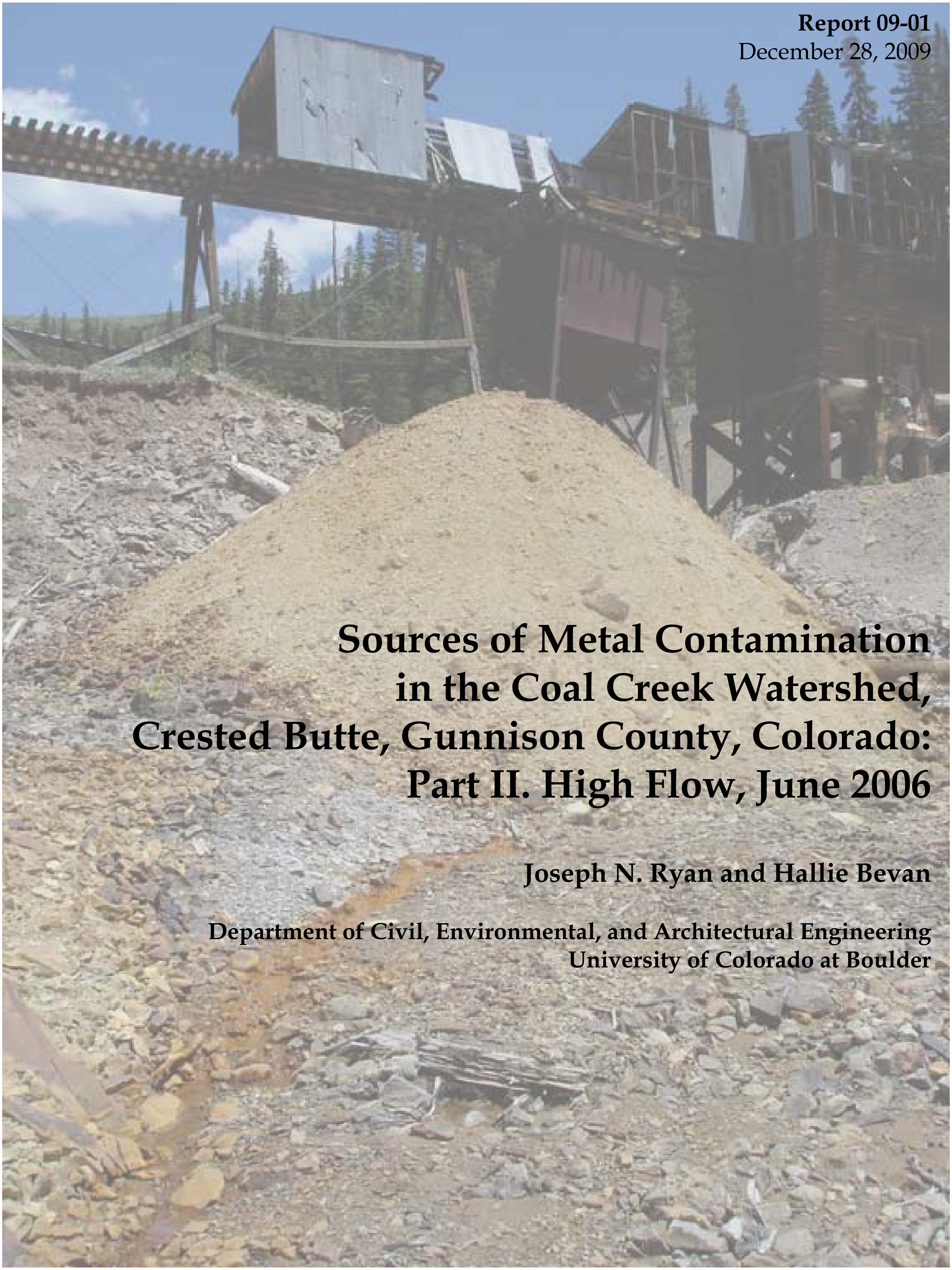
Report 09-01
December 28, 2009



Sources of Metal Contamination in the Coal Creek Watershed, Crested Butte, Gunnison County, Colorado: Part II. High Flow, June 2006

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EXECUTIVE SUMMARY

This report details 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 high flow in June 2006. 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.

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 naturally occurring iron fen and gossan 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 confirm these results and to locate any other inputs of metals and acidity to Coal Creek, a spatially detailed investigation of contaminant sources was performed by University of Colorado researchers in June 2006. The study was conducted at high flow to complement companion studies conducted at low flow in September 2005 (Shanklin and Ryan, 2006) and during snow melt in the watershed in April 2007 (Ryan et al., 2009).

Metal loading tracer-dilution tests on two reaches of Coal Creek allowed for the quantification of both surface and hyporheic flow and provided spatially detailed concentration and metal loading profiles for aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc along a 5.4 km reach of Coal Creek. Acute aquatic life toxicity standards were exceeded by cadmium and zinc, and chronic aquatic life toxicity standards were aluminum, cadmium, copper, lead, and zinc. Drinking water supply standards were never exceeded. Most of the exceedances occurred downstream of Elk Creek and an iron gossan tributary.

