



**Report 09-02**  
December 29, 2009

**Sources of Metal Contamination  
in the Coal Creek Watershed,  
Crested Butte, Gunnison County, Colorado:  
Part III. Early Spring Flow, April 2007**

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## EXECUTIVE SUMMARY

This report presents the results of a study conducted by University of Colorado researchers for the Coal Creek Watershed Coalition on the source of metals in the Coal Creek watershed during early spring runoff in April 2007. Coal Creek is the main water supply for the Town of Crested Butte in Gunnison County, Colorado. The study was funded by the University of Colorado's Outreach Committee and the Coal Creek Watershed Coalition.

Previous sampling has shown that Coal Creek is contaminated by metals and acidity from the Standard Mine on Elk Creek, a tributary of Coal Creek, and from a natural iron gossan and fen located just west of the Keystone Mine. Drainage from the Keystone Mine, which has been treated at the Mount Emmons treatment facility since 1981, also contributes metals to Coal Creek just downstream of Crested Butte's water supply intake. To further investigate the source of metals from the iron fen and gossan and the Keystone Mine property during a time of snow-melt and runoff in the Coal Creek watershed, a spatially detailed metal loading tracer test was performed by University of Colorado researchers in April 2007. The study was conducted during early spring flow to complement companion studies conducted at low flow in September 2005 and at high flow in June 2006.

The metal loading tracer dilution test was conducted on a 2.9 km reach of Coal Creek from just upstream of the iron fen to just downstream of the Keystone Mine property. The Coal Creek and tributary samples were analyzed for aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc. In this reach, chronic aquatic life toxicity standards were exceeded by aluminum, cadmium, copper, and zinc. Drinking water supply standards were not exceeded. The exceedances occurred downstream of the iron fen for aluminum, downstream of the iron gossan for cadmium, downstream of the tributary carrying the Mount Emmons treatment plant effluent and drainage from the Keystone Mine property for copper, and over the entire reach for zinc.

For all of the metals exceeding the chronic aquatic life standards, the Mount Emmons treatment plant effluent was a major or minor source. The effluent was sampled at near its expected maximum flow rate. For cadmium, copper, and zinc, a Keystone Mine surface drainage that combined with the treatment plant effluent to form the unnamed tributary at stream distance 5.368 km (stream distance datum was the injection point of the September 2005 metal loading tracer test) was a major or minor source. A tributary draining the iron gossan and possibly the western portion of the Keystone Mine property at 4.186 km was a minor source of aluminum and zinc. Other iron fen and gossan tributaries were trace sources for all of the metals.

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# TABLE OF CONTENTS

Executive Summary .....	iii
Acknowledgments .....	iv
Table of Contents .....	v
List of Tables .....	vi
List of Figures .....	vii
Introduction .....	1
Overview .....	1
Characterization of metal sources .....	3
Coal Creek watershed .....	4
Coal Creek stream flow .....	5
Metal loading tracer dilution method .....	5
Materials and Methods.....	7
Injection and synoptic sampling sites.....	7
Injection procedure.....	7
Water sampling procedures.....	8
Field laboratory procedures.....	11
Analytical procedures.....	12
Flow rate calculations .....	13
Metal loading calculations .....	14
Hardness and water quality standards .....	14
Results.....	17
Metal loading tracer dilution test details .....	17
Tracer dilution, bromide concentrations, and flow rate in Coal Creek .....	17
pH and hardness in Coal Creek .....	21
Metals in Coal Creek .....	23
Summary of metal loading contributions in Coal Creek .....	43
Discussion .....	45
Measurement of flow rate in Coal Creek .....	45
Mount Emmons treatment plant effluent and hardness.....	45
Sources of metals exceeding aquatic life toxicity standards.....	46
References .....	49

## LIST OF TABLES

Table 1. Record of injection for metal loading tracer test in Coal Creek on April 8, 2007 .....	9
Table 2. Equations used to calculate flow rates and mass loading rates (Kimball et al., 2002) for the Coal Creek tracer dilution study.....	13
Table 3. Hardness-based equations for calculating acute and chronic aquatic life toxicity standards. ....	15
Table 4. Coal Creek flow rates at sample sites and tributaries during the metal loading tracer dilution test in April 2007.....	20
Table 5. Dissolved calcium and magnesium and measured and estimated flow rates for the tributary UT-5.368 and the three drainages that combine to form UT-5.368.....	40
Table 6. Total and dissolved metal loading rates expressed as percentages of the cumulative total metal loading rate for Coal Creek. ....	44
Table 7. Coal Creek distances over which metals and arsenic exceed the Colorado chronic aquatic life toxicity standards.....	46
Table 8. Major, minor, and trace sources of metals that exceeded the chronic toxicity standards for aquatic life in Coal Creek. ....	48



## LIST OF FIGURES

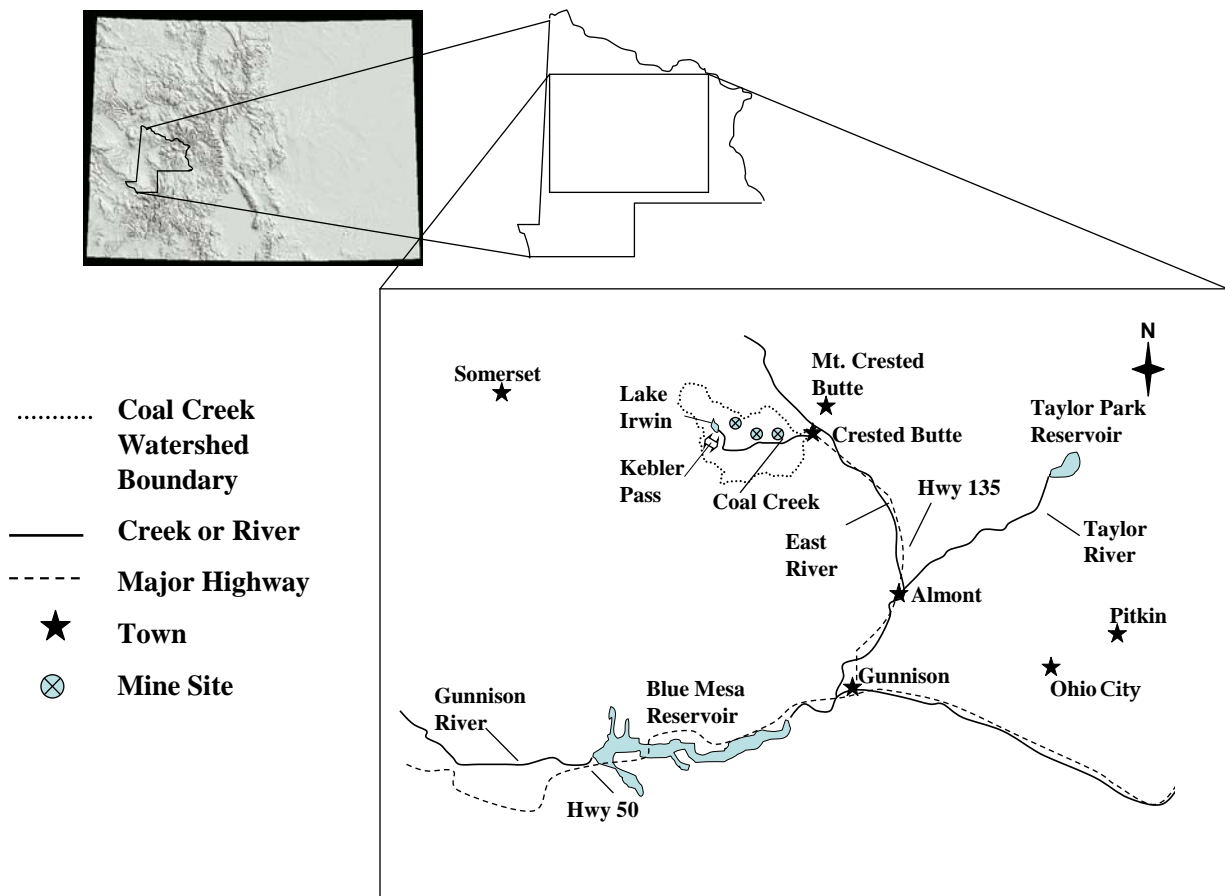
Figure 1. Maps showing the State of Colorado, Gunnison County, and the major rivers of the Gunnison-Crested Butte area.....	1
Figure 2. Key landmarks of the Coal Creek watershed, including Lake Irwin, the Forest Queen Mine, Kebler Pass, the Standard Mine, Elk Creek, Mount Emmons, the Keystone Mine, and the Town of Crested Butte.....	2
Figure 3. Aerial photograph of Coal Creek near the Keystone Mine at the base of Mount Emmons with tributaries present during the April 2007 metal loading tracer dilution test ....	3
Figure 4. The injection setup at CC-3.085 for the metal loading tracer dilution test on April 8, 2007.....	8
Figure 5. University of Colorado undergraduate research assistant Hallie Bevan samples Coal Creek from the downstream end during the synoptic sampling .....	10
Figure 6. University of Colorado graduate research assistant Tim Dittrich samples Coal Creek from the upstream end during the synoptic sampling .....	10
Figure 7. Unnamed tributary UT-3.212, the first and main iron fen tributary, followed a clear channel from the culvert under County Road 12 to Coal Creek .....	11
Figure 8. Unnamed tributary UT-3.595, the second iron fen tributary, did not follow a clear channel from the culvert to the Coal Creek.....	11
Figure 9. Unnamed tributary UT-3.895, which drains the iron fen and gossan, flows from a culvert as a thin sheet over saturated soil and peat down to Coal Creek .....	11
Figure 10. Marshy pool at the confluence of unnamed tributary UT-4.186, which drains the iron gossan, and Coal Creek .....	12
Figure 11. Concentration of bromide in injection solution as a function of time during the metal loading tracer dilution test in Coal Creek in April 2007 .....	17
Figure 12. Bromide concentration at the downstream end of the Coal Creek reach (CC-5.986) as a function of time during the metal loading tracer dilution test in April 2007.....	18
Figure 13. Bromide concentration in Coal Creek and its tributaries as a function of distance downstream during the metal loading tracer dilution test in April 2007 .....	18
Figure 14. Flow rate in Coal Creek and its tributaries during the metal loading tracer dilution test in April 2007.....	19
Figure 15. Coal Creek and tributary pH during the metal loading tracer dilution test in April 2007.....	21
Figure 16. Stream and tributary calcium concentrations as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007.....	22
Figure 17. Stream and tributary magnesium concentrations as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	22
Figure 18. Stream and tributary hardness as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	23
Figure 19. Stream and tributary aluminum concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	25
Figure 20. Stream and tributary arsenic concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	26
Figure 21. Stream and tributary barium concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	28
Figure 22. Stream and tributary cadmium concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	29

Figure 23. Stream and tributary chromium concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	31
Figure 24. Stream and tributary copper concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	32
Figure 25. Stream and tributary iron concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007.....	34
Figure 26. Stream and tributary lead concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007.....	35
Figure 27. Stream and tributary manganese concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	37
Figure 28. Stream and tributary nickel concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007 .....	38
Figure 29. Stream and tributary zinc concentrations and loading rates as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007.....	39
Figure 30. Photographs of the drainages combining to make up the tributary UT-5.368 .....	41
Figure 31. Total and dissolved metal concentrations for the three sources that combine to form the tributary UT-5.368.....	42
Figure 32. Photographs of the grit chamber and equalization pond used by the Mount Emmons treatment plant.....	47

# INTRODUCTION

## Overview

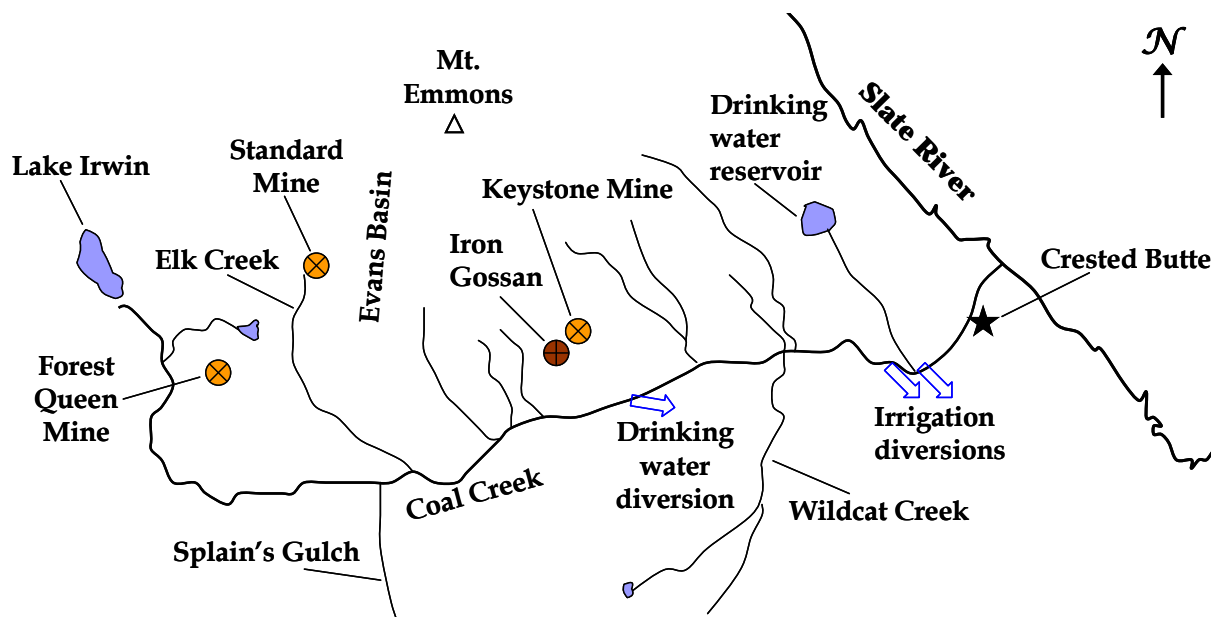
The Coal Creek watershed in northern Gunnison County near Crested Butte, Colorado (Figure 1) is contaminated by acid mine drainage (Wentz, 1974; Stantec, 2005; EPA, 2005a). Acid mine drainage results when sulfide minerals such as pyrite ( $\text{FeS}_2$ ) contact water and oxygen and are oxidized. The chemical processes are accelerated by the activities of microbes, and the results are high concentrations of metal ions and acidic compounds that contaminate groundwater and surface runoff. High concentrations of metals can be toxic to aquatic life and can pose health problems for humans if they contaminate drinking water sources.



**Figure 1.** Maps showing the State of Colorado (upper left), Gunnison County (upper right), and the major rivers of the Gunnison-Crested Butte area. The Coal Creek watershed is outlined by the dashed line west of Crested Butte (Shanklin and Ryan, 2006).

The Coal Creek watershed is located west of the Town of Crested Butte in Gunnison County, Colorado (Figure 2). Coal Creek is the main drinking water supply for the approximately 1,500 residents of Crested Butte. The watershed area, which

encompasses what was known as the Ruby Mining District, is rich in mineral resources. Hard rock mining began in this area in 1874 when the watershed belonged to the Ute Indian Reservation and continued until 1974 (EPA, 2005a). Vein deposits are contained in north-northeast-trending faults, dikes, and small stocks on the eastern faces of the Ruby Range. These veins are rich in copper, gold, lead, molybdenum, ruby, silver, and zinc (Streufert, 1999). The three largest mines were the Standard Mine, the Keystone Mine, and the Forest Queen Mine, all of which lie on the southern face of Scarp Ridge, and all of which are now inactive (EPA, 2005b). The watershed is now used primarily for residential development, recreation, and water supply.

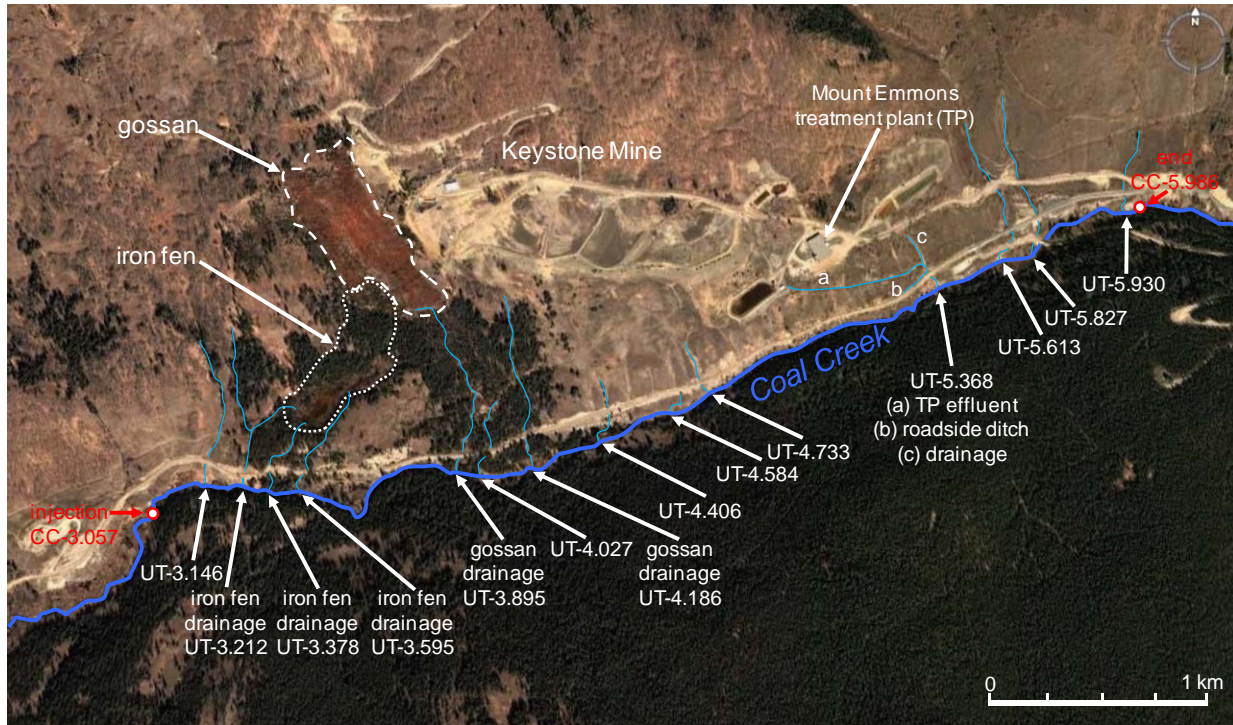


**Figure 2.** Key landmarks of the Coal Creek watershed, including Lake Irwin, the Forest Queen Mine, Kebler Pass, the Standard Mine, Elk Creek, Mount Emmons, the Keystone Mine, and the Town of Crested Butte (Shanklin and Ryan, 2006).

The Standard Mine, which is located 3.2 km north of Coal Creek along a tributary, Elk Creek, was added to the National Priority List (“Superfund”) in September 2005. The Standard Mine was a silver mine that was in operation until 1966. Since then, heavy metals and ground and surface water flow have contaminated Elk Creek and Coal Creek. Site remediation activities by the U.S. Environmental Protection Agency (EPA) were started in the summer of 2006 and continue to the present.

Drainage from the Keystone Mine is treated at the Mount Emmons Treatment Plant and released into Coal Creek just downstream of Crested Butte’s drinking water intake (Figure 3). The treatment plant was constructed in 1981 by Amax Gold, Inc., which merged into Cyprus Amax Minerals Company and was later acquired by the Phelps-Dodge Corporation. In February, 2006, Phelps-Dodge transferred ownership of property to the U.S. Energy Corporation. When the metal-loading tracer-dilution test described in this report was conducted, U.S. Energy was responsible for operation of the treatment plant.

A naturally occurring iron-rich surface deposit, or gossan, also drains into Coal Creek (Figure 3). Drainage from the gossan is characterized by low pH and high concentrations of aluminum, iron, manganese, zinc, and other metals. The gossan drainage lingers in a wetland, locally referred to as “the iron fen.” The iron fen is the home to an endangered plant species, the *Drosera rotundifolia* (USFS, 1981).



**Figure 3.** Aerial photograph of Coal Creek near the Keystone Mine at the base of Mount Emmons with tributaries present during the April 2007 metal loading tracer dilution test. The injection was made at a distance of 3.057 km downstream of the injection point for the September 2005 low flow test (Shanklin and Ryan, 2006). Unnamed tributaries (“UT-”) show distances from the September 2005 injection point. The path of the tributaries is approximate. Coal Creek flows from the southwest to the northeast. The aerial photo was retrieved using Google Earth™ (<http://earth.google.com>).