Water draining from the iron gossan near Keystone Mine was identified as the largest metal contributor in the watershed. It was a major source of aluminum, cadmium, copper, lead, manganese, and zinc to Coal Creek. Elk Creek, which carries metals from the Standard Mine drainage, was identified as a major source of cadmium, copper, lead, and zinc. Splains Gulch was the major source of barium and chromium, which were present at concentrations that did not exceed any standards. Detailed results are presented in Table 16. The Mount Emmons treatment plant effluent was a minor or trace source of aluminum, copper, iron, lead, and manganese.

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INTRODUCTION

Overview

The Coal Creek watershed in northern Gunnison County near Crested Butte, Colorado (Figure 1), is contaminated by acid mine drainage (Wentz, 1974). Acid mine drainage results when sulfide minerals such as pyrite (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.

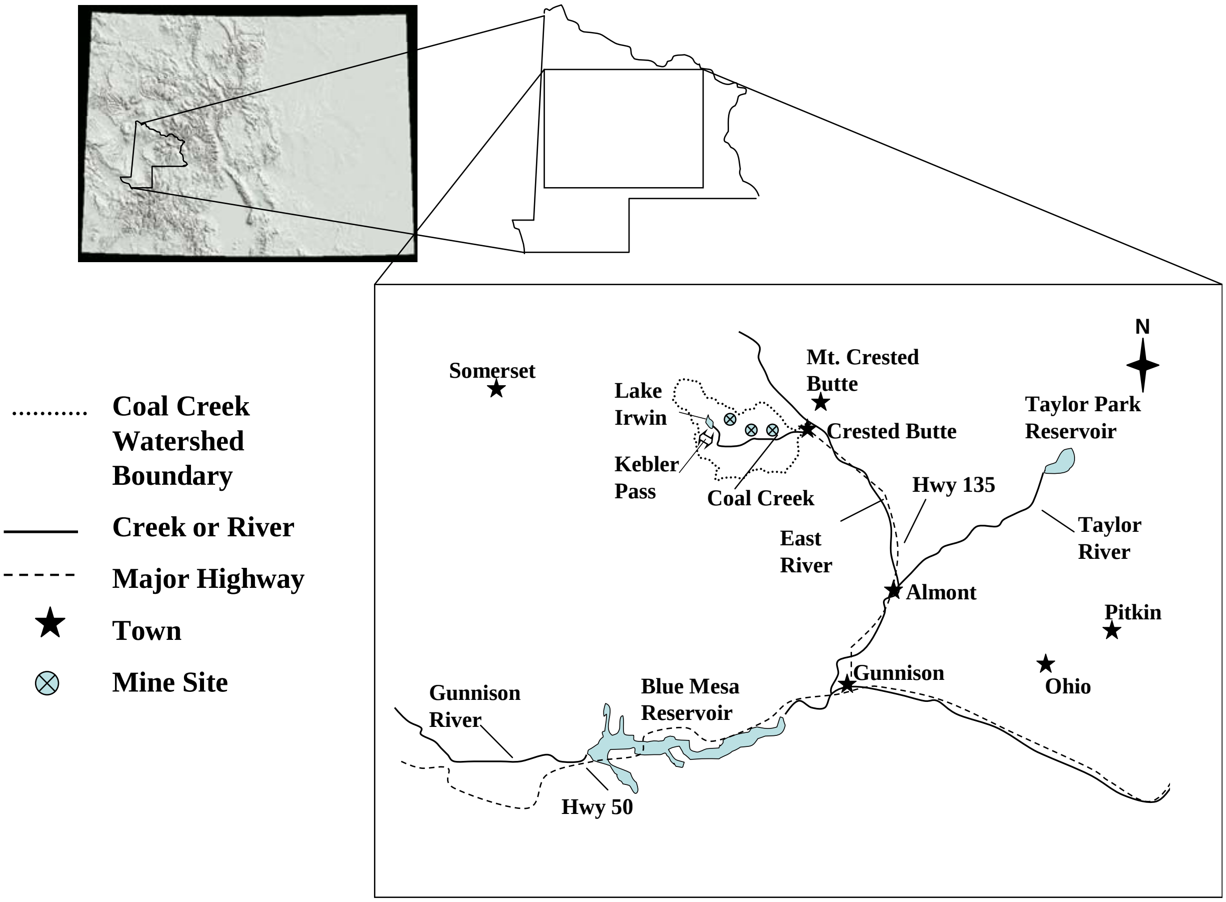

Figure 1. Maps showing the State of Colorado (upper left), Gunnison County (upper right), and the major rivers of the Gunnison-Crested Butte area. The Coal Creek watershed is outlined by the dashed line west of Crested Butte (Shanklin and Ryan, 2006).

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 (Figure 2) (EPA, 2005b). The watershed is now used primarily for residential development, recreation, and water supply.

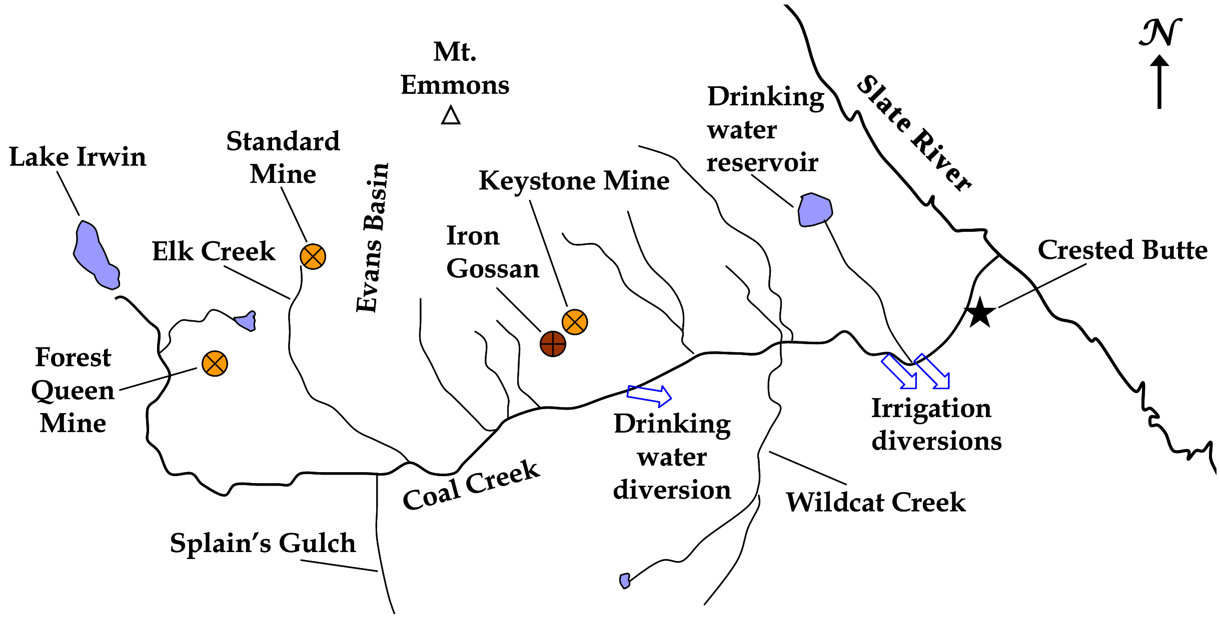

Figure 2. Key landmarks of the Coal Creek watershed, including Lake Irwin, the Forest Queen Mine, Kebler Pass, the Standard Mine, Elk Creek, Mount Emmons, the Keystone Mine, and the Town of Crested Butte (Shanklin and Ryan, 2006).

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 1974. Since then, heavy metals and ground and surface water flow have contaminated Elk Creek and Coal Creek. Metals of concern include arsenic, barium, cadmium, chromium, copper, lead, and zinc (EPA, 2006). Site remediation activities by the U.S. Environmental Protection Agency (EPA) were started in the summer of 2006.

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. 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. U.S. Energy was responsible for operation of the treatment plant at the time of the metal-loading tracer-dilution tests described in this report.

A naturally occurring iron-rich surface deposit, or gossan, also drains into Coal Creek. Drainage from the gossan is characterized by low pH and high concentrations of aluminum, iron, manganese, and zinc. Some of the water draining from the gossan flows into a wetland to the west of the gossan locally referred to as "the iron fen." The iron fen is the home to an endangered plant species, the *Drosera rotundifolia* (USFS, 1981). Some of the water draining from the gossan flows to the south into Coal Creek.

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, three metal loading tracer dilution experiments have been conducted at low flow (September 2005), high flow (June 2006), and during the start of snow melt and runoff in the lower elevations of the watershed (April, 2007). This report presents the results of the high-flow study conducted in June 2006. Shanklin and Ryan (2006) reported the results of the low-flow study. Ryan et al. (2009) reported the results of the April 2007 study.

The objectives of this June 2006 study were to (1) locate and quantify sources of metal input to Coal Creek at the time of the historically highest flow, (2) assess metal partitioning between the dissolved and colloidal phases, and (3) compare the results of the low-flow and high-flow studies to determine the effects of flow rate on the sources of metal input 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 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., μg 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.

BACKGROUND

Coal Creek Watershed

Coal Creek is fed by snow melt and springs in the surrounding Ruby-Anthracite Range of the greater Rocky 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^2. 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 $m^3\ s^{-1}$ 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 $m^3\ s^{-1}$. The minimum recorded flow was 0.030 $m^3\ s^{-1}$ during the winter months. During a sampling event, the EPA measured a flow of 2.38 $m^3\ s^{-1}$ on June 14, 2005 (EPA, 2005b).

Spring flow rates are important to consider in studying the metal loading of Coal Creek. During spring runoff, when snow melts from the peaks surrounding the watershed, springs and tributaries swell to flows much larger than normal. This increased volume of water can transport a greater quantity of metals picked up from bedrock, rocky slopes, and mine tailings. When Elk Creek swells during runoff, it may also flood the Standard Mine's tailings pond, causing an increase in metals transported from the mine site. Alternatively, it is possible that the greater volume of runoff may dilute the metals.

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 a rate of 0.079 m^3 s^{-1} (Shanklin and Ryan, 2006).

Mining Activities and Mineral Deposits

The major historical mines in the Coal Creek Watershed are the Standard Mine, the Keystone Mine, and the Forest Queen Mine, each of which are sources of contamination for Coal Creek. A natural feature, an iron gossan and fen, also contribute metal contaminants to Coal Creek.