### **Characterization of Metal Sources**

We are assisting the Coal Creek Watershed Coalition in an effort to identify the major sources of metal contamination in the watershed. To do this, a total of four metal loading tracer dilution experiments have been conducted: one 9.4 km reach at low flow (September 2005; Shanklin and Ryan, 2006), a 4.3 km reach and a 1.9 km reach at high flow (June 2006; Ryan and Bevan, 2009), and a 2.9 km reach in early spring during the start of snow melt and runoff in the lower elevations of the watershed (April, 2007; this report).

The objectives of this study were to (1) locate and quantify sources of metal input to Coal Creek at the time of the snow melt and runoff in the watershed, and (2) compare the results of the low flow and high flow studies with the results of this study to determine the effects of flow rate on the sources of metal input to Coal Creek. The

metal loading tracer dilution experiment was focused on a 2.9 reach extending from just upstream of the iron gossan and fen tributaries to just downstream of the Keystone Mine property to determine if surface runoff and seepage from the iron gossan and fen and the Keystone Mine property was carrying metals to Coal Creek.

For a metal loading tracer dilution experiment (Kimball, 1997), water is pumped from the stream and mixed with a high concentration of a tracer that remains dissolved in the water (e.g., a salt like sodium bromide or lithium chloride, or a fluorescent dye like rhodamine). The tracer solution is slowly pumped back into the stream until a steady concentration of the tracer is reached over the reach of the stream being investigated. When the tracer reaches a steady concentration, a synoptic sampling is conducted to provide a “snapshot” of concentration of the tracer and contaminants. If the synoptic sampling is conducted at a high spatial resolution, the source of the metal contaminants can be pin-pointed. The tracer concentrations are used to determine the stream flow rate – as tributaries without the tracer enter the stream, the tracer concentration decreases. With flow rates in units of volume per time (e.g.,  $L s^{-1}$ ) and metal concentrations in units of mass of metal per volume (e.g.,  $\mu g L^{-1}$ ), metal loading rates can be calculated in units of mass of metal passing the sampling point per time (e.g.,  $kg d^{-1}$ ; in the units used for total maximum daily load regulations,  $lb d^{-1}$ ). These metal loading rates allow identification of the major sources of metal contamination in the watershed.

### *Coal Creek Watershed*

Coal Creek is fed by snow melt and springs in the surrounding Ruby-Anthracite Range of the West Elk Mountains. The Coal Creek headwaters are located in the drainage southeast of Lake Irwin at an elevation just over 3,120 m. From the Lake Irwin area, Coal Creek runs eastward, is joined by Splains Gulch, Elk Creek, Wildcat Creek, and other tributaries, and continues through the Town of Crested Butte until reaching its confluence with the Slate River. The Slate River continues south to join the East River, the Gunnison River, and ultimately, the Colorado River. Running parallel to the majority of Coal Creek is County Highway 12, the Kebler Pass Road, a gravel road maintained by Gunnison County.

The watershed drainage area is approximately 22.4 km<sup>2</sup>. The watershed elevation is highest in the 4,300 m peaks of the Ruby-Anthracite Range and lowest at 2,900 m in the Town of Crested Butte. The valley creating the Coal Creek Watershed was shaped by glacial erosion during the Pleistocene epoch. The high peaks are characterized by laccoliths, dome-shaped igneous intrusions, and sedimentary and volcanic rock formations. The valley bottom is underlain by sand and gravel deposited by glacial ice and melt water (Streufert, 1999).

Regional vegetation is predominantly boreal forest. Aspen, fir, and spruce forests dominate the lower elevations, while alpine tundra is encountered at elevations above tree line. Microclimates vary with slope angle and aspect. This is demonstrated by the longer snowfall storage on north-facing slopes, which results in higher soil moisture contents and denser forest vegetation. On the contrary, snow on south-facing slopes

melts and runs off faster, resulting in drier soils, brush, and grass for vegetation (Soule, 1976).

### *Coal Creek Stream Flow*

Stream flow is not currently recorded for Coal Creek. The annual snowfall on the top of Kebler Pass, which is located just south of Lake Irwin at an elevation of 3,042 m, is about 12.7 m. The average annual watershed precipitation is 29.7 cm.

Between the years of 1941 and 1946, daily flow measures were taken from a location just upstream of the town's water intake, which is located 3.4 km downstream from the Elk Creek Confluence. These records indicate that the average maximum daily flow is  $3.31 \text{ m}^3 \text{ s}^{-1}$  and that the peak flows typically occur during the second week of June (USGS, 2006). The maximum daily flow recorded from 1941 to 1946 was  $4.87 \text{ m}^3 \text{ s}^{-1}$ . The minimum recorded flow was  $0.030 \text{ m}^3 \text{ s}^{-1}$  during the winter months. During a sampling event, the EPA measured a flow of  $2.4 \text{ m}^3 \text{ s}^{-1}$  on June 14, 2005 (EPA, 2005b).

There was one surface water diversion along the study reach of Coal Creek. This occurred at the Town of Crested Butte drinking water supply intake. Based on data provided by the Town of Crested Butte, the intake was estimated to divert water from Coal Creek at an average rate of  $0.079 \text{ m}^3 \text{ s}^{-1}$  (Shanklin and Ryan, 2006).

### *Metal Loading Tracer Dilution Method*

The tracer dilution method allows quantification of stream flow rate by monitoring dilution of a tracer as it moves downstream (Kimball, 1997). A specific concentration of tracer is injected at a constant rate to achieve steady-state conditions. This provides a known mass of tracer added to the stream. Tracer concentration is measured upstream and downstream of the injection site. Flow rate is quantified based on the dilution of the tracer by tributaries and groundwater input as it moves downstream from the injection site. The tracer dilution method accounts for flow through the hyporheic zone, or the layer of streambed sediment that rapidly exchanges water with the stream. Flow through the hyporheic zone is normally substantial for high-gradient, shallow mountain streams such as Coal Creek. Traditional current meter flow measurements for mountain streams are typically underestimates because flow through the hyporheic zone is not captured (Bencala et al., 1990).

The tracer dilution method accounts for tributaries and dispersed groundwater inputs as well as seeps or springs discharging over a large area. These non-point sources affect quantification of flow because they contribute to the dilution of the tracer; however, the portion of flow attributable to point versus non-point sources cannot be distinguished. All downstream reductions in tracer concentration are assumed to be a result of dilution from tributary and groundwater inflow (Kimball et al., 2002). When a surface tributary is present between two sample locations, the calculated inflow rate is assigned solely to the tributary despite the possibility of groundwater inputs. When no visible tributary is present, flow rate increases are assumed to be a result of groundwater inflow. Again, the tracer dilution method is unable to distinguish

between tributary and groundwater inflow if both occur between two synoptic sample sites. The method only accounts for the total inflow between two sample sites. The method also cannot specifically identify points where stream flow rates decrease from losses to groundwater. Only losses over an entire reach between two sample sites can be determined.

The tracer-injection method requires the tracer to be inert and transported downstream in a conservative fashion, unaffected by biogeochemical reactions. The injection must continue until all parts of the stream including the hyporheic zone and all surface storage zones become saturated with tracer. Under these saturation conditions, the in-stream tracer concentration is said to be at a steady-state, or plateau, concentration (Bencala et al., 1990). When the tracer concentration reaches a steady state, a synoptic sampling is conducted. A synoptic sampling is a spatially detailed sampling of stream sites and all tributary inflows to provide a “snapshot” of stream and tributary chemistry (Kimball, 1997). The “snapshot” is not actually instantaneous – sampling may actually occur over a period of several hours – but during the sampling, the tracer and metal concentrations are assumed to be at steady state. A sample site spacing of hundreds of meters is recommended for practical analysis of stream chemistry (Bencala et al., 1990). Synoptic sample sites are intended to bracket all tributary inflows. This allows for understanding and quantifying the impacts of many individual sources on the watershed as a whole.



## MATERIALS AND METHODS

### *Injection and Synoptic Sampling Sites*

On April 8, 2007, we conducted a metal loading tracer dilution test over a 2.9 km reach in Coal Creek from upstream of the iron gossan and fen drainages to downstream of the Keystone Mine. The injection site was located at a distance of 3.073 km downstream of the September 2005 injection site, which we used as a point of reference for the later tests. The downstream end of the reach was at a distance of 6.014 km downstream of the September 2005 injection site. The distance of the test reach was 2.941 km. The tributaries at which water samples were collected during the synoptic sampling are shown in Figure 3.

Sample sites in Coal Creek were generally located every 200 m or less. A sample site was established in every tributary and in the creek downstream of every tributary discovered during a walking survey of the creek. Sampling sites downstream of the tributaries were usually located within 50-100 m of the tributary unless another tributary downstream required closer placement. There were 44 sampling sites, 30 in Coal Creek and 14 in tributaries.

The latitude and longitude of each sampling site was measured using a global positioning system (GPS) receiver (Garmin GPS12). Photographs of the tributaries and prominent landmarks were taken. The GPS points were transposed onto a topographic map and relabeled with distances downstream of the upstream site used by the September 2005 study (Shanklin and Ryan, 2006). All sample sites along Coal Creek were designated "CC- " and labeled with the appropriate distance. Sample sites at unnamed tributaries were labeled "UT- ".

### *Injection Procedure*

The tracer used in this study was sodium bromide (NaBr). The previous tracer tests were conducted with lithium chloride (September 2005, low flow; Shanklin and Ryan, 2006) and sodium chloride (June 2006, high flow; Ryan and Bevan, 2009). Lithium was an unreliable tracer because it was attenuated in wetlands near Coal Creek. Chloride was used to determine flow rate in the September 2005 and June 2006 tests. It was a marginally suitable tracer because we could not add it at sufficiently high concentration to exceed background chloride concentrations in some of the tributaries. In this April 2007 early spring runoff test, bromide was an effective tracer - it was transported conservatively and we were able to inject it at concentrations well above background concentrations in the stream and tributaries.

To prepare the tracer solution, 1,135 L (about 300 gallons) of stream water was pumped from Coal Creek into a polyethylene tank using a garden hose and gasoline-powered water pump on the day before the injection. Sodium bromide (234 kg; 520 pounds; Ameribrom, Inc., Fort Lee, NJ) was added to the stream water to create a bromide solution of 2.0 M concentration, stirred using a paddle, and left in the tank overnight to dissolve. On the day of the injection, April 8, 2007, the tracer solution was continuously injected into Coal Creek using a piston-driven metering pump (Fluid Metering, Inc.; QV pump; QCKC pump head with ceramic and polyvinylidene difluoride parts; V200 stroke rate controller) and Tygon<sup>®</sup> tubing (Fisherbrand, 12.7 mm inside diameter). The injection began at 8:00 and continued for 7.5 h. Injection flow rates were determined by measuring the amount of time needed to fill a 500 mL graduated cylinder with the injectate. The time-weighted average flow rate of the injection was 2.24 L min<sup>-1</sup> with a range of 2.20 L min<sup>-1</sup> to 2.30 L min<sup>-1</sup>. The tank was stirred with a paddle every 15-30 min. The injection setup is shown in Figure 4 and the injection details are recorded in Table 1. A rented snowmobile and sled were used to transport the injection equipment along County Road 12 over the snow-covered portions of the road.



**Figure 4.** The injection setup at CC-3.085 for the metal loading tracer dilution test on April 8, 2007. From left to right, the tube delivering the injection solution to Coal Creek, the generator that powered the injection pump (in the background), the injection pump in the open container, and the 330 gallon injection tank (dark green, right foreground).

The weather on the day of the injection was recorded as varying from overcast to light rain to snow flurries with an estimated temperature of 1-4°C. No accumulation of snowfall occurred during the injection. The north-facing south bank of Coal Creek was entirely covered by snow, and the south-facing north bank was about 20% covered by snow. At 1-5 °C, it was unlikely that much, if any, melting snow was added to the tributaries, but tributary flow was fed by warmer temperatures of the previous week (average high of 15.6°C with mostly clear skies during the days).

### ***Water Sampling Procedures***

At the upstream end of the injection reaches, samples were taken from the injection tubing and from Coal Creek upstream of the injection. Samples were collected on the half-hour from the injection tubing in 60 mL high-density polyethylene Nalgene bottles

to monitor the consistency of the injection chloride concentration. “Background” samples were collected nearly hourly from the sites CC-3.503 located just upstream of the injection sites in 250 mL samples high-density polyethylene Nalgene bottles to monitor changes in upstream chloride concentration. Specific conductance was measured at the end of the injection tubing and in the injection tank at various times throughout the injection periods using a Thermo Orion 105A+ meter and Orion 010510 conductivity cell calibrated with Traceable One-Shot™ 1409  $\mu\text{S cm}^{-1}$  conductivity calibration standard.

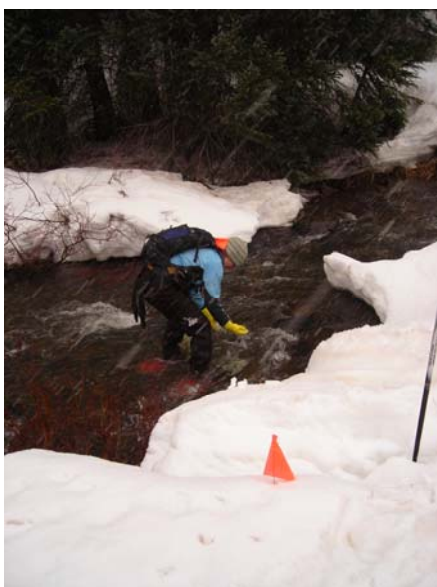
**Table 1.** Record of injection for metal loading tracer test in Coal Creek on April 8, 2007.

clock time	experiment time (h)	flow rate ( $\text{L min}^{-1}$ )	conductivity ( $\text{mS cm}^{-1}$ )	activity
8:00	0.00	2.20	189.0	Started injection at CC-3.057
8:30	0.50	2.24	190.3	
9:00	1.00	2.20	181.9	
9:15	1.25			Flow interruption for three minutes caused by tripped circuit breaker on generator; changed injection pump
9:18	1.30	2.22		Flow resumed
9:40	1.67	2.20	179.0	
10:00	2.00	2.30	177.9	
10:30	2.50	2.30	175.9	
11:00	3.00	2.30	185.0 (top) 187.0 (bottom)	Conductivity measurements made at top and bottom of injection tank
11:30	3.50	2.22		Conductivity meter read over maximum; replaced electrode
12:00	4.00	2.20	176.2	
12:30	4.50	2.28	176.4 (before stirring) 177.8 (after stirring)	Conductivity measured in tank before and after stirring
12:45	4.75			Debris removed from pump line; no flow interruption
13:00	5.00	2.20	177.3	
13:15	5.25			Synoptic sampling begins from upstream and downstream ends
13:30	5.50	2.22	178.0	Ended sampling of upstream (background) sampling point
14:00	6.00	2.20	175.3	
14:30	6.50	2.24	174.4	
15:00	7.00	2.20	175.1	
15:30	7.50	2.28	172.9	Synoptic sampling completed; injection ended

At the downstream end of the injection reaches, samples were collected every 15 min from site CC-5.986 in 60 mL high-density polyethylene Nalgene bottles. The conductivity and bromide concentrations of these samples were measured in the field to track the arrival of the tracer and determine the proper time to start the synoptic sampling. A Thermo Orion 250A+ or 290A+ meter and Orion 9435BN bromide electrode with an Orion 900200 double-junction reference electrode were used to

measure the bromide concentrations. The electrode was calibrated with sodium bromide standards. The standards were equilibrated to the temperature of the stream water (about 2 °C).

When the bromide concentration reached a plateau at the downstream end of the injection reach, synoptic sampling of the reach was begun. Synoptic sampling lasted two hours. Two teams of two people carried out the sampling from the downstream and upstream ends of the reach. Two water samples were collected from each synoptic sample site in 250 mL high-density polyethylene Nalgene bottles. Accumulation of snow over the creek made sampling challenging. Samples were obtained by wading in the stream from the downstream end and by using a pole from the upstream end (Figures 5 and 6).



**Figure 5.** University of Colorado undergraduate research assistant Hallie Bevan samples Coal Creek from the downstream end during the April 8, 2007, synoptic sampling using snow shoes and chest waders.



**Figure 6.** University of Colorado graduate research assistant Tim Dittrich samples Coal Creek from the upstream end during the April 8, 2007 synoptic sampling using snow shoes and a pole to extend the sample bottle into the stream without collapsing the snow accumulated on the north bank.

Sampling of the tributaries was often complicated by dispersal of flow from culverts under County Road 12 and snow cover. As observed during the previous metal loading tracer dilution tests, seepage from north bank slopes flows into road-side ditches and through culverts under the road. Water flowing out of the culverts flows to Coal Creek in clear channels in some cases (Figure 7), but in other cases, flows from the culverts is low and no clear channel to the creek is present (Figure 8). Where no clear tributary channel was present near Coal Creek, the tributary sample was collected from the culvert opening. In some cases, tributaries from culverts spread out as broad sheet flows over saturated soil and peat (Figure 9) or as marshy pools near the creek (Figure 10); these tributaries were also sampled at the culvert opening. The tributary

samples collected at the culvert openings may not accurately reflect the concentration of metals reaching Coal Creek because contact with soils and peat may remove some metals; however, it is likely that these soils and peat are saturated with metals and removal of metals is negligible. Over time, these peats may release metals to Coal Creek. Often, de-watering of peats leads to oxidation and release of metals (Tipping et al., 2003).

All samples were collected after rinsing the sample bottles and lids three times in the waters being sampled. The rinse water was discarded downstream of the sample site, and then the sample bottle was filled. Bottles were labeled with date, time, sample location name, and the name of the sampler. Samples were stored in coolers on ice to preserve them in the field.

### *Field Laboratory Procedures*

For each synoptic sample site, portions of one of the two 250 mL samples were tested for pH and specific conductance, filtered, and acidified, and the other 250 mL sample was set aside as a “backup.” The pH was measured using a Thermo Orion 250A+ or 290A+ meter and Thermo 91-57BN electrode. The meter and triode were calibrated with pH 4 and 7 buffers with an ambient room temperature of approximately 20 °C. The pH measurements were made after the water reached room temperature. Specific conductance was measured with an Orion 105A+ meter and Orion 010510 Conductivity Cell calibrated with a Traceable One-Shot™ conductivity calibration standard (1409  $\mu\text{S cm}^{-1}$ ) at room temperature.

Following pH and specific conductance measurement, the sample was divided into two 60 mL samples. One of



**Figure 7.** Unnamed tributary UT-3.212, the first and main iron fen tributary, followed a clear channel from the culvert under County Road 12 to Coal Creek; the sample was taken at the location of the orange flag within about 2 m of the creek’s north bank.



**Figure 8.** Unnamed tributary UT-3.595, the second iron fen tributary, did not follow a clear channel from the culvert to the Coal Creek; therefore, the sample was taken at the culvert opening.



**Figure 9.** Unnamed tributary UT-3.895, which drains the iron fen and gossan, flows from a culvert as a thin sheet over saturated soil and peat down to Coal Creek. This tributary was sampled at the culvert under the road. Graduate research assistant Chase Gerbig collected samples while negotiating the terrain on snow shoes.

the two 60 mL samples was filtered using a syringe (30 mL BD Luer-Lok syringes) and a membrane filter (Fisherbrand nylon, 0.45  $\mu\text{m}$  pore diameter, 25 mm diameter) for determination of dissolved bromide (total bromine) and major cations and metals by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The second 60 mL sample was not filtered for measurement of total major cations and metals by ICP-AES and ICP-MS. The dissolved and total major cation and metal samples were acidified to  $\text{pH} < 2$  by adding 1 mL of concentrated nitric acid (Fisher Chemical, trace metal-grade). The pH and specific conductivity measurements, filtration, and acidification were conducted in a field laboratory within 24 h of collecting the samples.

For every tenth sample, the “backup” sample was processed as described above to provide duplicate samples for ICP-AES and ICP-MS measurements. After every twenty samples, a blank sample (high purity water, Millipore, Milli-Q,  $>18$  Mohm resistivity) was processed for bromide and dissolved and total major cations and metals. All lab personnel wore gloves during the pH, specific conductance, filtration, and acidification processes. The acidified major cation and metal samples were stored at room temperature until analysis.

The 60 mL injection tank and downstream end samples as well as the 250 mL upstream samples were also filtered and acidified for measurement of bromide by ICP-MS. No cation or metals measurements were made for these samples.