The Standard Mine sits on 4 ha of land located approximately 16 km northwest of Crested Butte. The Standard Metals Corporation owns the patented mining claims. The surrounding land is owned by the U.S. Forest Service. The mine site contains many open adits and shafts and, until recently, a non-engineered, unlined surface impoundment, or tailings pond (90 m diameter by 4.5 m deep). Popular hiking trails parallel the site and no access restrictions are in place. On-site wastes include about 41,000 m^3 of waste rock and 22,000 m^3 of mill tailings. Acidic, metal-laden water previously flowed out of open adits and into Elk Creek, which is devoid of all aquatic life (CDPHE, 2006). Elk Creek flows into Coal Creek 3.2 km downstream of the Standard Mine site. The drinking water intake for the Town of Crested Butte is 3.4 km downstream of this confluence. Flow from the Standard Mine into Elk Creek ranges from 550 to 1,100 m^3 d^{-1} during the high flow season to 5.5 to 55 m^3 d^{-1} during low flow. Suspected contaminants include arsenic, barium, cadmium, chromium, copper, lead, and zinc. The Standard Mine was added to the U.S. Environmental Protection Agency National Priority List in September 2005. During the summer of 2006, the EPA directed remediation activities that included channelizing and re-directing Elk Creek and hillside surface drainage with cement blocks to protect it from mine site contamination; tearing down the old mill, rail trestle bridge, and several structures and moving them to a centralized location pending further removal of the debris; and improving the only access road to the Standard Mine site. Water was also removed from the tailings pond for future mine tailings removal and a pilot bioreactor for metals removal was installed and operated. Future remediation plans include the selection and construction of a contaminated soils repository site, Standard Mine site revegetation, and diversion and stabilization of the mine adit and drainage.

The Keystone Mine is located approximately 5.0 km northwest of Crested Butte under the south slope of Mount Emmons (Streufert, 1999). Lead, zinc, and silver were extracted from the Keystone Mine until the mid-1970s (U.S. Energy, 2006). Acid mine drainage from the abandoned Keystone Mine contains high concentrations of lead, zinc, and cadmium. The drainage is treated at the Mount Emmons Treatment Plant, which was built in 1981 (CCWC, 2006). The Mount Emmons Treatment Plant also treats flow emitted from exploratory cores drilled in the 1970s by Amax Gold, Inc., as part of a feasibility study investigating the extent of molybdenum and diamond deposits. The plant cost $14 million to build and the yearly operational costs are about $1 million (U.S. Energy, 2006). On February 28, 2006, U.S. Energy Corporation and Crested Corporation re-acquired the Mount Emmons property from the Phelps-Dodge Corporation. According to U.S. Energy Corporation, this 2,185 ha property contains a "world-class" molybdenum deposit. Reserves are estimated at 140 million tonnes of 0.44 percent molybdenum disulfide (MoS_2) (Streufert, 1999). The owners have been pursuing development and mining.

The former Forest Queen Mine is located 19 km west of Crested Butte near Lake Irwin. Silver was the main metal extracted at the Forest Queen Mine. A mill was located on the site (Hornbaker, 1984). One adit drains into Coal Creek just below the Irwin town site southeast of Lake Irwin. The flow appears to be quite low. Ongoing studies aim to determine how this drainage impacts Coal Creek (CCWC, 2006).

An iron gossan and fen is located just west of the Keystone Mine at an elevation of 2,911 m (Figure 3). Its surface area is approximately 1.2 ha. An iron gossan is formed by the flow of springs through highly mineralized and fractured bedrock rich in pyrite (FeS_2) (CCCOSC, 2006). This process forms peat terraces composed of limonite, a natural aggregate of hydrous ferric oxides lacking crystallization (Kelly, 1958). Pyrite oxidation produces acidic byproducts that lower the pH of the water. Pyritic gossans are characterized by a very dusky red to dark reddish brown or moderate brown color. A wetland area locally referred to as "the iron fen" is present below the gossan. The iron fen is a peat wetland with high nutrient content fed from upslope mineral-rich soil and groundwater movement. Sampling revealed acidic water (pH 3.4) with elevated concentrations of aluminum, iron, manganese, and zinc concentrations draining from the iron fen into Coal Creek (EPA, 2005a). At low flow in September 2005, drainage from the gossan entered Coal Creek via a single surface tributary and drainage from the iron fen entered Coal Creek via two surface tributaries (Shanklin and Ryan, 2006). We observed that some of the surface flow from the iron fen and gossan did not reach Coal Creek as surface flow, and we surmise that a significant fraction of this flow enters Coal Creek as subsurface flow. The fen supports a unique vegetative community including a round-leafed sundew, *Drosera rotundifolia*. This small, carnivorous plant has not been found anywhere else in the Central or Southern Rocky Mountains in spite of extensive searches in similar acidic fens. The U.S. Forest Service is concerned that molybdenum mining on Mount Emmons may threaten the sundew population. Another concern is the alteration of groundwater flow by mining operations, which may remove water from springs that feed the fen (USFS, 1981).

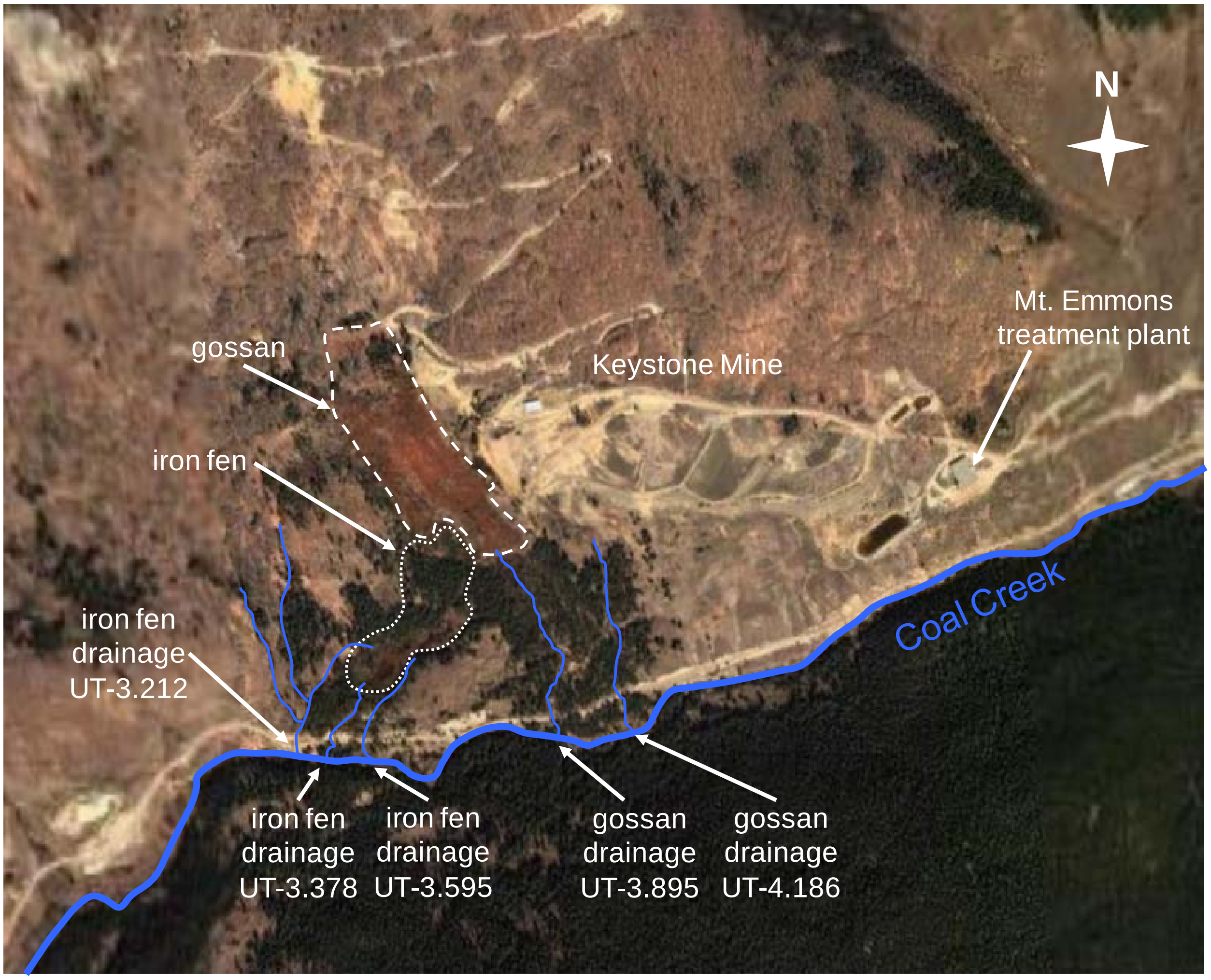

Figure 3. Aerial photograph of Coal Creek near the Keystone Mine at the southern base of Mount Emmons in June 2006 at high flow. The figure includes the iron gossan and fen located just west of the Keystone Mine, approximate paths of unnamed tributaries at Coal Creek distances 3.212, 3.378, 3.595, 3.895, and 4.186 km downstream of the September 2005 injection site, and the Mount Emmons treatment plant. Coal Creek flows from the southwest to the northeast. The aerial photo was retrieved using Google Earth™ (http://earth.google.com).

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

We conducted two metal loading tracer dilution experiments in Coal Creek during June 2006. During the previous low flow experiment, we made a single injection and conducted synoptic sampling over the full 9 km reach of Coal Creek from upstream of Elk Creek to downstream of the Town of Crested Butte (Shanklin and Ryan, 2006). Monitoring the tracer injection over 9 km of Coal Creek proved challenging at low flow, so for the June 2006 experiments, we broke the 9 km of Coal Creek into two reaches and performed separate metal loading tracer dilution studies in each reach.

The lower Coal Creek injection site was located 4.324 km downstream of the September, 2005, upstream site. Synoptic sampling of lower Coal Creek occurred along 5.063 km of Coal Creek from the injection site to just downstream of the Town of Crested Butte. Due to sampling errors, only the first 1.616 km of lower Coal Creek were analyzed for flow rates and metal loading. All other site data was discarded. Figure 4 shows the sample sites of the lower Coal Creek tracer reach with a cutoff at 5.940 km. The blue dots indicate samples taken from Coal Creek; the red arrows indicate samples taken from tributaries. The lower reach injection was performed prior to the upper reach injection to prevent detection of the tracer.