### *Analytical Procedures*

Calcium, iron, and magnesium were measured by ICP-AES (Applied Research Laboratories ARL 3410+) in the Laboratory for Environmental and Geological Studies (LEGS) at University of Colorado at Boulder. Three standards and blanks (high-purity water) were run between every ten samples. A 2% nitric acid (trace metal-grade) solution was run through the system for 10 s between each sample. The detection limits for ICP-AES were similar to those presented by Ryan and Bevan (2009) for the June 2006 metal loading tracer dilution tests.

Bromide and aluminum, arsenic, barium, cadmium, chromium, copper, lead, manganese, nickel, and zinc, were measured by ICP-MS (PerkinElmer SCIEX Elan DRC-e) in the Laboratory for Environmental and Geological Studies (LEGS) at University of Colorado at Boulder. Four standards were used to calibrate the ICP-MS. A blank (high-purity water) and a  $100 \mu\text{g L}^{-1}$  standard were run between every ten samples. Each sample was spiked (1:9) with an internal standard consisting of  $160 \mu\text{g L}^{-1}$  of gallium, scandium, and indium and  $80 \mu\text{g L}^{-1}$  bismuth in 2% nitric acid



**Figure 10.** Marshy pool at the confluence of unnamed tributary UT-4.186, which drains the iron gossan, and Coal Creek. The tributary sample was taken at the culvert under County Road 12.

(trace metal-grade). A 2% nitric acid (trace metal-grade) solution was run through the system for 10 s between each sample. The detection limits for ICP-MS were similar to those presented by Ryan and Bevan (2009) for the June 2006 metal loading tracer dilution tests.

### Flow Rate Calculations

The tracer dilution method assumes conservation of mass between upstream and downstream sample locations (Kimball, 1997; Kimball et al., 2002). Conservation of mass requires that flow or mass at a downstream sample location is equal to flow or mass at an upstream sample location plus the flow or mass entering the stream at the injection site. Steady-state conditions dependent upon a constant injection tracer concentration and a constant tracer injection rate are assumed. The equations used for determining flow are presented in Table 2.

**Table 2.** Equations used to calculate flow rates and mass loading rates (Kimball et al., 2002) for the Coal Creek tracer dilution study.

Calculated Variable	Equations	Variable Definition
Mass balance downstream from injection site	$M_{down} = Q_{down} C_{down}$ (1)	$C_{up}$ , tracer concentration upstream of injection site
	$M_{down} = Q_{up} C_{up} + Q_{inj} C_{inj}$ (2)	$C_{down}$ , tracer concentration downstream of injection site
	$Q_{down} = Q_{up} + Q_{inj}$ (3)	$C_{inj}$ , injectate tracer concentration
Flow rate at first site downstream of injection site with uniform background concentration	$Q_{down} = Q_{inj} \frac{C_{inj} - C_{up}}{C_{down} - C_{up}}$ (4)	$M_{down}$ , mass loading rate downstream of injection site
		$Q_{up}$ , flow rate upstream of injection site
		$Q_{down}$ , flow rate downstream of injection site
		$Q_{inj}$ , injection flow rate
Flow rate at subsequent downstream sites with uniform background concentration and upstream surface inflow contribution	$Q_{down} = Q_{up} \frac{C_{up} - C_{in}}{C_{down} - C_{in}}$ (5)	$C_{down}$ , tracer concentration at downstream site
		$C_{up}$ , tracer concentration at upstream site
		$C_{in}$ , tracer concentration of inflow
		$Q_{up}$ , flow rate at upstream site
		$Q_{down}$ , flow rate at downstream site
Metal loading rates	$M_i = Q_i C_i$ (6)	$M_i$ , metal loading rate of site $i$ $Q_i$ , flow rate of site $i$ $C_i$ , metal concentration of site $i$
Tributary loading contribution	$tributary\ load\ (\%) = \frac{load_i}{\sum_i load} \times 100$ (7)	$load_i$ (kg d <sup>-1</sup> ), loading rate at a specific tributary $\sum load$ , cumulative total of all tributary inputs (kg d <sup>-1</sup> )

All inflow between two sites bracketing a visible tributary was assumed to be due to tributary inflow. This may not actually be the case, however, because the tracer dilution

method quantifies flow from point sources as well as flow from distributed groundwater input, springs, or seeps discharging over a large area. The fraction of flow input attributable to dispersed sources cannot be quantified using tracer dilution. Tributary flow rates were calculated as the difference between flow at the sample location upstream of the tributary and flow at the sample location downstream of the tributary.

### *Metal Loading Calculations*

Stream flow rate and metal concentration at each synoptic sample site were multiplied to obtain a metal loading rate ( $\text{kg d}^{-1}$ ) for each site (Equation 6). These metal loading rates produce a metal loading profile for the length of the study reach. The load at the downstream end of a stream reach is equal to the load at the upstream end plus load contributions from all sources between the ends of the reach. The load is used to identify metal sources within the watershed. Increases in the metal load between sites indicate a metal source. Metal load decreases indicate a net loss of dissolved metal resulting from precipitation, sorption, or chemical reactions. The downstream load minus the upstream load between two sites is defined as the net load change.

The cumulative load is the sum of the positive load changes for the entire study reach, including both the upper and lower Coal Creek tributaries. The cumulative load is held constant for a negative load change between sites. The cumulative load approximates the minimum possible metal load contributed to the stream (Kimball et al., 2002). The tributary loading contribution (Equation 7) is the percentage of the cumulative metal loading for each metal. The calculation of tributary loading contributions allows the prioritization of major sources of metal contamination.

### *Hardness and Water Quality Standards*

All surface waters in the State of Colorado must meet physical and chemical water quality requirements set by the Colorado Department of Public Health and Environment (CDPHE). Coal Creek is classified as a “Class 1 - Cold Water Aquatic Life” stream because the summer water temperature does not often exceed  $20\text{ }^{\circ}\text{C}$  and as a “Domestic Water Supply” because Coal Creek supplies the Town of Crested Butte’s drinking water. As such, Coal Creek must meet all requirements put forth by the CDPHE for these stream types. For protection of aquatic life, CDPHE gives chronic and acute toxicity limits for metals. The chronic standard is defined as the concentration limit that protects 95% of the genera from the chronic toxic effects of metals. Acute toxicity is defined as the concentration limit that protects 95% of the genera from the lethal affects of metals. Standard exceedances should not occur more than once every three years on average (CDPHE, 2008).

Many of the CDPHE metal standards are based on hardness measured in units of milligrams of calcium carbonate per liter ( $\text{mg CaCO}_3\text{ L}^{-1}$ ). Hardness was calculated as the sum of the dissolved calcium and magnesium ion concentrations:



$$\text{Hardness (mg CaCO}_3\text{ L}^{-1}) = 50,050 \times ([\text{Ca}] + [\text{Mg}]) \quad (8)$$

where [Ca] and [Mg] are the dissolved concentrations of the calcium and magnesium ions in units of equivalents per liter (eq L<sup>-1</sup>).

Using the calcium and magnesium concentrations measured for each synoptic sample site, a hardness profile for the entire length of the stream was calculated. The standard and acute toxicity limits calculated as a function of hardness were compared to the measured dissolved metal concentrations along Coal Creek for cadmium, copper, lead, manganese, and zinc (Table 3). There are two acute toxicity standards given for cadmium, with one specifically pertaining to trout. The chronic toxicity standard for cadmium applies to all aquatic life. Parameters that are not hardness-based included pH and the acute and chronic toxicity standards for aluminum, barium, chromium(VI), and iron. The non-hardness based toxicity standards were also compared to the measured metal concentrations along Coal Creek when possible. The CDPHE does not provide toxicity standard information for barium.

**Table 3.** Hardness-based equations for calculating acute and chronic aquatic life toxicity standards (CDPHE, 2008).

<b>Metal</b>	<b>Acute Aquatic Life Toxicity Standard (µg L<sup>-1</sup>)</b>
Cadmium	$(1.136672 - [\ln(\text{hardness}) \times 0.041838]) \times e^{0.9151[\ln(\text{hardness})] - 3.1485}$
(trout)	$(1.136672 - [\ln(\text{hardness}) \times 0.041838]) \times e^{0.9151[\ln(\text{hardness})] - 3.6236}$
Copper	$e^{0.9422[\ln(\text{hardness})] - 1.7408}$
Lead	$(1.46203 - [\ln(\text{hardness}) \times 0.145712]) \times e^{1.273[\ln(\text{hardness})] - 1.46}$
Manganese	$e^{0.3331[\ln(\text{hardness})] + 6.4676}$
Nickel	$e^{(0.846[\ln(\text{hardness})] + 2.253)}$
Zinc	$0.978 \times e^{0.8525[\ln(\text{hardness})] + 1.0617}$
<b>Metal</b>	<b>Chronic Aquatic Life Toxicity Standard (µg L<sup>-1</sup>)</b>
Cadmium	$(1.101672 - [\ln(\text{hardness}) \times 0.041838]) \times e^{0.7998[\ln(\text{hardness})] - 4.4451}$
Copper	$e^{0.8545[\ln(\text{hardness})] - 1.7428}$
Lead	$(1.46203 - [\ln(\text{hardness}) \times 0.145712]) \times e^{1.273[\ln(\text{hardness})] - 4.705}$
Manganese	$e^{0.3331[\ln(\text{hardness})] + 5.8743}$
Nickel	$e^{(0.846[\ln(\text{hardness})] + 0.0554)}$
Zinc	$0.986 \times e^{0.8525[\ln(\text{hardness})] + 0.9109}$

The Mount Emmons treatment plant adds lime (CaO) to raise the pH of Keystone Mine drainage to between 10 and 10.5 to precipitate and remove cadmium and

manganese (other metals are effectively removed at lower pH values). The addition of calcium results in a significant increase in the hardness of Coal Creek downstream of the treatment plant effluent, which enters Coal Creek as part of UT-5.368. The increase in hardness increases the CDPHE hardness-based aquatic life standards. Competition between calcium and other metals for binding sites on colloids is expected to reduce the toxicity of metals to aquatic life.

## RESULTS

### *Metal Loading Tracer Dilution Test*

The results of a metal loading tracer dilution tests conducted over a 2.9 km reach of Coal Creek in April 2007 are presented in this section. The test measured metal loading rates during the early spring runoff in the area of iron gossan and fen and the Keystone Mine property. These results can be compared to similar metal loading tracer dilution tests conducted during low flow in September 2005 (Shanklin and Ryan, 2006) and during high flow in June 2006 (Ryan and Bevan, 2009).

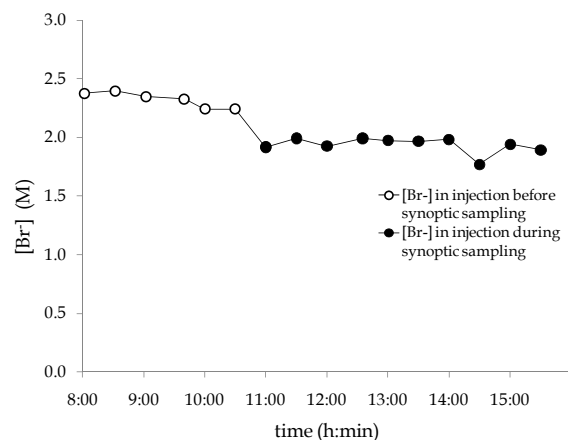
All distances presented in the following results were measured in units of kilometers from the injection site used for the September 2005 metal loading tracer test (Shanklin and Ryan, 2006). The September 2005 injection point was used at the point of reference to allow easy comparison of tributary metal loads between the tests at different flow. All distances are presented to the nearest 1 m (0.001 km) to facilitate a clear downstream order; however, the actual distance precision is estimated at 50 m (0.050 km) because the latitude and longitude of the sampling sites was measured with a global position system (GPS) instrument of relatively low precision.

### *Tracer Dilution, Bromide Concentrations, and Flow Rate in Coal Creek*

*Bromide concentration in Coal Creek upstream of the injection.* The bromide concentration in Coal Creek at sampling site CC-3.025 about 30 m upstream of the injection ranged from below the detection limit ( $5.0 \times 10^{-7}$  M) to  $6.7 \times 10^{-6}$  M. The average bromide concentration used for the flow calculations was  $2.0 \times 10^{-6}$  M for which the bromide concentrations measured below the detection limit were calculated with values of the detection limit.

*Bromide concentration in injection solution.* The average bromide concentration for the upper Coal Creek tracer injection ranged from 1.77 M to 2.40 M (Figure 11). Over the entire injection period, the average bromide concentration was 2.08 M. Because the bromide concentration decreased to a new plateau at 11:00 and because the bromide in Coal Creek during the synoptic sampling was injected after 11:00, the average bromide concentration used for the flow calculations was calculated to be 1.94 M using only the bromide concentrations measured at 11:00 and later.

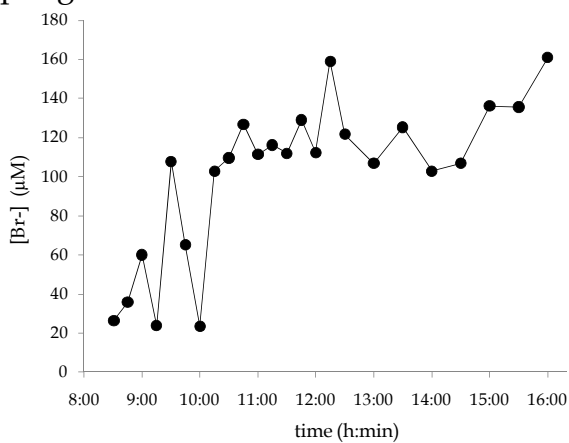
*Bromide concentration at downstream end of the reach.* At the downstream end of the Coal Creek reach at CC-5.986, the bromide concentration ranged from



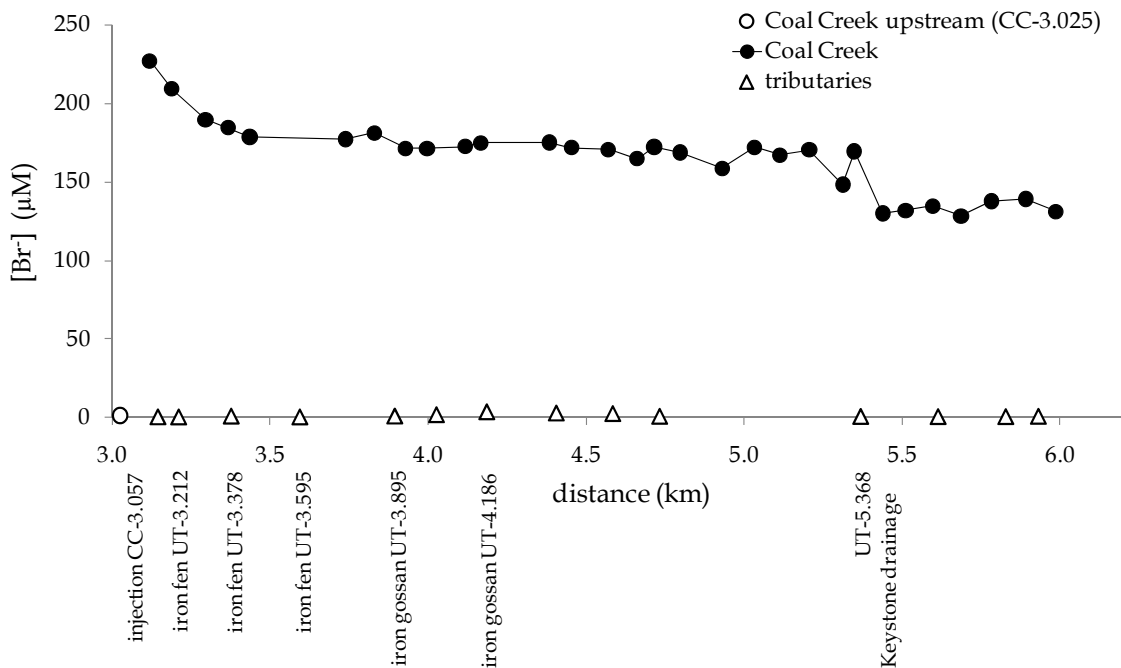
**Figure 11.** Concentration of bromide in injection solution as a function of time during the metal loading tracer dilution test in Coal Creek in April 2007. The bromide concentrations represented by the filled circles were used to calculate the average bromide concentration for the injection.

26  $\mu\text{M}$  to 160  $\mu\text{M}$  (Figure 12). Bromide concentration increased to a plateau of about 120  $\mu\text{M}$  at about 10:30, which indicated that the bromide in the injection solution reached the downstream end of the reach. To be sure that a steady-state bromide concentration was reached, the synoptic sampling was not commenced until 13:15.

*Bromide concentration in Coal Creek and the tributaries.* The injection of the bromide solution initially increased the concentration of bromide in Coal Creek by a factor of 114, from the average background concentration of  $2 \times 10^{-6}$  M at CC-3.025 to  $2.27 \times 10^{-4}$  M at CC-3.147, the first downstream sampling site following the injection in Coal Creek (Figure 13). Downstream of the injection, the concentration of bromide in Coal Creek was at least about 50 times greater than the concentration of bromide in the tributaries. Problems encountered using chloride as a tracer in Coal Creek (Shanklin and Ryan, 2006; Ryan and Bevan, 2009) were not encountered with bromide.



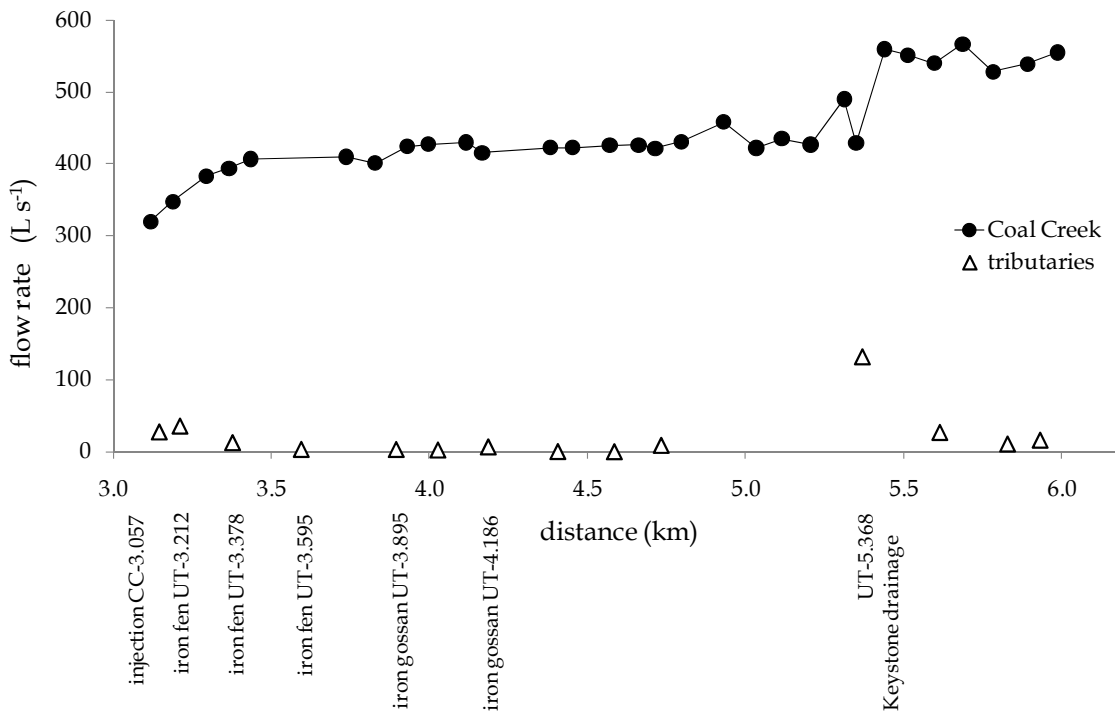
**Figure 12.** Bromide concentration at the downstream end of the Coal Creek reach (CC-5.986) as a function of time during the metal loading tracer dilution test in April 2007. Synoptic sampling commenced at 13:15.



**Figure 13.** Bromide concentration in Coal Creek and its tributaries as a function of distance downstream during the metal loading tracer dilution test in April 2007.

*Flow rate in Coal Creek.* Flow rates in Coal Creek were calculated using the bromide concentrations measured during the synoptic sampling (Table 4). One manual adjustment to the flow rate had to be made for the Town of Crested Butte’s drinking water intake located at 5.296 km. The drinking water intake flow was estimated at 79 L s<sup>-1</sup> based on communications with the Town of Crested Butte. This diverted flow was subtracted from the Coal Creek flow rate.