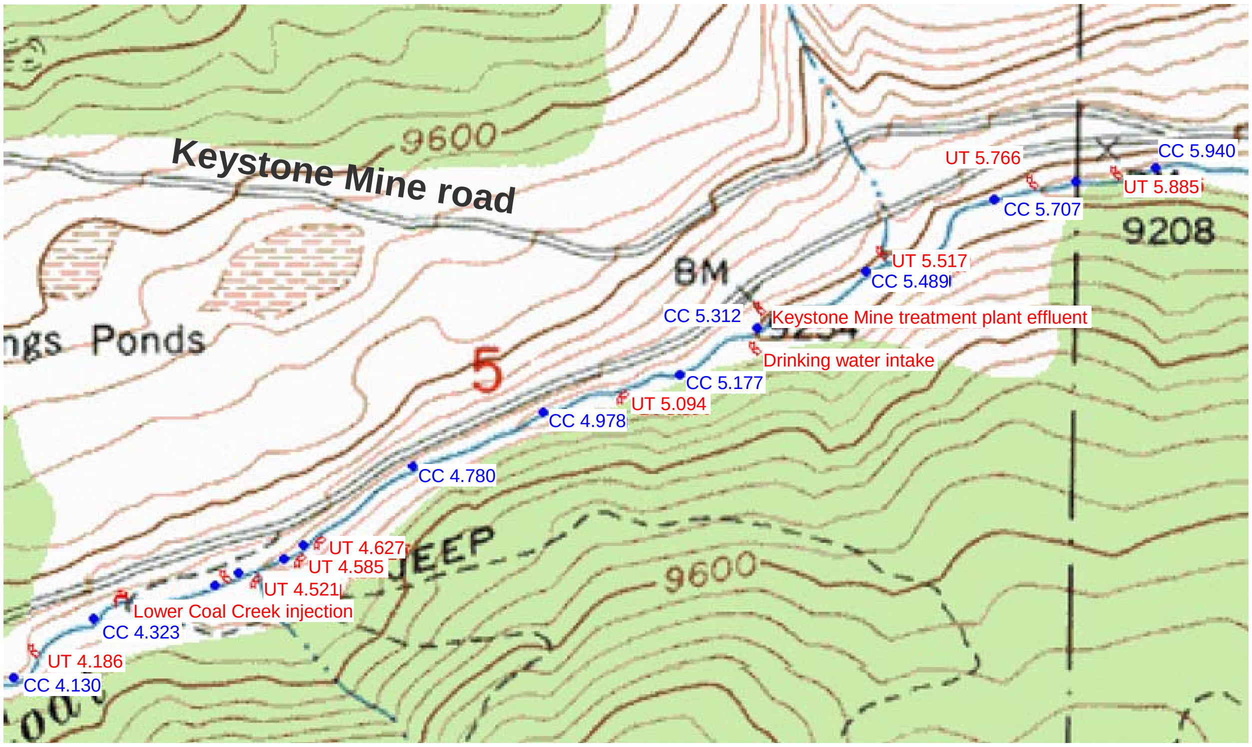

Figure 4. Sample sites for the lower Coal Creek injection experiment. The injection was made at a distance of 4.324 km downstream of the injection point for the low-flow September 2005 experiment (Shanklin and Ryan, 2006). Blue "CC- " labels show sampling sites in Coal Creek; red labels show tributary sampling sites, including unnamed tributaries ("UT- ").

The upper injection site was located 0.561 km downstream of the September 2005, upstream site. Synoptic sampling for the upper tracer injection was conducted along the upper stretch of Coal Creek for 3.781 km from the upper tracer injection site to the lower tracer injection site. Figure 5 shows the sample sites of the upper tracer injection reach of synoptic sampling.