Corresponding with the decrease in bromide concentration with distance, flow rate in Coal Creek increased with distance (Figure 14). Some of the flow decreases may be attributed to uncertainty in the measurement of the bromide concentrations. At the upstream end of the reach, the flow rate was 320 L s<sup>-1</sup>. At the downstream end (CC-5.986), the flow rate was 560 L s<sup>-1</sup> (0.56 m<sup>3</sup> s<sup>-1</sup>, or 20 ft<sup>3</sup> s<sup>-1</sup>). These flow rates are about one-third of the flow rates measured for this reach at high flow in June 2006. Tributary flows ranged from 0.2 L s<sup>-1</sup> to 131 L s<sup>-1</sup>. The maximum tributary flow rate was measured in tributary UT-5.368, which receives water from three sources: (1) the effluent from the Mount Emmons treatment plant, (2) a roadside ditch that flows along County Road 12 from the west, and (3) a channel draining Keystone Mine property to the north.



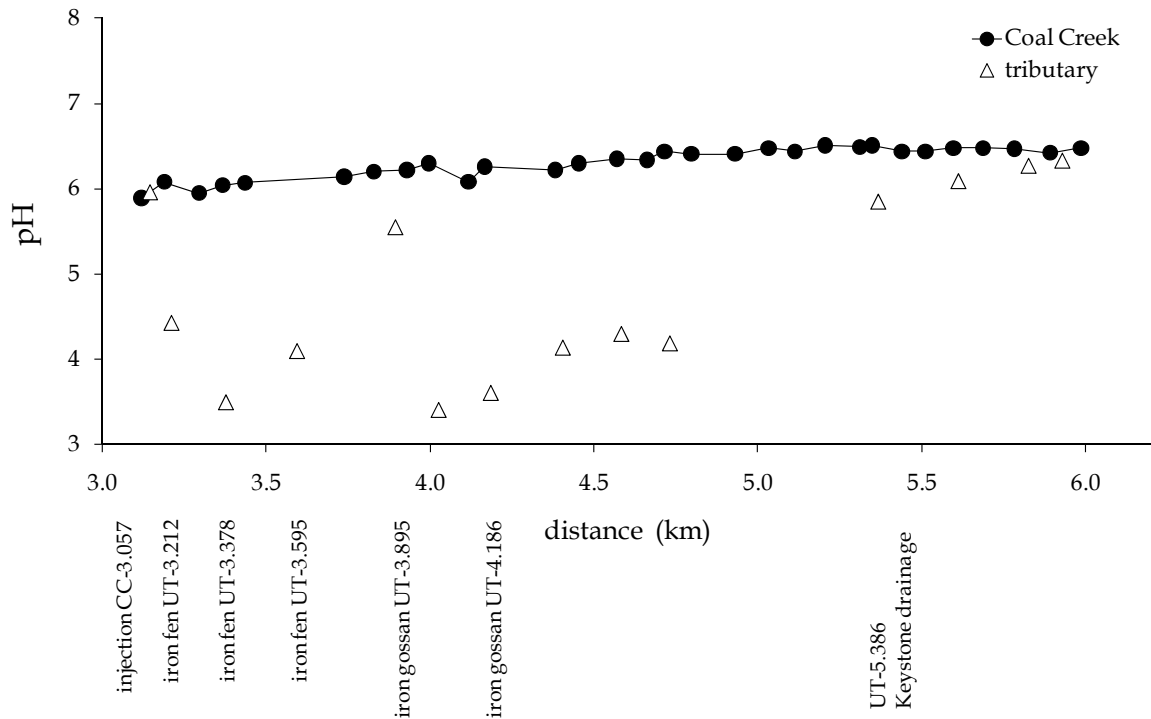
**Figure 14.** Flow rate in Coal Creek and its tributaries during the metal loading tracer dilution test in April 2007. Flow rates were calculated based on the dilution of the bromide tracer with distance downstream of the injection sites.

**Table 4.** Coal Creek flow rates at sample sites and tributaries during the metal loading tracer dilution test in April 2007. Site names are “CC-” for samples from Coal Creek and “UT-” for samples from unnamed tributaries.

site name	latitude	longitude	site description	Coal Creek flow rate (L s <sup>-1</sup> )	tributary flow rate (L s <sup>-1</sup> )
CC-0.000			September 2005 upstream sample site		
CC-3.057	38° 51' 42.3"	107° 2' 45.0"	April 2007 injection site		
CC-3.119	38° 51' 43.8"	107° 2' 43.8"		320	
UT-3.146	38° 51' 44.3"	107° 2' 43.1"	tributary draining area west of iron fen		28
CC-3.189	38° 51' 44.8"	107° 2' 41.3"		347	
UT-3.212	38° 51' 45.7"	107° 2' 40.4"	first iron fen tributary		36
CC-3.296	38° 51' 43.8"	107° 2' 37.3"		383	
CC-3.367	38° 51' 44.1"	107° 2' 34.5"		394	
UT-3.378	38° 51' 45.6"	107° 2' 31.7"	second iron fen tributary		13
CC-3.435	38° 51' 41.7"	107° 2' 32.3"		407	
UT-3.595	38° 51' 44.2"	107° 2' 26.6"	third iron fen tributary		3.4
CC-3.738	38° 51' 45.1"	107° 2' 23.1"		410	
CC-3.829	38° 51' 45.8"	107° 2' 19.7"		401	
CC-3.875	38° 51' 45.7"	107° 2' 15.5"		424	
UT-3.895	38° 51' 45.9"	107° 2' 14.9"	first iron gossan tributary		3.4
CC-3.997	38° 51' 45.0"	107° 2' 12.9"		427	
UT-4.027	38° 51' 45.6"	107° 2' 11.8"	drains area south of iron gossan		2.6
CC-4.117	38° 51' 44.9"	107° 2' 08.0"		430	
CC-4.167	38° 51' 45.6"	107° 2' 06.3"		415	
UT-4.186	38° 51' 46.6"	107° 2' 06.8"	second iron gossan tributary		6.9
CC-4.383	38° 51' 49.6"	107° 2' 00.1"		422	
UT-4.406	38° 51' 49.6"	107° 1' 59.3"	Keystone Mine drainage		0.5
CC-4.453	38° 51' 50.0"	107° 1' 57.2"		423	
CC-4.570	38° 51' 51.1"	107° 1' 52.7"		426	
UT-4.584	38° 51' 51.2"	107° 1' 52.3"	seepage from north bank of creek		0.2
CC-4.662	38° 51' 52.3"	107° 1' 49.3"		441	
CC-4.715	38° 51' 53.3"	107° 1' 47.5"		422	
UT-4.733	38° 51' 53.7"	107° 1' 47.0"	Keystone Mine drainage		8.9
CC-4.797	38° 51' 54.7"	107° 1' 44.8"		431	
CC-4.930	38° 51' 56.5"	107° 1' 39.6"		458	
CC-5.033	38° 51' 58.0"	107° 1' 36.1"		422	
CC-5.114	38° 51' 59.0"	107° 1' 33.0"		435	
CC-5.206	38° 51' 59.7"	107° 1' 29.4"		427	
CC-5.312	38° 52' 00.4"	107° 1' 27.5"		490	
CC-5.349	38° 52' 01.4"	107° 1' 24.4"		429	
UT-5.368	38° 52' 01.9"	107° 1' 24.1"	Tributary made up by (a) Mount Emmons treatment plant effluent, (b) a roadside ditch, (c) a tributary draining the eastern portion of the Keystone Mine property		131
CC-5.439	38° 52' 02.6"	107° 1' 21.1"		560	
CC-5.511	38° 52' 03.4"	107° 1' 18.7"		551	
CC-5.597	38° 52' 04.9"	107° 1' 15.9"		540	
UT-5.613	38° 52' 04.8"	107° 1' 15.4"	Keystone Mine drainage		27
CC-5.687	38° 52' 05.9"	107° 1' 12.9"		567	
CC-5.782	38° 52' 07.9"	107° 1' 09.9"		528	
UT-5.827	38° 52' 08.3"	107° 1' 08.2"	Keystone Mine drainage		11
CC-5.891	38° 52' 08.6"	107° 1' 05.3"		539	
UT-5.930	38° 52' 08.7"	107° 1' 03.8"	Keystone Mine drainage		16
CC-5.986	38° 52' 8.9"	107° 1' 1.5"		555	

### *pH and Hardness in Coal Creek*

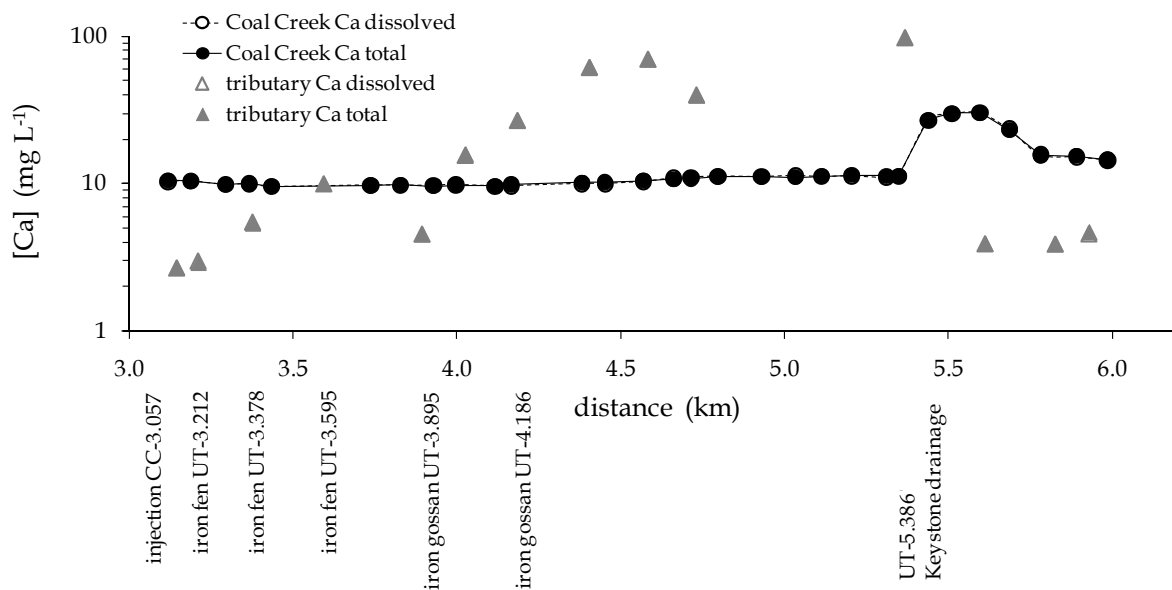
*pH in Coal Creek.* The pH in Coal Creek steadily increased from 5.9 to 6.5 over the distance downstream during the April 2007 metal loading tracer dilution test (Figure 15). Just upstream of the Town of Crested Butte’s drinking water intake at CC-5.114, the pH was measured as 6.4, which falls within the domestic drinking water supply pH range of 5.0 to 9.0 set by the Colorado Department of Public Health and Environment. The pH range established for cold water aquatic life is 6.5 to 9.0 (CDPHE, 2008). Only the downstream end of the reach sampled during this metal loading tracer dilution test meets this standard, and most of the tributaries are in violation of this standard.



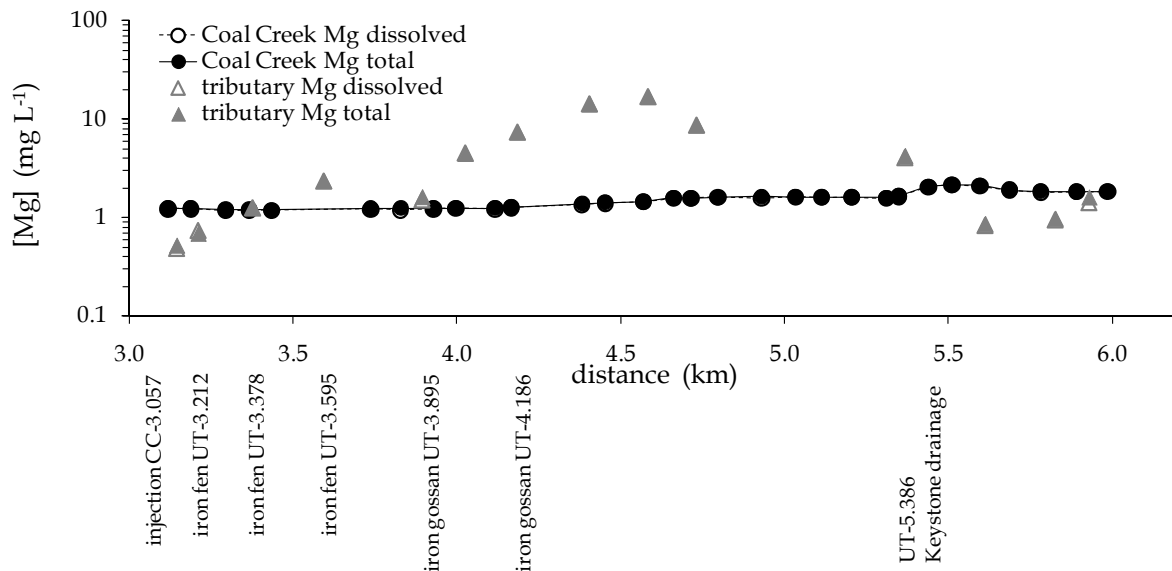
**Figure 15.** Coal Creek and tributary pH during the metal loading tracer dilution test in April 2007.

*Calcium, magnesium, and hardness in Coal Creek.* The concentration of calcium averaged about 10 mg L<sup>-1</sup> from the upstream end of the reach to UT-5.368, the tributary that includes the Mount Emmons treatment plant effluent. The addition of the UT-5.368 flow (98 mg L<sup>-1</sup> total calcium) increased the concentration of calcium in Coal Creek by about a factor of three. Further tributary inputs of lower calcium concentration resulted in a decrease in calcium concentration downstream of UT-5.368. The dissolved and total calcium concentrations were nearly equal.

The concentration of magnesium increased gradually with stream distance from about 1.2 mg L<sup>-1</sup> to 2.1 mg L<sup>-1</sup> owing to magnesium inputs from the tributaries draining the iron gossan and western side of the Keystone Mine.



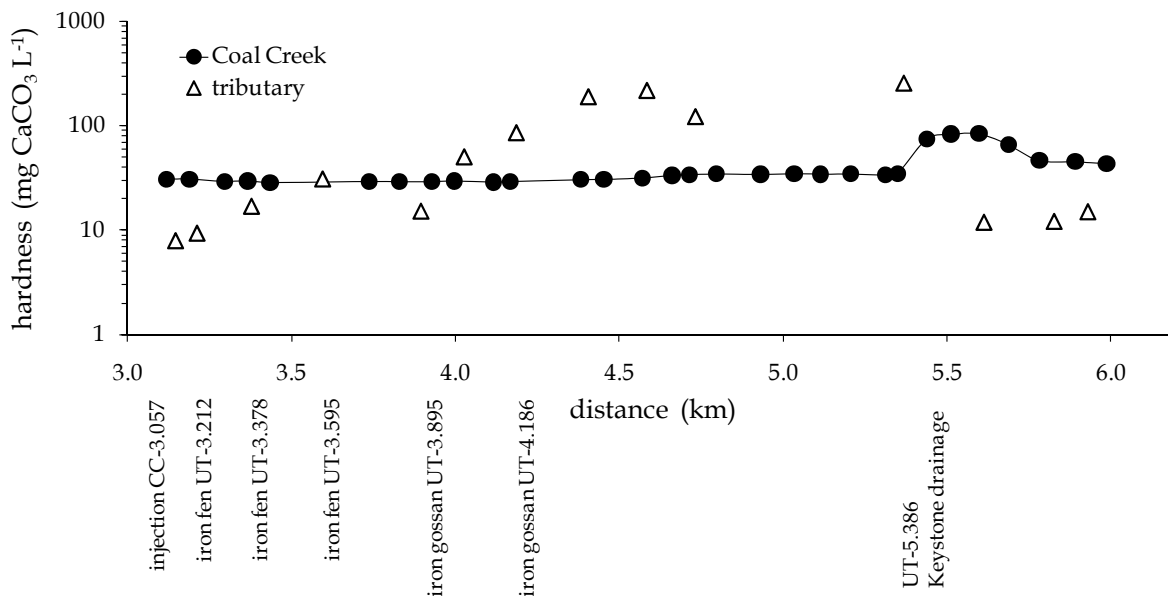
**Figure 16.** Stream and tributary calcium concentrations as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines.



**Figure 17.** Stream and tributary magnesium concentrations as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines.



Hardness was calculated as the sum of the dissolved calcium and magnesium concentrations (Equation 8). The concentration of calcium exceeded the concentration of magnesium by about 10-15 times over the reach of the metal loading tracer dilution test; therefore, hardness varied with stream distance similarly to calcium (Figure 18). Because the addition of UT-5.368, which includes the Mount Emmons treatment plant effluent, increases the calcium concentration in Coal Creek, the hardness in Coal Creek increases. The increase in hardness resulted in increases in the hardness-based standards for metal toxicity to aquatic organisms downstream of the effluent at UT-5.368.



**Figure 18.** Stream and tributary hardness as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. The stream concentrations are connected by lines.

### *Metals in Coal Creek*

For the April 2007 metal loading tracer dilution test, we measured the total and dissolved concentrations of aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc. Dissolved metal concentrations were operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The metal concentrations are compared to chronic toxicity standards for aquatic life (CDPHE, 2008), some of which were calculated using the measured hardness (Figure 18). The metal loading rates were calculated as the product of the metal concentrations and flow rates (Equation 7) for each stream and tributary sampling site.

*Aluminum.* The concentration of aluminum in Coal Creek ranged from 27 to 230  $\mu\text{g L}^{-1}$  for dissolved aluminum and from 310 to 1,060  $\mu\text{g L}^{-1}$  for total aluminum (Figure 19). The tributary concentrations were typically higher than the stream concentrations, which resulted in a steady increase in aluminum concentration in Coal Creek along the test reach. The total aluminum concentrations were always greater

than the dissolved aluminum concentrations in the stream and some of the tributaries; therefore, most of the aluminum was in the colloidal form (retained on 0.45  $\mu\text{m}$  filters). In some tributaries, particularly those with lower pH, total and dissolved aluminum concentrations were similar.

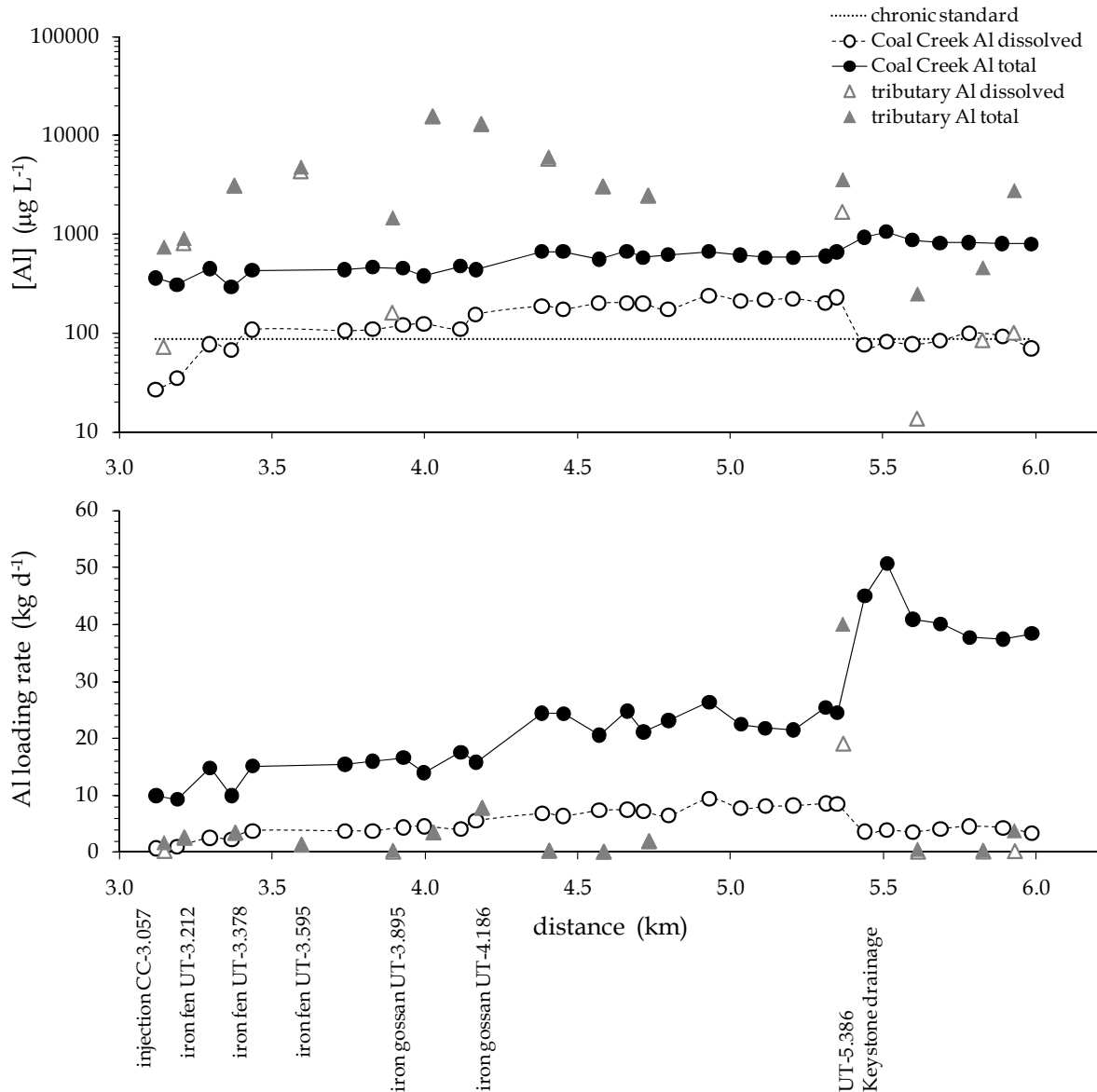
For most of the Coal Creek reach tested, dissolved aluminum concentrations were higher than the chronic toxicity standard for aquatic life ( $87 \mu\text{g L}^{-1}$  for waters of pH below 7.0; CDPHE, 2008). The addition of the Mount Emmons treatment plant effluent as part of UT-5.368 resulted in a significant decrease in the dissolved aluminum concentration even as it increased the total aluminum concentration. There is no drinking water supply standard for Colorado (CDPHE, 2008).

The loading rates for total and dissolved aluminum gradually increased over the Coal Creek reach down to UT-5.368. UT-5.368, which includes the Mount Emmons treatment plant effluent, was the largest aluminum load over the study reach (59% of the total loading rate from the tributaries). Slightly less than half of the aluminum from the effluent was dissolved and the effluent addition resulted in an increase in the total aluminum loading rate, but a decrease in the dissolved aluminum loading rate. The iron gossan tributary UT-4.186 contributed 12% of the aluminum to Coal Creek, all in the dissolved form because of the low pH of this tributary, and the other iron fen and gossan tributaries combined to contribute nearly 17% of the total aluminum, nearly all in the dissolved form. The tributaries draining the Keystone Mine property to the west and east of the treatment plant did not contribute significant amounts of aluminum.

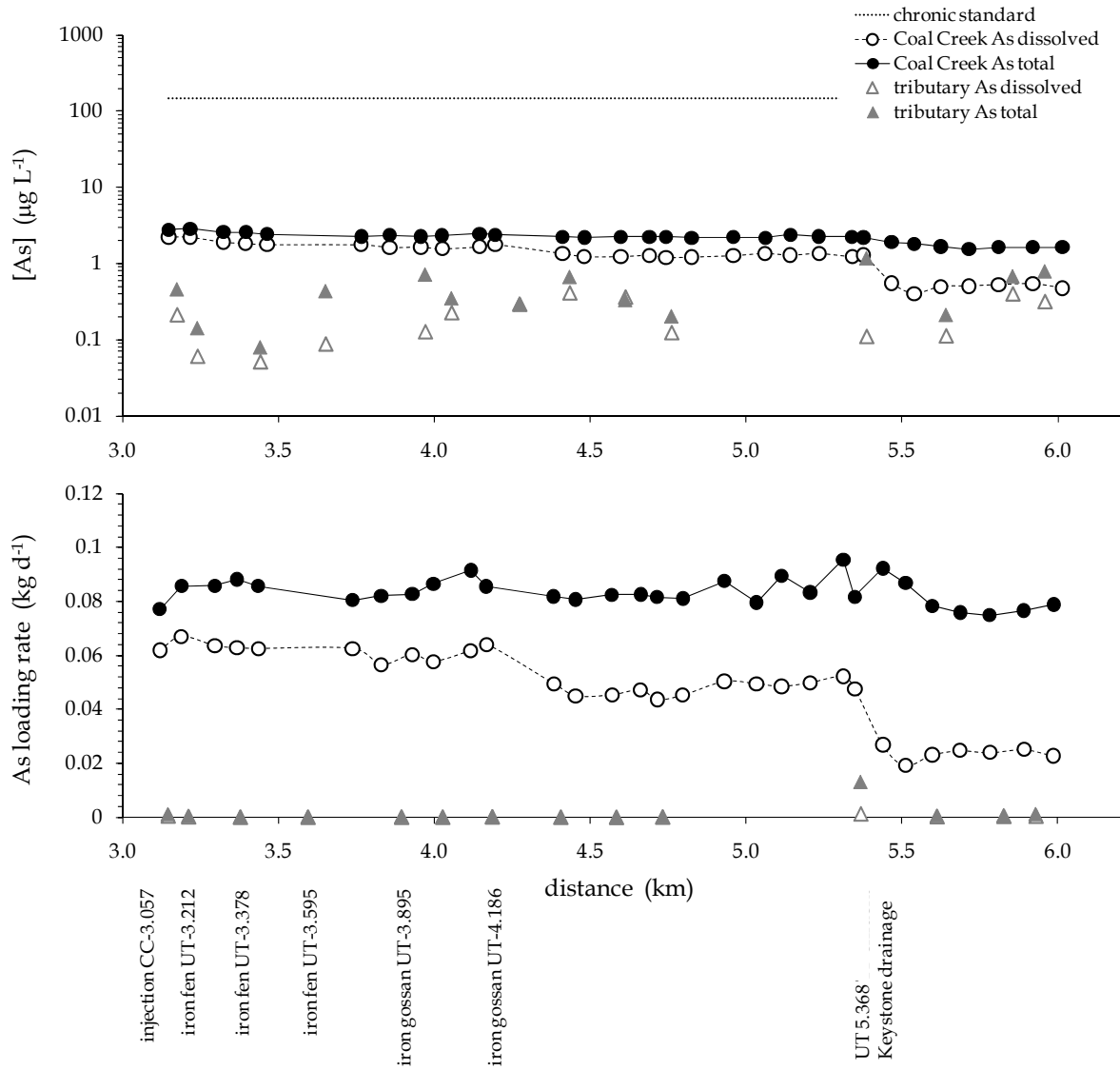
*Arsenic.* The concentration of arsenic in Coal Creek ranged from the detection limit to  $2.2 \mu\text{g L}^{-1}$  for dissolved arsenic and from  $1.6$  to  $2.9 \mu\text{g L}^{-1}$  for total arsenic (Figure 20). The tributary concentrations were typically lower than the stream concentrations, which resulted in a steady decrease in arsenic concentration over the test reach. The total arsenic concentrations were slightly greater than the dissolved concentrations in the stream and some of the tributaries; therefore, some of the arsenic was in colloidal form (retained on  $0.45 \mu\text{m}$  filters). In some tributaries, particularly those with lower pH, total and dissolved arsenic concentrations were similar.

For all of the Coal Creek reach tested, dissolved arsenic concentrations were much lower than the chronic toxicity standard for aquatic life ( $150 \mu\text{g L}^{-1}$ ; CDPHE, 2008). Arsenic did not exceed the 30-day drinking water supply standard of  $10 \mu\text{g L}^{-1}$  based on Safe Drinking Water Act maximum contaminant levels, but the CDPHE human health-based standard of  $0.02 \mu\text{g L}^{-1}$  was exceeded throughout the reach.

The only significant arsenic loading came from UT-5.368, which includes the Mount Emmons treatment plant effluent, but this loading rate is based on total arsenic concentration of only  $1.2 \mu\text{g L}^{-1}$ , just above the detection limit. None of the tributaries significantly changed the arsenic loading rate in Coal Creek.



**Figure 19.** Stream and tributary aluminum concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by  $0.45 \mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The chronic standard for toxicity to aquatic life (CDFPHE, 2008) is shown on the concentration graph.



**Figure 20.** Stream and tributary arsenic concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by  $0.45 \mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.

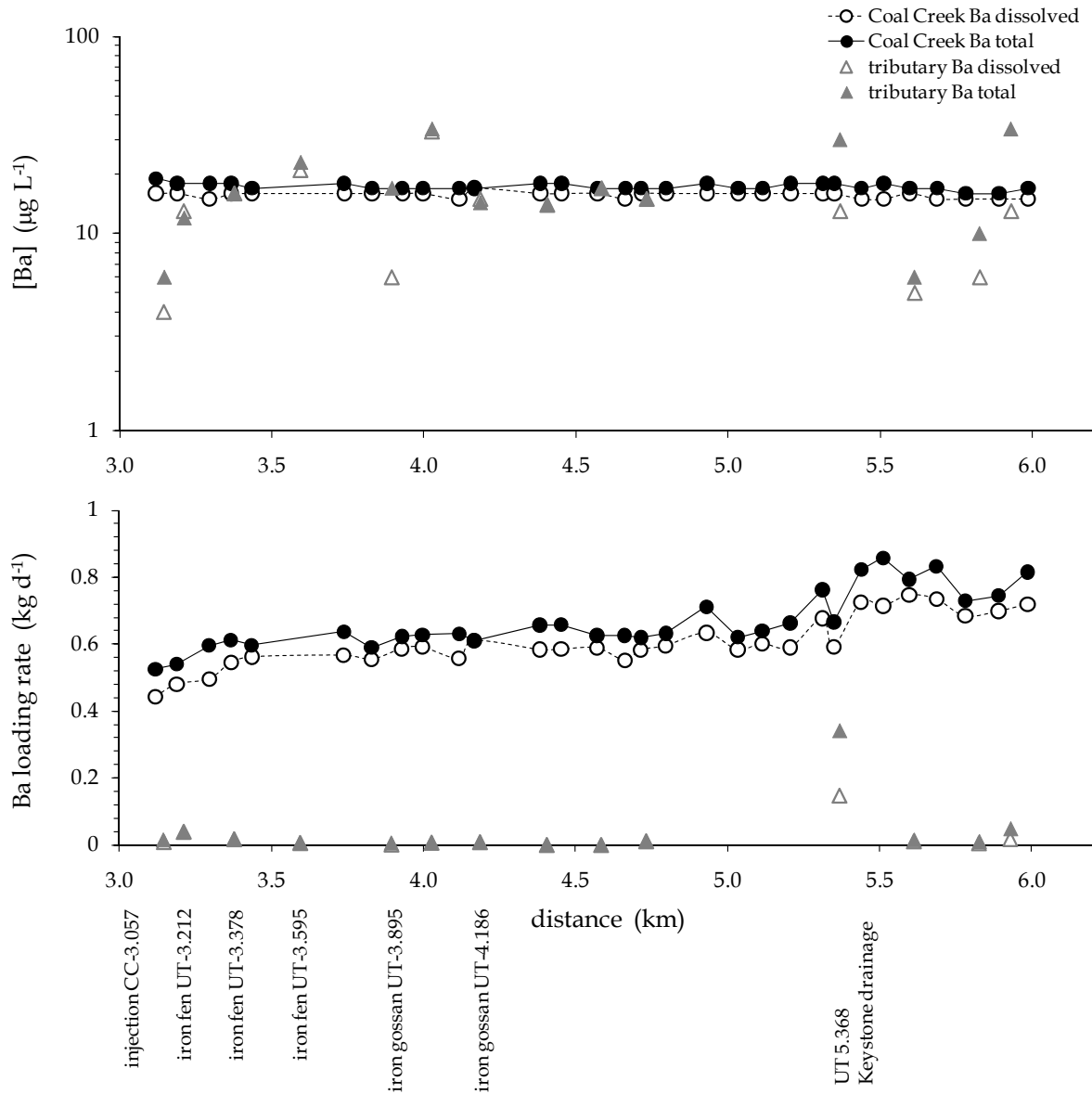
*Barium.* The concentration of barium in Coal Creek ranged from 15 to 17  $\mu\text{g L}^{-1}$  for dissolved barium and from 16 to 19  $\mu\text{g L}^{-1}$  for total barium (Figure 21). Some of the tributary concentrations were higher than and some were lower than the narrow range of barium concentrations in the stream. The total barium concentrations were slightly greater than the dissolved concentrations in the stream and some of the tributaries; therefore, a small fraction of the barium was in colloidal form (retained on 0.45  $\mu\text{m}$  filters). In some tributaries, particularly those with lower pH, total and dissolved barium concentrations were similar. There is no toxicity standard for aquatic life for barium in Colorado (CDPHE, 2008). Barium did not exceed the drinking water supply standards of 1,000  $\mu\text{g L}^{-1}$  (1-day) or 490  $\mu\text{g L}^{-1}$  (30-day) in the study reach.

The only significant barium loading came from UT-5.368, which includes the Mount Emmons treatment plant effluent (65% of the total load). The addition of UT-5.368 caused a small increase in the Coal Creek barium concentration. None of the other tributaries significantly changed the barium loading rate in Coal Creek.

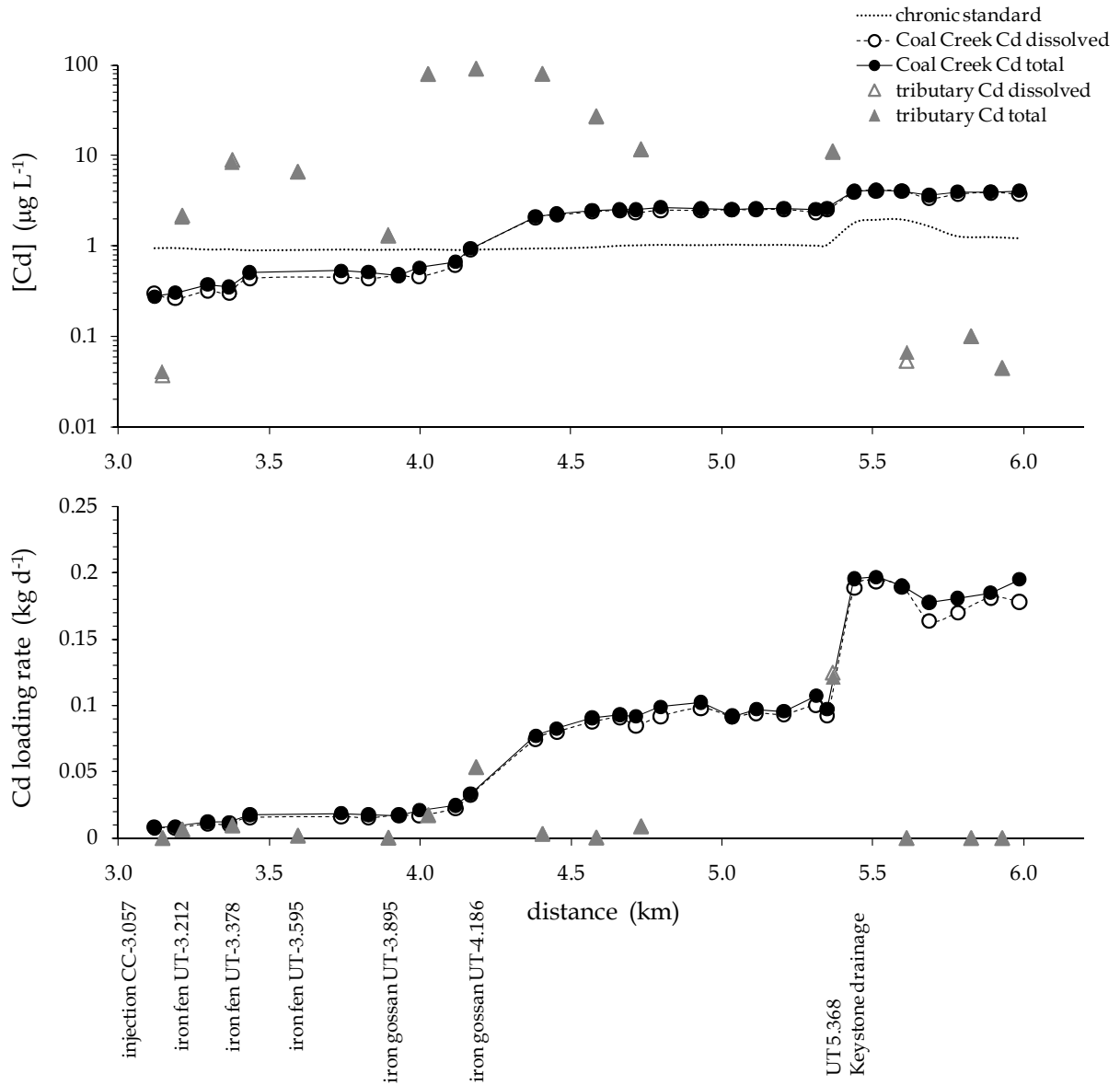
*Cadmium.* Over the 2.9 km of Coal Creek examined in this metal loading tracer dilution test, cadmium concentration increased from about 0.3 to 4.1  $\mu\text{g L}^{-1}$  (Figure 22). Most of the tributaries over the upper 2 km of the reach contained higher concentrations of cadmium than Coal Creek. Downstream of UT-5.368, the cadmium concentrations in the tributaries draining the eastern Keystone Mine property were lower than those in Coal Creek. In the stream and in the tributaries, the total and dissolved cadmium concentrations were the same – the colloidal fraction of cadmium was essentially zero.

From the tributary draining the iron gossan at 4.186 km, the dissolved cadmium concentration in Coal Creek exceeded the chronic aquatic life standard. Even below UT-5.368, where the increase in calcium results in an increase in hardness and an increase in the toxicity standard, the cadmium concentration exceeded the standard because the effluent also adds cadmium to Coal Creek. The 1-day drinking water supply standard of 5.0  $\mu\text{g L}^{-1}$  cadmium (CDPHE, 2008) was not exceeded in Coal Creek.

The two main contributions to the cadmium loading rate in Coal Creek are UT-4.186, one of the tributaries draining the iron gossan (24%), and UT-5.368, which includes the Mount Emmons treatment plant effluent (54%). The flow rate of the iron gossan tributary is low and the cadmium concentration is high (about 95 times greater than the Coal Creek concentration). For UT-5.368, the cadmium concentration is only 4 times greater than the Coal Creek concentration, but the flow rate is 19 times greater than the flow rate of the iron gossan tributary.



**Figure 21.** Stream and tributary barium concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. There is no acute or chronic standard for toxicity to aquatic life for Colorado (CDPHE, 2008).



**Figure 22.** Stream and tributary cadmium concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The hardness-based chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.

*Chromium.* The chromium concentration in Coal Creek was highest at the upstream end of the reach examined in this metal loading tracer dilution test – 1.5  $\mu\text{g L}^{-1}$  dissolved and 3.4  $\mu\text{g L}^{-1}$  total – and declined rapidly by about a factor of ten to chromium concentrations near the detection limit (Figure 23). The tributary chromium concentrations are similar to those in the stream. In the stream and in the tributaries, the total chromium concentrations typically exceed the dissolved chromium concentrations, which indicated that some of the chromium was in the colloidal fraction.

Aquatic life standards exist for chromium(III) and chromium(VI) (CDPHE, 2008). In a stream open to the atmosphere, we can assume that most of the chromium is present in the oxidized hexavalent chromium form, which is the more toxic oxidation state of chromium. The chronic aquatic life toxicity standard is 11  $\mu\text{g L}^{-1}$ , and this standard was not exceeded in Coal Creek. The 1-day drinking water supply standards of 50  $\mu\text{g L}^{-1}$  for chromium(III) or chromium(VI) (CDPHE, 2008) were not exceeded in Coal Creek.