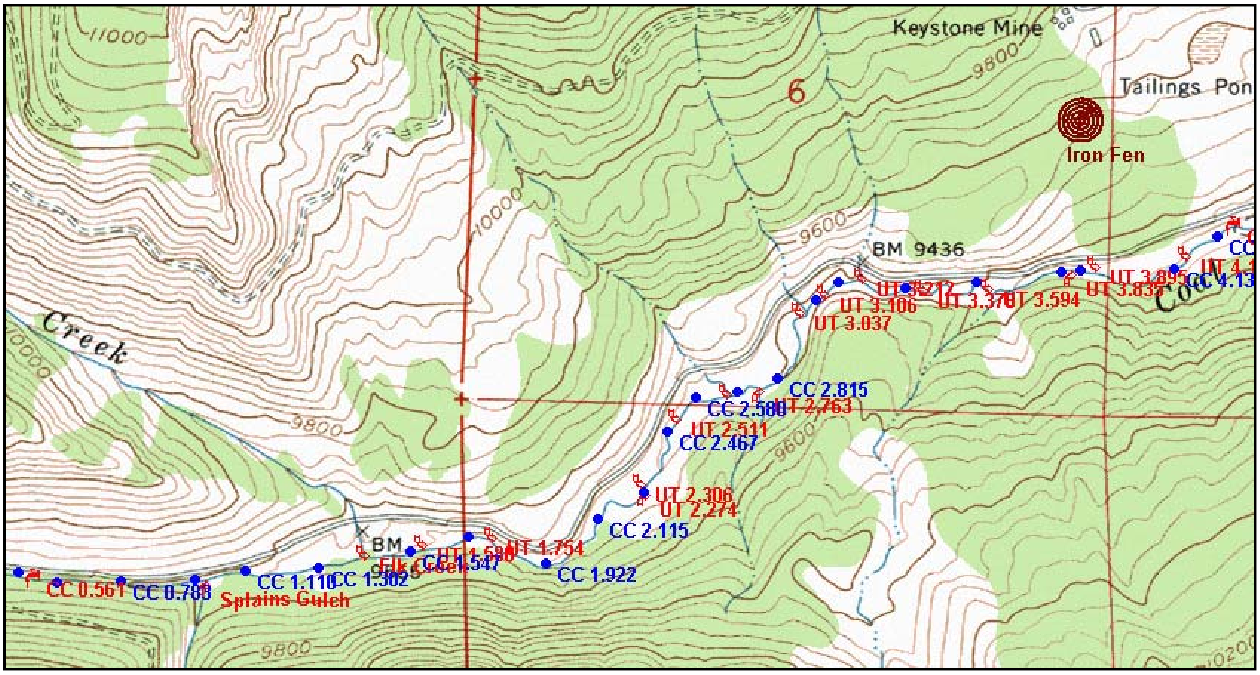

Figure 5. Sample sites for the upper Coal Creek injection reach. The injection was made at a distance of 0.561 km downstream of the injection point for the low-flow September 2005 experiment (Shanklin and Ryan, 2006). Blue "CC- " labels show sampling sites in Coal Creek; red labels show tributary sampling sites, including unnamed tributaries ("UT- ").

Sample sites along Coal Creek were generally located every 200 m, beginning at the injection sites. A sample site was established at and between every tributary, usually following closer than 200 m. There were 48 sampling sites on the lower reach (22 of which the samples were analyzed) and 40 sampling sites on the upper reach. 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- ". Splains Gulch, Elk Creek, and the drinking water intake were identified by name. The tributary draining the Mount Emmons treatment plant effluent, a road-side drainage ditch, and a surface tributary from the eastern portion of the Keystone Mine proper were identified as the "Mount Emmons tributary."

Injection Procedure

The tracer used in this study was sodium chloride (NaCl). The September, 2005, tracer study along Coal Creek used lithium chloride (LiCl) as a tracer with the intent of analyzing lithium dilution with distance downstream to determine flow rates (Shanklin and Ryan, 2006). The 2005 study found though that the lithium was attenuated in several marshy areas and was an unreliable tracer. Chloride analysis was therefore used for determining flow rates. Chloride's adequate performance as a tracer lead to its use for this study, although better, less reactive tracers are known. One such tracer is sodium bromide, which was used for the April 2007 study.

To prepare the tracer solutions, stream water was pumped from Coal Creek into a 1,250 L polyethylene tank using a garden hose and gasoline-powered Honda water pump. Sodium chloride (Morton Safe-T-Salt®) was then added to the nearly-full tank, stirred using a paddle, and left in the tank overnight to dissolve. On the day of the injections, the tracer solution was continuously injected from the storage tank 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® tubing (Fisherbrand, 12.7 mm inside diameter). Injection flow rates were determined by measuring the amount of time needed to fill a 500 mL graduated cylinder with the injectate.

To prepare the tracer solution for the lower reach of Coal Creek, 283 kg of sodium chloride were added to the tank. The desired tank chloride concentration was 3.87 M, which yielded a 100:1 ratio of chloride concentration downstream of the injection to the concentration upstream of the injection. Although calculations indicated the 3.87 M concentration was less than the NaCl solubility of 6.15 M at the anticipated water temperature, a large quantity of salt remained undissolved in the bottom of the tank. Two other injection solutions were prepared during the injection.

The lower Coal Creek injection began at 8:35 on June 11, 2006, and continued for 8.55 h. The weather was recorded as clear skies with a temperature of 15°C. No precipitation occurred during the injection. Patches of snow were observed on north-facing slopes; however, south facing slopes were fully melted. The average flow rate from the metering pump was time weighted and found to be 2.00 L min^{-1} with a range of 1.56 L min^{-1} to 2.44 L min^{-1}. Injection details are shown in Table 1.

The upper Coal Creek tracer solution used 113 kg of NaCl mixed with stream water in the 1,250 L tank. The tank was left overnight to allow the salt to dissolve; however, a small amount of salt remained undissolved the next morning. Before the injection, the solution was mixed for approximately 2 min, at which time its specific conductance was measured at 113.0 mS cm^{-1}. The upper injection began at 7:45 on June 13, 2006, and continued for 9.17 h. The weather was recorded as clear and warm with a slight breeze and ambient temperatures estimated at 18 to 21°C. A second tracer solution was prepared at 15:00 by mixing 36.3 kg NaCl with stream water in the 379 L tank until the specific conductivities of the 1,250 L tank and the 379 L tank matched at 111.3 mS cm^{-1}. No precipitation occurred during the injection. Patches of snow were observed on north-facing slopes; however, south facing slopes were fully melted. Average flow rate was 2.40 L min^{-1} with a range of 2.30 to 2.48 L min^{-1}. The upper Coal Creek synoptic sampling and injection concluded at 16:55. Table 2 summarizes the upper Coal Creek injection and synoptic sampling flow rates, specific conductivities, and activities.