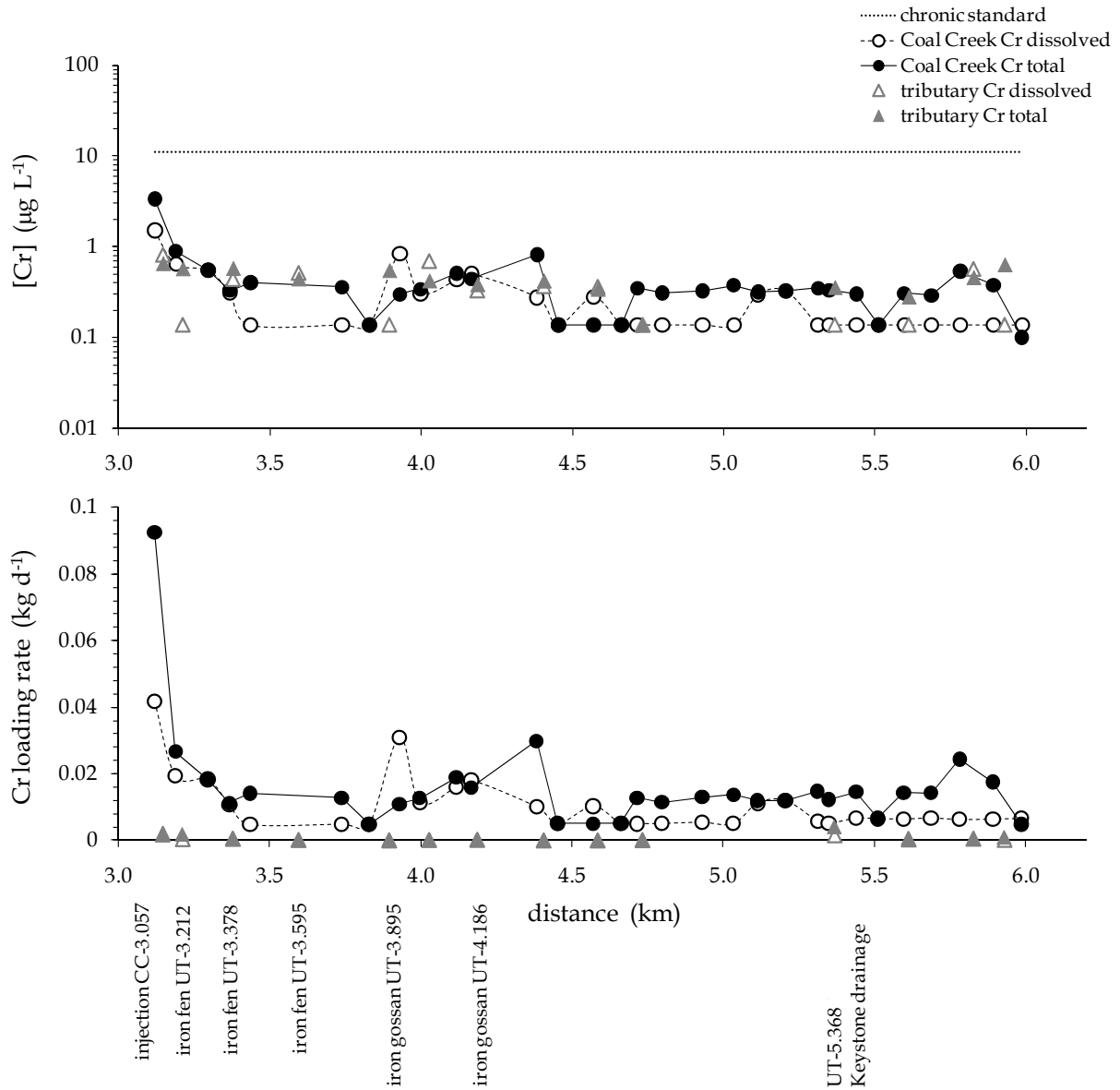
The main contributor of chromium to Coal Creek is UT-5.368, which includes the Mount Emmons treatment plant effluent, but this contribution is small and it did not increase the concentration of chromium in Coal Creek.

*Copper.* Over the 2.9 km of Coal Creek examined in this metal loading tracer dilution test, the concentration of copper increased from about 0.9 to 20  $\mu\text{g L}^{-1}$  (Figure 24). Most of the tributaries over the upper 2 km of the reach contained higher concentrations of copper than Coal Creek. Downstream of UT-5.368, the copper concentrations in the tributaries draining the eastern Keystone Mine property were lower than those in Coal Creek. In the stream and in the tributaries, the total copper concentration typically exceeded the dissolved concentration by 20-100%, which resulted in a maximum of about half of the copper in the colloidal fraction.

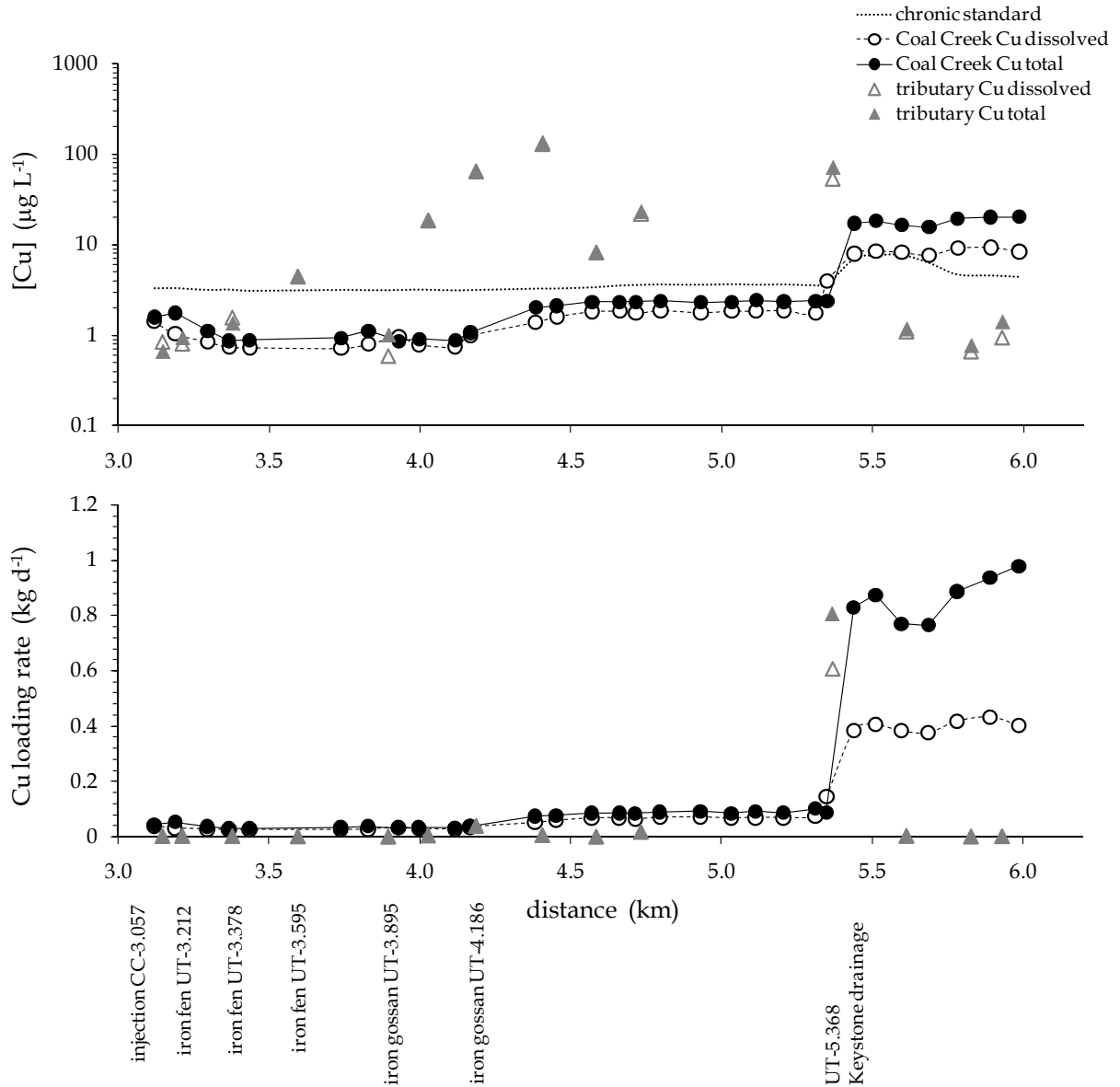
The dissolved copper concentration in Coal Creek exceeded the chronic aquatic life standard below UT-5.368, which includes the Mount Emmons treatment plant effluent, even though the effluent adds hardness and results in a higher copper standard. Copper did not exceed the 30-day drinking water supply standard of 1,000  $\mu\text{g L}^{-1}$  in the study reach.

The main copper contributor is the UT-5.368, which includes the Mount Emmons treatment plant effluent (91%). The iron gossan tributary at 4.186 km roughly doubles the copper loading rate in Coal Creek by adding 4.3% of the total copper load.





**Figure 23.** Stream and tributary chromium concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45 µm membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.



**Figure 24.** Stream and tributary copper concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The hardness-based chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.

*Iron.* The total concentration of iron in Coal Creek ranged from 220 to 320  $\mu\text{g L}^{-1}$ . The dissolved iron concentration ranged from 5 to 130  $\mu\text{g L}^{-1}$  (Figure 24). Total iron concentration increased by about 50% and dissolved iron decreased by about a factor of 10 downstream of UT-5.368, which includes the Mount Emmons treatment plant effluent. Some tributaries contained concentrations of total iron in excess of the stream concentrations, and other tributaries had lower concentrations of total iron. In the stream and in most of the tributaries, the total iron concentration exceeded the dissolved iron concentration by a factor of 2-4, which indicated that most of the iron was in the colloidal fraction. Most of the other metals in colloidal form are expected to be associated with iron in the colloidal form. Only in the iron gossan tributaries was most of the iron dissolved.

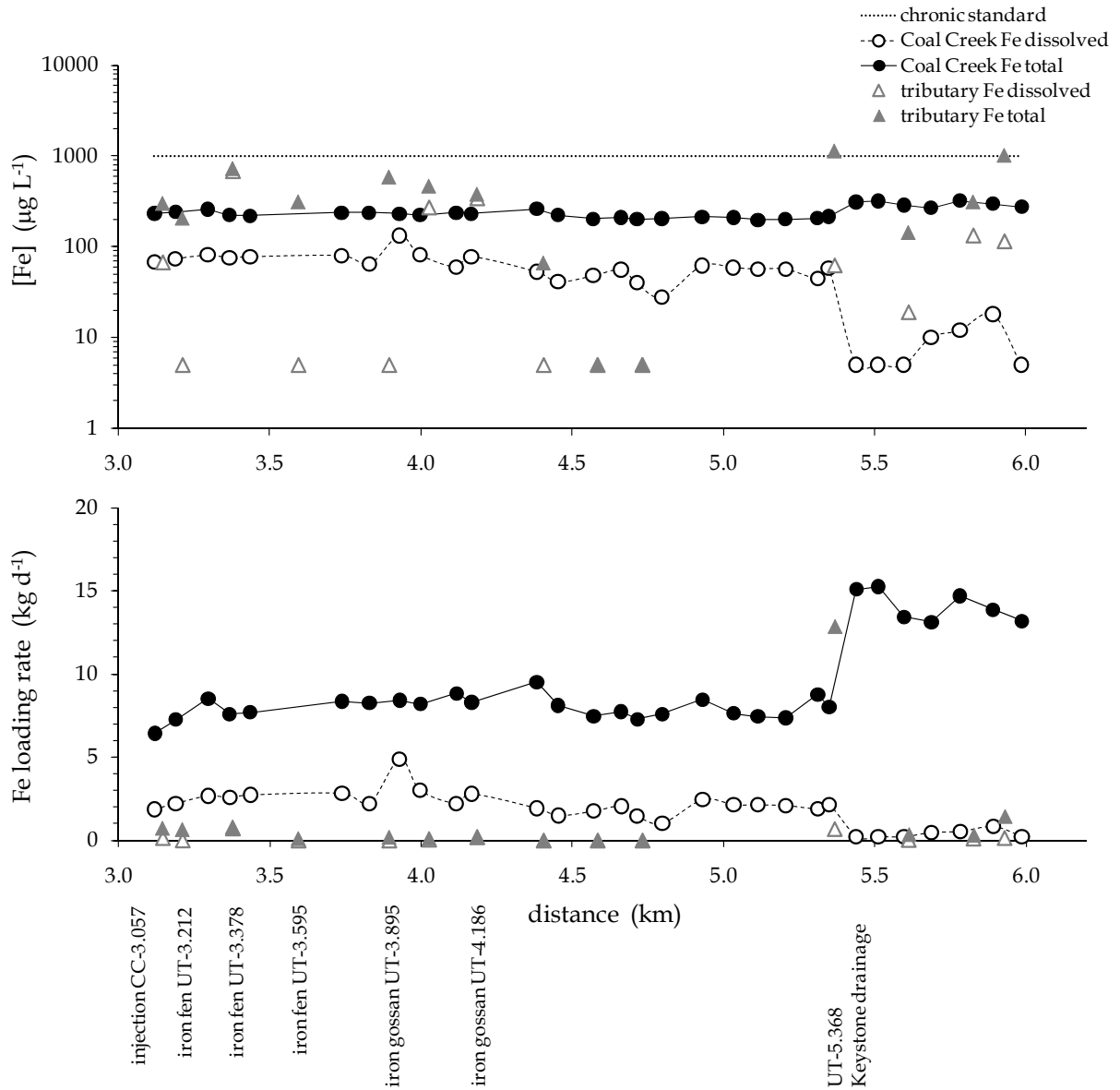
The chronic aquatic life toxicity standard for iron is 1,000  $\mu\text{g L}^{-1}$  total recoverable iron (CDPHE, 2008). The “total recoverable” iron concentration is determined by a heated digestion of the water sample. Our total iron is determined by acidification of the water sample to a pH of less than 2 for about two weeks before analysis. If we had subjected our samples to the “total recoverable” procedure, our iron concentrations might have been slightly higher, but it would be unlikely that the “total recoverable” procedure would have resulted in exceedance of the standard. The 30-day drinking water supply standard for dissolved iron, 300  $\mu\text{g L}^{-1}$  (CDPHE, 2008), was not exceeded in Coal Creek.

The main contributor of iron to Coal Creek is UT-5.368, which includes the Mount Emmons treatment plant effluent (73%). One of the tributaries draining the east side of the Keystone Mine property, UT-5.930, contributed 8.1% of the total iron loading rate.

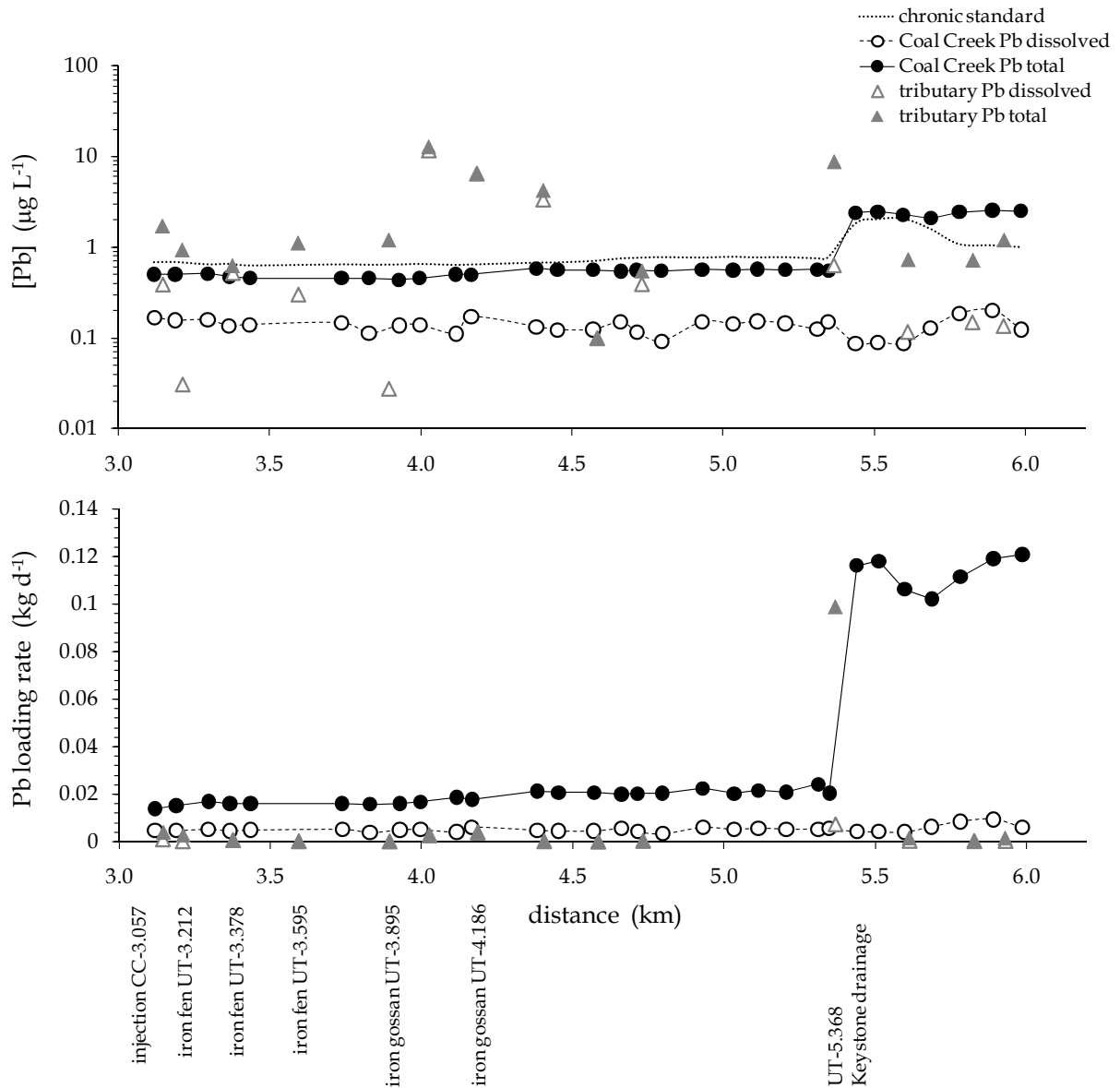
*Lead.* Over the 2.9 km of Coal Creek examined in this metal loading tracer dilution test, the total concentration of lead increased from about 0.5 to 2.5  $\mu\text{g L}^{-1}$  and the dissolved concentration decreased from about 0.2 to 0.1  $\mu\text{g L}^{-1}$  (Figure 26). Some tributary lead concentrations were higher than those in Coal Creek, and other tributary lead concentrations were lower than those in Coal Creek. Immediately downstream of UT-5.368, the total lead concentration increased by a factor of four and the dissolved lead concentration decreased by a factor of about two. In the stream and in most of the tributaries (except those of low pH), the total lead concentration exceeded the dissolved concentration by a factor of 4-12, which indicates that most of the lead was in the colloidal fraction.

The dissolved lead concentrations in Coal Creek never exceeded the hardness-based chronic aquatic life toxicity standard. Lead did not exceed the 1-day drinking water supply standard of 50  $\mu\text{g L}^{-1}$  in the study reach.

Downstream of UT-5.368, the total lead concentration did exceed the standard, but 90-95% of that lead is colloidal, and colloidal metals are not considered toxic to aquatic life. The main lead contributor is UT-5.368, which includes the Mount Emmons treatment plant effluent (84%).



**Figure 25.** Stream and tributary iron concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45  $\mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.



**Figure 26.** Stream and tributary lead concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by  $0.45 \mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The hardness-based chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.

*Manganese.* Over the Coal Creek reach examined in this metal loading tracer dilution test, the total concentration of manganese increased from 25 to 460  $\mu\text{g L}^{-1}$  and the dissolved concentration decreased from 20 to 460  $\mu\text{g L}^{-1}$  (Figure 27). The concentrations of manganese increased just downstream of the iron gossan tributary at 4.186 km and UT-5.368, which includes the Mount Emmons treatment plant effluent. Most of the tributaries contained concentrations of manganese that were higher than the concentrations of manganese in the stream. With the exception of a few tributaries, the total and dissolved manganese concentrations were similar, which indicates that the manganese was not present in the colloidal fraction.

The dissolved manganese concentrations in Coal Creek never exceeded the hardness-based chronic aquatic life toxicity standard. In contrast, the 30-day drinking water supply standard, 50  $\mu\text{g L}^{-1}$  for dissolved manganese (CDPHE, 2008), was exceeded from CC-4.167 to the downstream end of the reach.

The main contributors of manganese to Coal Creek are UT-4.186, the iron gossan tributary (15%); UT-4.733, a tributary draining the western part of the Keystone Mine property (19%); and UT-5.368, which includes the Mount Emmons treatment plant effluent (59%).

*Nickel.* The total concentrations of nickel ranged from 0.7 to 3.5  $\mu\text{g L}^{-1}$  and the dissolved concentrations were similar; therefore, very little of the nickel was in the colloidal phase (Figure 28). The highest concentration of nickel was found at the upstream end of the reach. Increases in nickel concentration occurred just downstream of the iron gossan tributary at 4.186 km and UT-5.368, which includes the Mount Emmons treatment plant effluent. Most of the tributaries contained concentrations of nickel that were higher than the concentrations of nickel in the stream.

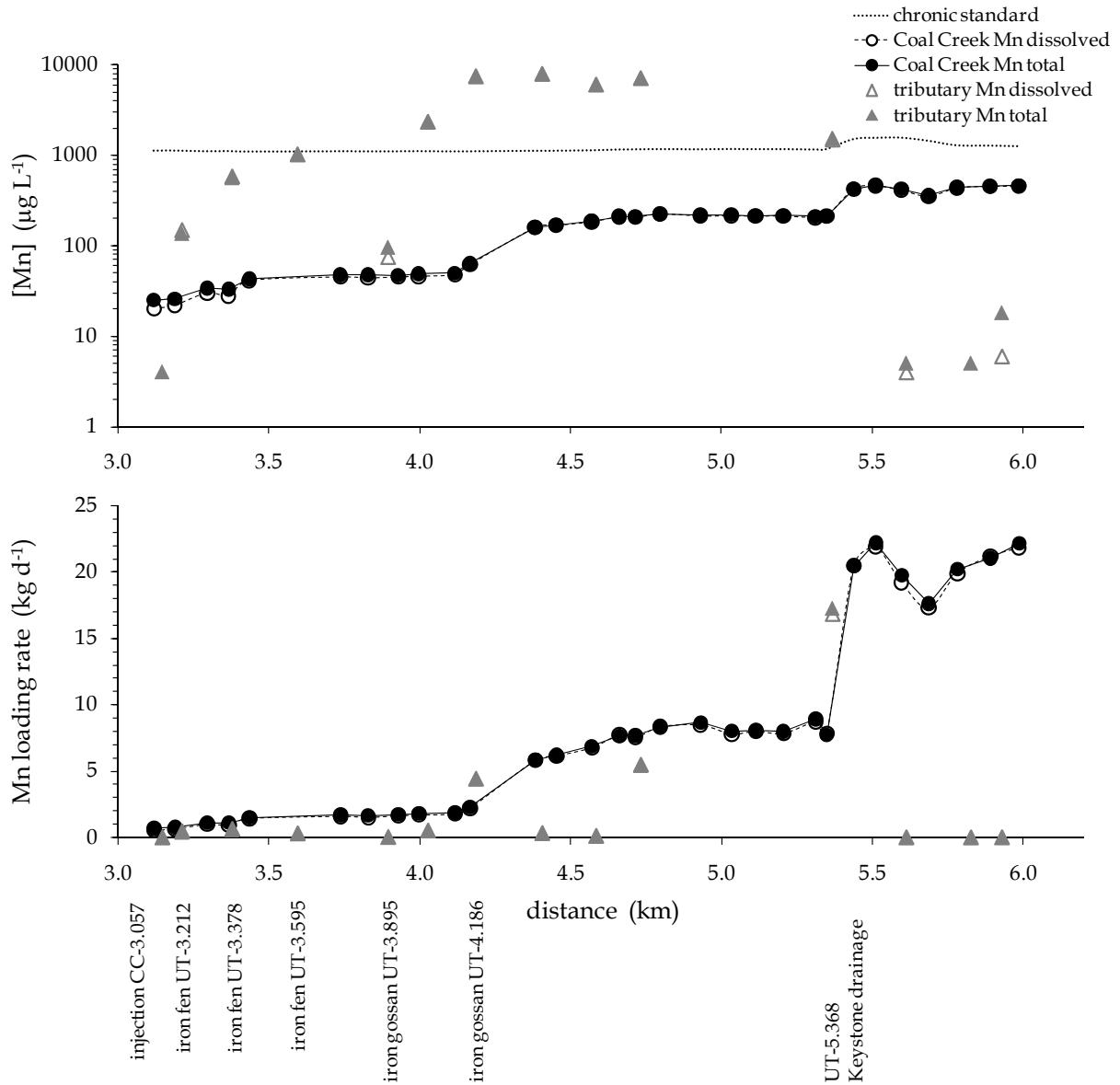
The dissolved nickel concentrations in Coal Creek never exceeded the hardness-based chronic aquatic life toxicity standard or the 30-day drinking water supply standard, 100  $\mu\text{g L}^{-1}$  for dissolved nickel (CDPHE, 2008).

The main contributors of nickel to Coal Creek are UT-4.186, the iron gossan tributary (15%); UT-4.733, a tributary draining the western part of the Keystone Mine property (19%); and UT-5.368, which includes the Mount Emmons treatment plant effluent (59%).

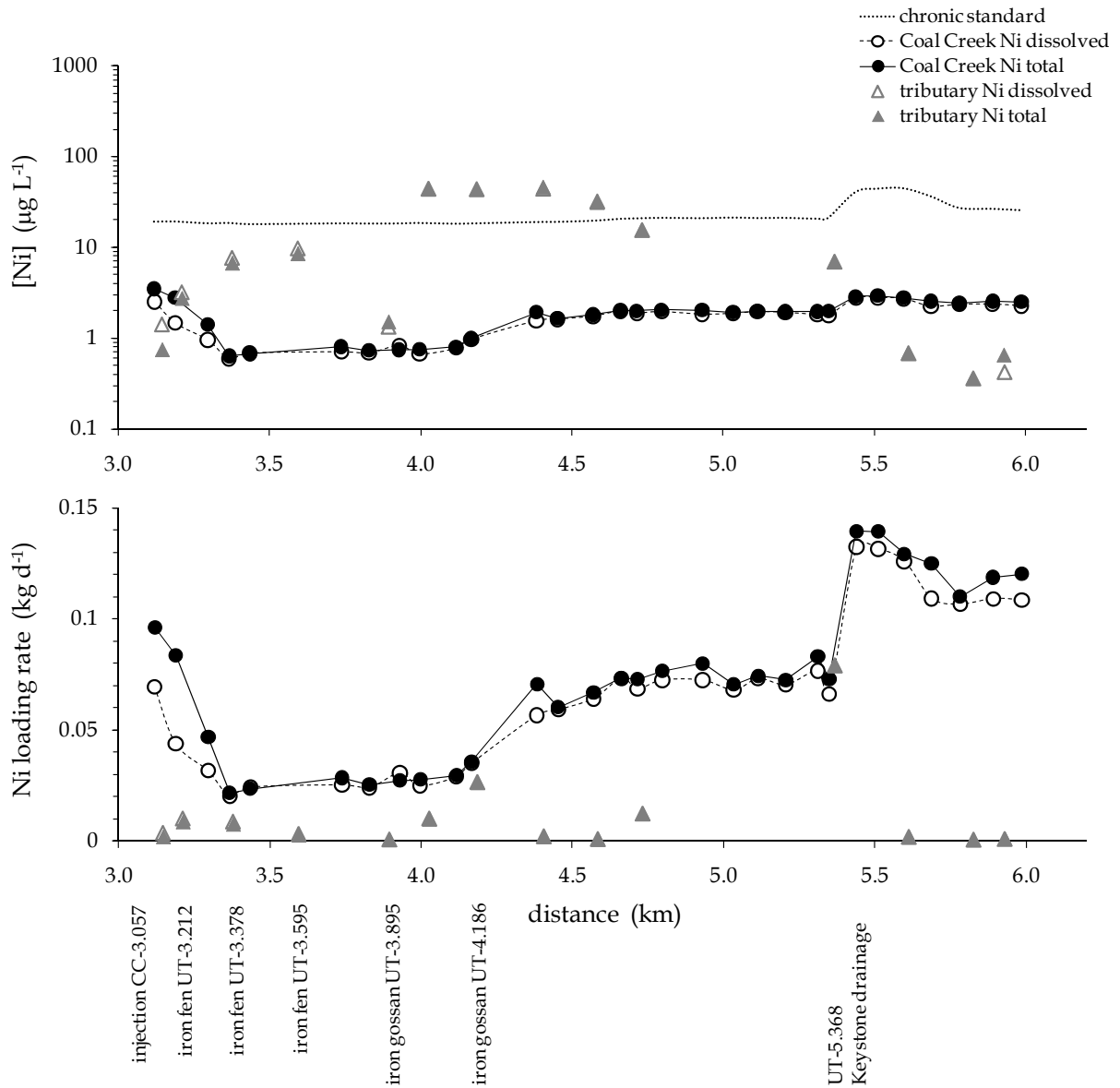
*Zinc.* Over the reach of Coal Creek examined in this metal loading tracer dilution test, the total concentration of zinc increased from 80 to 780  $\mu\text{g L}^{-1}$  (Figure 29). The dissolved zinc concentrations were 5-10% lower than the total zinc concentrations, which indicates that a small fraction of the zinc was in the colloidal phase. Most of the tributaries over the upper 2 km of the reach contained higher concentrations of zinc than Coal Creek. Downstream of UT-5.368, which includes the Mount Emmons treatment plant effluent, the zinc concentrations in the tributaries draining the eastern Keystone Mine property were lower than those in Coal Creek.

Throughout this reach of Coal Creek, the dissolved zinc concentration exceeded the chronic aquatic life standard. Zinc did not exceed the 30-day drinking water supply standard of 5,000  $\mu\text{g L}^{-1}$  in the study reach (CDPHE, 2008).

The main zinc contributor was UT-5.368, which includes the Mount Emmons treatment plant effluent (50%). The iron gossan tributary at 4.186 km contributed 24% of the zinc to Coal Creek.

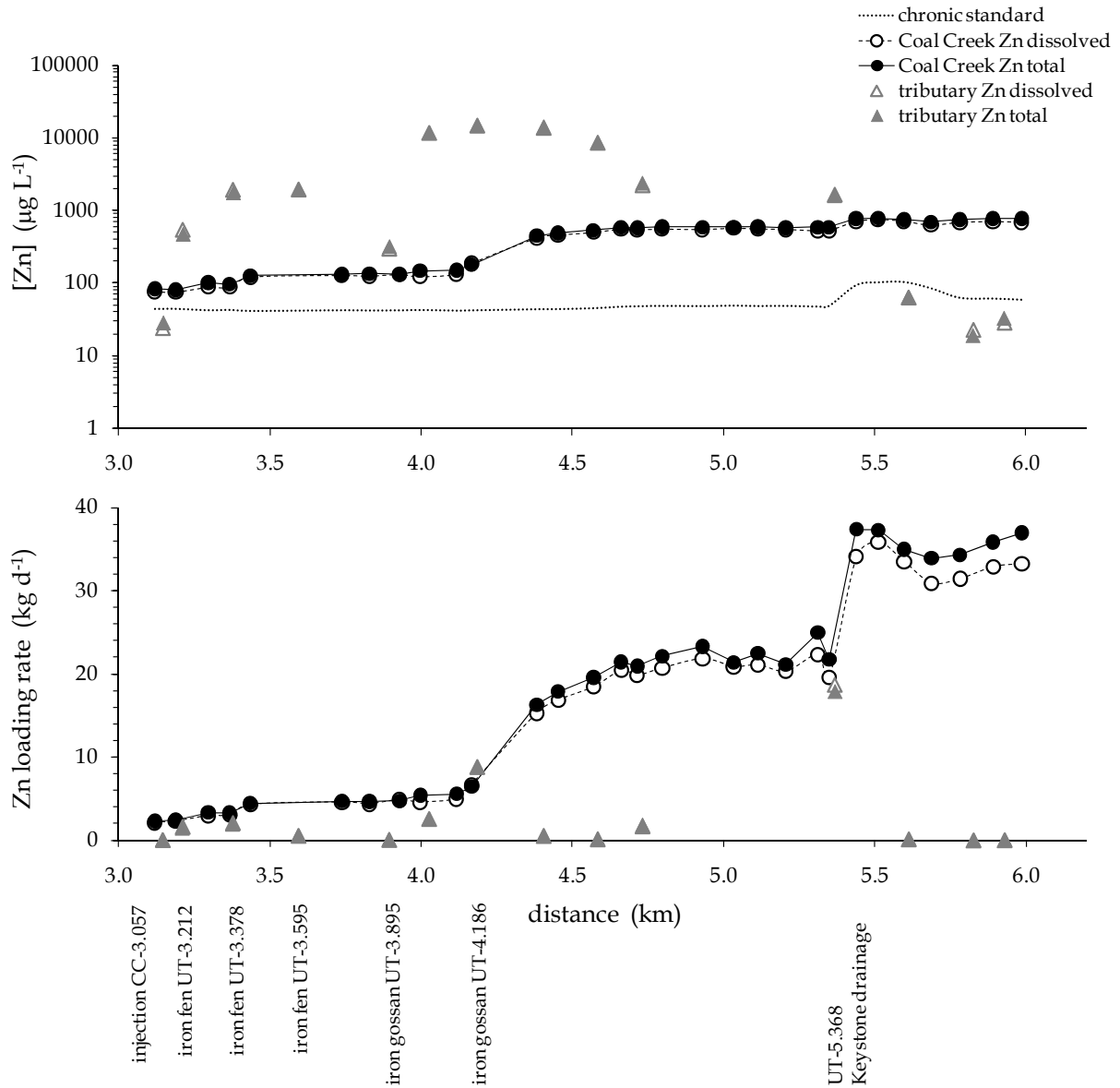


**Figure 27.** Stream and tributary manganese concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by  $0.45 \mu\text{m}$  membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The hardness-based chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.



**Figure 28.** Stream and tributary nickel concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45 µm membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The hardness-based chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.





**Figure 29.** Stream and tributary zinc concentrations (upper) and loading rates (lower) as a function of distance in Coal Creek during the metal loading tracer dilution test in April 2007. Dissolved concentrations operationally defined by 0.45 µm membrane filtration. The concentrations are displayed on a logarithmic axis. The stream concentrations are connected by lines. The hardness-based chronic standard for toxicity to aquatic life (CDPHE, 2008) is shown on the concentration graph.

*Metal contributions from Tributary UT-5.368.* The tributary UT-5.368 is a combination of three sources: (1) the effluent from the Mount Emmons treatment plant, which may collect some surface runoff, (2) a roadside ditch draining the north side of County Road 12 west of the tributary, and (3) a channel draining part of the eastern half of the Keystone Mine property (Figure 30). The treatment plant effluent contained the highest concentrations of aluminum, cadmium, manganese, nickel, and zinc (Figure 31). The roadside ditch contained the highest concentrations of arsenic, barium, and chromium, which are all present at low concentrations. The channel draining the eastern Keystone mine property contained the highest concentrations of copper, iron, and lead.

The flow rate of UT-5.368 was measured as 131 L s<sup>-1</sup>. The samples collected from the effluent, roadside ditch, and drainage did not contain any added bromide and were not measured for any constituents that would work well as conservative tracers. At the pH of these waters, however, calcium and magnesium are expected to be adequately conservative. Using the calcium and magnesium concentrations of the three sources and the total flow rate, the flow rates of the three sources were estimated (Table 5) by finding a unique trio of flow rates that satisfied the following equations:

$$[\text{Ca}]_{\text{METP}} Q_{\text{METP}} + [\text{Ca}]_{\text{ditch}} Q_{\text{ditch}} + [\text{Ca}]_{\text{KM}} Q_{\text{KM}} = [\text{Ca}]_{5.368} Q_{5.368} \quad (10)$$

$$[\text{Mg}]_{\text{METP}} Q_{\text{METP}} + [\text{Mg}]_{\text{ditch}} Q_{\text{ditch}} + [\text{Mg}]_{\text{KM}} Q_{\text{KM}} = [\text{Mg}]_{5.368} Q_{5.368} \quad (11)$$

$$Q_{\text{METP}} + Q_{\text{ditch}} + Q_{\text{KM}} = Q_{5.368} \quad (12)$$

where  $Q$  is the flow rate and the subscripts *METP*, *ditch*, *KM*, and *5.368* refer to the Mount Emmons treatment plant effluent, the roadside ditch, the Keystone Mine drainage, and the combined tributary UT-5.368, respectively. The Mount Emmons treatment plant effluent contains a high concentration of calcium because lime (CaO) is used to form metal hydroxide solids at high pH. The roadside ditch contains a high concentration of magnesium because of the use of magnesium chloride for dust suppression on County Road 12.

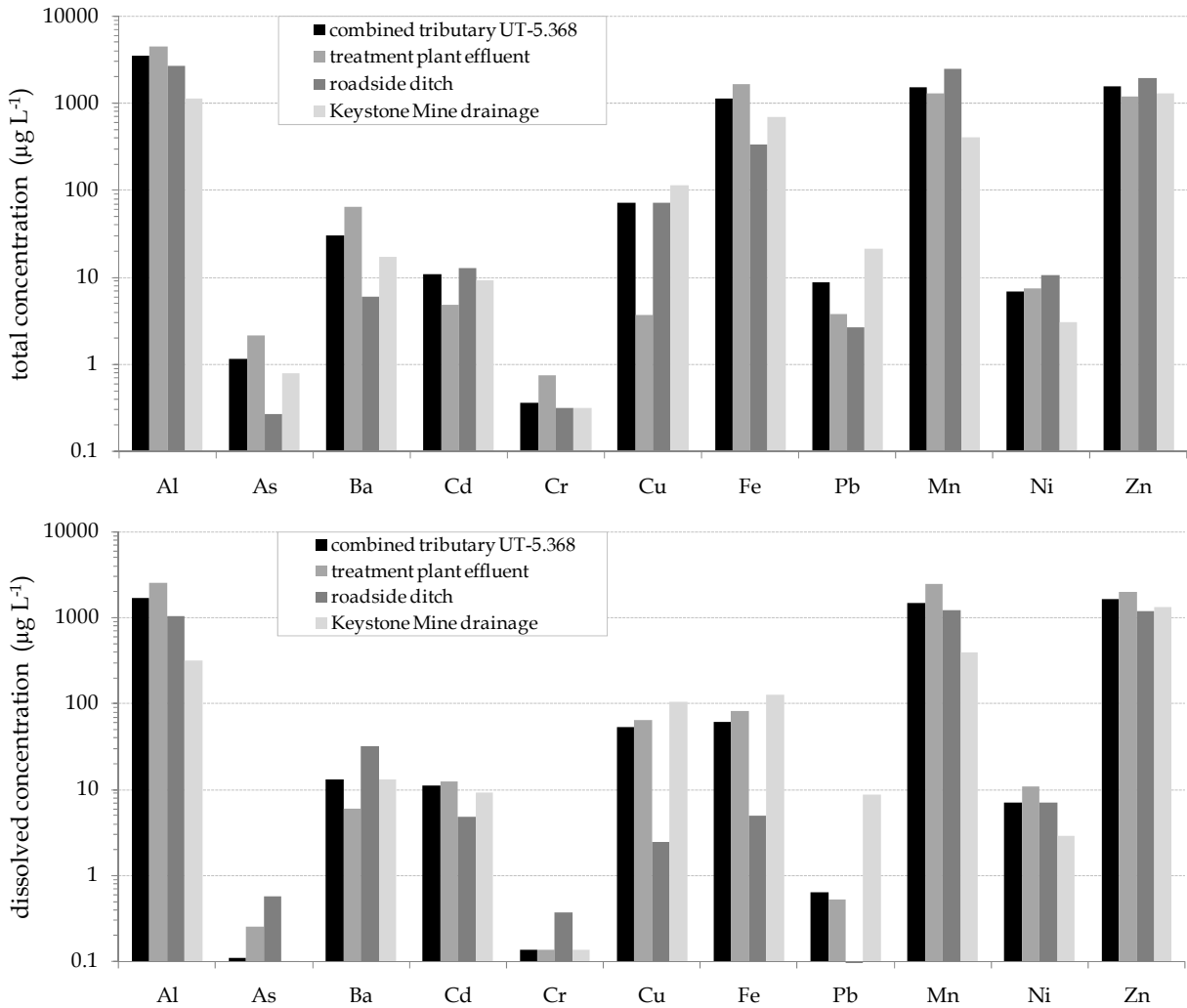
The differences in the calcium and magnesium concentrations between the three drainages allowed identification of a unique trio of flow rates (Table 5). The release of effluent from the treatment plant is not steady; it varies from 0 to 79 L s<sup>-1</sup> over each day and concludes at 16:00 (John Perusek, personal communication, July 15, 2005). Based on the estimated flow rate of 69.3 L s<sup>-1</sup> for the treatment plant effluent, our synoptic sampling occurred at a time of near-peak effluent discharge.

**Table 5.** Dissolved calcium and magnesium and measured and estimated flow rates for the tributary UT-5.368 and the three drainages that combine to form UT-5.368. The flows were estimated using Equations 10, 11, and 12. The estimated flows are shown in italic font for the three drainages.

<b>designation: tributary</b>	<b>dissolved [Ca] (mg L<sup>-1</sup>)</b>	<b>dissolved [Mg] (mg L<sup>-1</sup>)</b>	<b>flow rate (L s<sup>-1</sup>)</b>
UT-5.368: combined tributary at 5.368 km	97.5	4.04	131.0
METP: Mount Emmons treatment plant effluent	179	5.86	<i>69.30</i>
ditch: roadside ditch	42.5	13.78	<i>2.45</i>
KM: channel draining eastern Keystone Mine property	6.00	1.50	<i>59.25</i>



**Figure 30.** Photographs of the drainages combining to make up the tributary UT-5.368: (upper left) view from the south side of County Road 12 where the oval culvert in left background drains the road-side ditch and the cast-iron pipes drain the treatment plant effluent and the Keystone Mine drainage; (upper right) view of the road-side ditch on the north side of County Road 12 which drains through the oval culvert; (lower left) close-up view of the Mount Emmons treatment plant effluent; and (lower right) the Keystone Mine drainage which is joined by the treatment plant effluent at the blue arrow.



**Figure 31.** Total (upper) and dissolved (lower) metal concentrations for the three sources that combine to form the tributary UT-5.368. The concentrations are shown on logarithmic axes. The combined tributary is formed by the confluence of (1) the Mount Emmons treatment plant effluent, (2) the roadside ditch along County Road 12, and (3) a Keystone Mine drainage.

### *Summary of Metal Loading Contributions in Coal Creek*

To quantify the contribution of each tributary to the overall Coal Creek metal loading, tributary loading rates were expressed as percentages of the cumulative loading rates for total and dissolved metals using Equation 7. The metal loading contributions are presented in Table 6.

The tributary UT-5.368 was a major source of all of the metals measured as total, and a major source of all but two of the metals measured as dissolved (0.45  $\mu\text{m}$ -filtered). For dissolved chromium and iron, this tributary was a minor source. Three drainages combined to make this tributary to Coal Creek – the treatment plant effluent, the roadside ditch, and a Keystone Mine drainage. On its own, the treatment plant effluent was a major source of aluminum, cadmium, copper, manganese, and nickel. The roadside ditch was a trace source for all of the metals measured. The Keystone Mine drainage was a major source of barium, copper, and lead and total arsenic and iron.

The iron gossan tributary UT-4.186 was a minor metal source for cadmium, manganese, nickel, and zinc in the total and dissolved forms and aluminum and lead in the dissolved form. The low pH of UT-4.186 (3.61) resulted in dissolved metal concentrations approximately equal to total metal concentrations for nearly all of the metals, even those that were found predominantly in the colloidal form in other tributaries and in Coal Creek.

In addition to the major metal contributions from UT-5.368 (the treatment plant effluent and the Keystone Mine drainage) and UT-4.186, the iron gossan drainage, a few other tributaries made minor contributions to the metal loading in Coal Creek.

- UT-3.146, the first tributary sampled downstream of the injection, was a minor contributor of dissolved arsenic and chromium;
- UT-3.212, the first iron fen tributary, was a minor contributor of dissolved barium and total chromium;
- UT-3.378, the second iron fen tributary, was a major contributor of dissolved iron;
- UT-4.027, a tributary south of the iron gossan, was a minor contributor of dissolved lead;
- UT-4.733, a tributary draining the western part of the Keystone Mine property, was a minor contributor of manganese; and
- UT-5.930, a tributary draining the eastern part of the Keystone Mine property, was a minor contributor of dissolved arsenic.

**Table 6.** Total (“Tot”) and dissolved (“Diss”) metal loading rates expressed as percentages of the cumulative total metal loading rate for Coal Creek as determined by Equation 7. Percentages between 12% and 33% are highlighted in italic font (“minor” sources); percentages greater than 33% are highlighted in bold font (“major” sources). Percentages of less than 0.1% are shown as blank entries. Percentages are shown in grey for the three sources that combine to form the tributary UT-5.368. The cumulative total loading rate is shown on the final line of the table.

Source / Tributary	Tot Al (%)	Tot As (%)	Tot Ba (%)	Tot Cd (%)	Tot Cr (%)	Tot Cu (%)	Tot Fe (%)	Tot Pb (%)	Tot Mn (%)	Tot Ni (%)	Tot Zn (%)
UT-3.146	2.6	6.1	2.7		14.5	0.2	4.0	3.4		1.2	0.2
UT-3.212 1 <sup>st</sup> iron fen	4.1	2.4	7.1	2.9	16.5	0.3	3.6	2.4	1.4	5.5	4.0
UT-3.378 2 <sup>nd</sup> iron fen	4.9	0.5	3.4	4.1	5.9	0.2	4.5	0.6	2.1	4.9	5.3
UT-3.595 3 <sup>rd</sup> iron fen	2.1	0.7	1.3	0.9	1.2	0.1	0.5	0.3	1.0	1.7	1.6
UT-3.895 1 <sup>st</sup> iron gossan	0.6	1.2	0.9	0.2	1.5		1.0	0.3	0.1	0.3	0.3
UT-4.027	5.1	0.4	1.4	7.9	0.9	0.5	0.6	2.4	1.7	6.4	7.1
UT-4.186 2 <sup>nd</sup> iron gossan	11.4	1.0	1.6	23.8	2.1	4.3	1.3	3.3	15.0	17.1	24.4
UT-4.406 west Keystone Mine	0.4	0.2	0.1	1.5	0.2	0.6		0.1	1.1	1.2	1.6
UT-4.584 west Keystone Mine	0.1		0.1	0.2	0.1				0.4	0.4	0.4
UT-4.733 west Keystone Mine	2.8	0.9	2.2	4.1	1.0	2.0		0.4	18.5	8.0	5.0
UT-5.368 combined tributary	<b>58.9</b>	<b>74.2</b>	<b>65.4</b>	<b>54.4</b>	<b>37.7</b>	<b>91.1</b>	<b>72.9</b>	<b>83.5</b>	<b>58.5</b>	<b>51.5</b>	<b>49.6</b>
treatment plant effluent	41.3	19.5	17.2	33.3	19.4	39.0	24.5	10.6	50.5	40.6	31.0
roadside ditch	2.5	5.5	6.6	0.5	1.6	0.1	4.3	0.5	0.9	1.0	0.7
Keystone Mine drainage	15.1	49.2	41.6	20.7	16.7	52.0	44.1	72.3	7.1	9.9	17.9
UT-5.613 east Keystone Mine	0.8	2.7	2.7	0.1	6.1	0.3	1.9	1.4		1.1	0.4
UT-5.827 east Keystone Mine	0.6	3.6	1.8		4.0	0.1	1.7	0.6		0.2	
UT-5.930 east Keystone Mine	5.6	6.2	9.1		8.3	0.2	8.1	1.4	0.1	0.6	0.1
<b>Cumulative total load (kg d<sup>-1</sup>)</b>	<b>68.1</b>	<b>0.02</b>	<b>0.52</b>	<b>0.22</b>	<b>0.01</b>	<b>0.88</b>	<b>17.7</b>	<b>0.17</b>	<b>29.5</b>	<b>0.15</b>	<b>36.1</b>

Source / Tributary	Diss Al (%)	Diss As (%)	Diss Ba (%)	Diss Cd (%)	Diss Cr (%)	Diss Cu (%)	Diss Fe (%)	Diss Pb (%)	Diss Mn (%)	Diss Ni (%)	Diss Zn (%)
UT-3.146	0.4	14.5	3.3		31.8	0.3	7.2	5.6		2.1	0.2
UT-3.212 1 <sup>st</sup> iron fen	6.2	5.4	14.0	2.9	6.9	0.4	0.7	0.6	1.6	6.3	4.5
UT-3.378 2 <sup>nd</sup> iron fen	8.5	1.6	6.1	4.3	7.9	0.3	33.4	3.5	2.2	5.4	5.7
UT-3.595 3 <sup>rd</sup> iron fen	3.2	0.7	2.2	0.8	2.5	0.2	0.1	0.5	1.0	1.8	1.5
UT-3.895 1 <sup>st</sup> iron gossan	0.1	1.1	0.6	0.2	0.6		0.1		0.1	0.2	0.2
UT-4.027	8.6	1.4	2.5	7.6	2.5	0.6	2.7	15.8	1.8	6.3	7.0
UT-4.186 2 <sup>nd</sup> iron gossan	19.4	5.0	3.1	23.6	3.2	5.7	9.1	23.6	15.2	16.8	23.7
UT-4.406 west Keystone Mine	0.6	0.5	0.2	1.4	0.2	0.8		0.8	1.1	1.2	1.5
UT-4.584 west Keystone Mine	0.1	0.2	0.1	0.2	0.1				0.4	0.4	0.4
UT-4.733 west Keystone Mine	4.7	2.8	4.0	3.9	1.7	2.5	0.2	1.9	18.8	7.7	4.6
UT-5.368 combined tributary	<b>47.5</b>	<b>36.0</b>	<b>51.4</b>	<b>54.9</b>	<b>25.4</b>	<b>88.7</b>	<b>31.8</b>	<b>43.9</b>	<b>57.8</b>	<b>50.3</b>	<b>50.2</b>
treatment plant effluent	42.4	25.5	16.9	33.4	13.0	37.2	13.8	2.8	50.0	40.2	31.7
roadside ditch	0.6	2.0	3.2	0.5	1.3				0.9	0.9	0.7
Keystone Mine drainage	4.5	8.6	31.3	21.0	11.1	51.4	18.0	41.1	6.9	9.2	17.9
UT-5.613 east Keystone Mine	0.1	7.5	4.0	0.1	5.2	0.4	2.0	1.7		1.0	0.4
UT-5.827 east Keystone Mine	0.2	10.7	2.0		8.8	0.1	5.6	0.9		0.2	0.1
UT-5.930 east Keystone Mine	0.3	12.7	6.3		3.1	0.2	7.2	1.2		0.4	0.1
<b>Cumulative total load (kg d<sup>-1</sup>)</b>	<b>40.0</b>	<b>0.003</b>	<b>0.29</b>	<b>0.23</b>	<b>0.006</b>	<b>0.69</b>	<b>2.21</b>	<b>0.016</b>	<b>29.2</b>	<b>0.16</b>	<b>37.3</b>

## DISCUSSION

### *Measurement of Flow Rate in Coal Creek*

*Suitability of bromide as a tracer in Coal Creek.* Bromide was used as the tracer in this April 2007 metal loading tracer dilution test to avoid the problems encountered with lithium and chloride in the previous tests (Shanklin and Ryan, 2006; Ryan and Bevan, 2009). An appropriate tracer must be (1) conservative (non-reactive, non-sorbing), (2) present at concentrations several times greater than background concentrations, (3) cost-effective, and (4) safe (no risk to human health or aquatic life) (Bencala et al., 1990). Bromide and chloride have been shown to be conservative over a wide range of conditions, but lithium was not conservative in Coal Creek (Shanklin and Ryan, 2006). The addition of bromide and lithium resulted in stream concentrations much greater than concentrations in the tributaries. Bromide, added as sodium bromide, was more expensive than sodium chloride, but less expensive than lithium chloride. Bromide, lithium, and chloride were all considered to be safe at the concentrations resulting from injection in Coal Creek. For bromide, there was initial concern about oxidation into bromate ( $\text{BrO}_3^-$ ), a carcinogen, during chlorination in the Town of Crested Butte's drinking water treatment plant, but calculation of the bromide dilution in Coal Creek and in the town's drinking water reservoir indicated that no risk was present even if all of the bromide were oxidized to bromate.

*Steady-state conditions for bromide injection in Coal Creek.* During a metal loading tracer dilution test, the tracer concentration must reach steady-state concentrations for the tracer dilution method to properly work. For this April 2007 test, the results indicated that steady-state bromide concentrations were achieved in Coal Creek. The bromide solution was injected at a fairly constant flow rate and concentration (Table 1, Figure 11) and the bromide concentration at the downstream end of the reach achieved a clear plateau (Figure 12).

### *Mount Emmons Treatment Plant Effluent and Hardness*

The Mount Emmons treatment plant adds lime ( $\text{CaO}$ ) during the treatment process to achieve a pH greater than 10 (John Perusek, personal communication, July 15, 2005). The pH is increased to precipitate and remove cadmium and manganese in the plant's flotation process. Cadmium and manganese require higher pH for precipitation than most other metals. The calcium is released to Coal Creek with the treatment plant effluent as part of tributary UT-5.368. The release of effluent is not steady; it varies from 0 to  $79 \text{ L s}^{-1}$  over each day and concludes at 16:00 (John Perusek, personal communication, July 15, 2005). During the synoptic sampling conducting for this April 2007 metal loading tracer dilution test, the treatment plant was discharging effluent at a flow rate estimated at  $69.3 \text{ L s}^{-1}$  (Table 5). The variation in effluent release also results in differences in calcium concentration along the length of Coal Creek. During this test, the calcium concentration downstream of UT-5.368 was about 3 times greater than the upstream calcium concentration, and just about 400 m downstream of UT-5.368, the calcium concentration decreased by a factor of about two relative to the peak calcium

concentration (Figure 16). The decrease in calcium concentration may be attributed to either calcium removal by geochemical processes in the stream or to variations in the effluent release.

The hourly variation in calcium concentration in Coal Creek results in hourly variation in hardness and, hence, the protection of hardness for uptake of toxic metals by aquatic life. When treatment plant effluent is being discharged to Coal Creek, aquatic life is afforded greater protection from toxic metals. When effluent is not being discharged, aquatic life is at greater risk from toxic metals. According to CDPHE (2008), hardness-based toxicity standards should be calculated using the hardness corresponding to “the lower 95 per cent confidence limit of the mean hardness value at the periodic low flow criteria as determined from a regression analysis of site-specific data.” The aquatic toxicity standards shown for the metals in the Results section were calculated using the hardness measured during the synoptic sampling. For a permit effluent calculation for the Mount Emmons treatment plant, the periodic input of calcium and hardness could not be used to lessen the stringency of the toxicity standards.

### *Aquatic Life Toxicity and Drinking Water Supply Standard Exceedances*

During the early spring runoff in April 2007, concentrations of aluminum, cadmium, copper, and zinc exceeded the CDPHE chronic aquatic life toxicity standards in the reach of Coal Creek examined during the metal loading tracer dilution test (Table 7). The CDPHE drinking water supply standards were not exceeded by any of the metals or arsenic, although the arsenic concentrations did exceed the CDPHE human health-based standard for drinking water (0.02 µg L<sup>-1</sup>) throughout Coal Creek.

### *Sources of Metals Exceeding Aquatic Life Toxicity Standards*

For the metals that exceeded the chronic toxicity standard for aquatic life – aluminum, cadmium, copper, and zinc – the major, minor, and trace sources are presented in Table 8. “Major” sources were classified as sources that caused water quality standard exceedances or contributed more than 33% of the cumulative tributary metal loading rate. “Minor” sources were classified as sources that contributed 12-33% of the cumulative tributary metal loading rate. “Trace” sources were classified as sources that contributed 5-12% of the cumulative tributary metal loading rate.

**Table 7.** Coal Creek distances over which metals and arsenic exceed the Colorado chronic aquatic life toxicity standards (CDPHE, 2008).

<b>metal</b>	<b>chronic toxicity standard exceeded</b>
aluminum	3.435 to 5.439 km
arsenic	none
barium <sup>1</sup>	--
cadmium	4.167 km to end
chromium	none
copper	5.349 km to end
iron	none
lead	none
manganese	none
nickel	none
zinc	entire reach

<sup>1</sup> No aquatic life toxicity standard.



During early spring runoff in April 2007, the major sources of toxic metal contamination in Coal Creek were the Mount Emmons treatment plant effluent and a Keystone Mine drainage that combined to form unnamed tributary UT-5.368.

The treatment plant effluent was a major contributor of aluminum, cadmium, and copper and a minor contributor of zinc. The treatment plant effluent is a major contributor to the metal loading rate in Coal Creek because the lime/flotation treatment process does not achieve complete metal removal and because the effluent flow rate is high. The release of effluent is not steady; it varies from 0 to 79 L s<sup>-1</sup> over each day and concludes at 16:00 (John Perusek, personal communication, July 15, 2005); therefore, the metal loading from the treatment plant effluent varies during the day.

The Keystone Mine drainage that forms part of the flow in unnamed tributary UT-5.368 appears to drain an area containing the grit chamber and equalization pond associated with the Mount Emmons treatment plant (Figure 32). The exact area drained by this tributary was not determined because access to the Keystone Mine property is controlled. Further reconnaissance is needed to determine the source of toxic metals in this drainage.



**Figure 32.** Photographs of the grit chamber (left) and equalization pond (right) used by the Mount Emmons treatment plant. The chamber and pond are located above the Keystone Mine drainage that forms part of unnamed tributary UT-5.368.

The unnamed tributary UT-4.186 that drains the iron gossan and possibly the western part of the Keystone Mine property was a minor source of aluminum and zinc and a trace source of cadmium and copper. The exact source of the metal-contaminated water in this tributary is not clear. Most of the water appeared to be flow into the tributary from the iron gossan to the west, but seepage and runoff from the exposed terrain of the Keystone Mine could also be a source. Further examination of the source of this water with high metal concentrations and low pH is recommended.

Unnamed tributaries draining the iron fen (UT-3.212, UT-3.378) and the iron gossan (UT-4.027) were trace contributors of toxic metals. Because of the low pH in the iron fen water, the tributaries UT-3.212 and UT-3.378 were trace contributors of dissolved aluminum. Metals are more soluble in waters of low pH and high dissolved organic

matter concentration. The unnamed tributary UT-4.027 drains an area south of the iron gossan. We did not observe a direct connection between the gossan and this tributary, but we assume it is fed by water draining over the iron gossan.

**Table 8.** Major, minor, and trace sources of metals that exceeded the chronic toxicity standards for aquatic life in Coal Creek. Sources classified as “major” include those that caused water quality standard exceedances or contributed more than 33% of the cumulative metal loading rate; those classified as “minor” contributed 12-33% of the cumulative metal loading rate; and those classified as “trace” contributed 5-12% of the cumulative metal loading rate.

<b>metal</b>	<b>major sources</b>	<b>minor sources</b>	<b>trace sources</b>
aluminum, total	UT-5.368 (Mount Emmons treatment plant effluent)		UT-4.027 (iron gossan?) UT-4.186 (iron gossan) UT-5.368 (Keystone Mine drainage) UT-5.930 (Keystone Mine east)
aluminum, dissolved	UT-5.368 (Mount Emmons treatment plant effluent)	UT-4.186 (iron gossan)	UT-3.212 (iron fen) UT-3.378 (iron fen) UT-4.027 (iron gossan?)
cadmium, total	UT-5.368 (Mount Emmons treatment plant effluent)	UT-5.368 (Keystone Mine drainage)	UT-4.027 (iron gossan?) UT-4.186 (iron gossan)
cadmium, dissolved	UT-5.368 (Mount Emmons treatment plant effluent)	UT-5.368 (Keystone Mine drainage)	UT-4.027 (iron gossan?) UT-4.186 (iron gossan)
copper, total	UT-5.368 (Mount Emmons treatment plant effluent) UT-5.368 (Keystone Mine drainage)		
copper, dissolved	UT-5.368 (Mount Emmons treatment plant effluent) UT-5.368 (Keystone Mine drainage)		UT-4.186 (iron gossan)
zinc, total		UT-4.186 (iron gossan) UT-5.368 (Mount Emmons treatment plant effluent) UT-5.368 (Keystone Mine drainage)	UT-3.378 (iron gossan) UT-4.027 (iron gossan?) UT-4.733 (Keystone Mine west)
zinc, dissolved		UT-4.186 (iron gossan) UT-5.368 (Mount Emmons treatment plant effluent) UT-5.368 (Keystone Mine drainage)	UT-3.378 (iron gossan) UT-4.027 (iron gossan?)

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