Table 1. Details of the metal loading tracer dilution test conducted on the lower reach of Coal Creek on June 11, 2006.

date	clock time	experiment time (h)	flow rate (L min^{-1})	conductivity (mS cm^{-1})	activity
6/10/2006	13:00				Lower Coal Creek injection solution prepared; 283 kg NaCl added to stream water in nearly full 1,250 L tank
6/11/2006	7:45				Noted substantial amount of undissolved salt in bottom of tank
	8:35	0.00	2.30		Lower Coal Creek tracer injection started
	8:42	0.12	2.14		
	9:22	0.78	2.34		
	9:42	1.12	2.34		
	10:12	1.62	2.40		
	10:35	2.00	2.44		
	11:10	2.58	2.54	57.5	
	11:20	2.75			Second injection solution prepared; 22.7 kg NaCl added to stream water in nearly full 379 L tank
	11:37	3.03	2.36	53.7	
	11:45	3.17			Approximately 13 min decrease in injection flow rate
	12:00	3.42	2.40	54.8	
	12:25	3.83	2.36 (first tank) 1.88 (second tank)	51.8 (first tank) 65.8 (second tank)	Switched from first solution injection in 1,250 L tank to second solution injection in 379 L tank
	12:33	3.97	1.90		
	12:50	4.25			Lower Coal Creek synoptic sampling started
	12:55	4.33	1.96	65.9	
	13:00	4.42			Third injection solution prepared, added stream water to remaining undissolved NaCl in 1,250 L tank
	13:21	4.77		66.5	
	13:33	4.97	1.92	83.4	
	14:05	5.50	2.00	74.8	
	14:33	5.97	1.90	73.4	
	15:07	6.53	1.70	72.3	
	15:37	7.03	1.90	71.8	
	16:05	7.50	1.84	74.7	Switched from second solution in 379 L tank to third solution in 1,250 L tank
	16:35	8.00	1.92	75.7	
	17:08	8.55	1.96	74.8	End of Lower Coal Creek synoptic sampling and injection

Table 2. Details of the metal loading tracer dilution test conducted on the lower reach of Coal Creek on June 13, 2006.

date	clock time	experiment time (h)	flow rate (L min^{-1})	conductivity (mS cm^{-1})	activity
6/12/2006					Upper Coal Creek injection solution prepared; 113 kg NaCl added to stream water in 1,250 L tank
6/13/2006	7:45	0.00	2.40	113.0	Upper Coal Creek tracer injection started
	8:00	0.25	2.30		
	8:33	0.80	2.40		
	9:00	1.25	2.36		
	9:30	1.75	2.40		
	10:00	2.25	2.40		
	10:33	2.80	2.44		
	11:00	3.25	2.40		
	11:30	3.75	2.40		
	12:00	4.25	2.40		
	12:30	4.75	2.40		
	13:03	5.30	2.40		
	13:30	5.75	2.40		
	14:00	6.25	2.40	111.5	Upper Coal Creek synoptic sampling started
	14:30	6.75	2.36		
	15:00	7.25	2.40	111.3 (first and second tank)	Second injection solution prepared, 36.3 kg NaCl added to stream water in 379 L tank
	15:10	7.42	2.40		Switched from first injection solution in 1,250 L tank to second solution in 379 L tank
	15:30	7.75	2.44	111.2	
	16:00	8.25	2.48	110.9	
	16:35	8.83	2.44	111.2	
	16:55	9.17			End of Upper Coal Creek synoptic sampling and injection

Water Sampling Procedure

At the upstream end of the injection reaches, samples were taken from the injection tubing and Coal Creek upstream of the injection. Samples were collected hourly 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-0.519 and CC-4.323 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 in the injection tanks at various times throughout the injection periods using a Thermo Orion 105A+ meter and Orion 010510 conductivity cell calibrated with Traceable One-Shot™ 1409 µS cm^{-1} conductivity calibration standard.

At the downstream end of the injection reaches, samples were collected every 15 min from sites CC-4.284 and CC-9.387 in 60 mL high-density polyethylene Nalgene bottles. The conductivity and chloride 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 94-17B chloride electrode with an Orion 90-02 double-junction reference electrode were used to measure the chloride concentrations. The lower Coal Creek chloride calibration involved measuring four chloride standards (0.14 M, 0.014 M, 0.0014 M, and 0.00014 M) made from Morton Safe-T-Salt® and Milli-Q water. The upper Coal Creek chloride calibration standards were 0.1 M, 0.01 M, 0.001 M, and 0.0001 M made from Morton Safe-T-Salt® and Milli-Q water. The standards were equilibrated to the temperature of the stream water (about 12 °C for both tests).

When the chloride concentration reached a plateau at the downstream end of the injection reach, synoptic sampling of the reach was begun. For the lower reach, synoptic sampling lasted 4.3 h, and for the upper reach, it lasted 2.9 h. A team of three people carried out the sampling by working their way from the injection site to the downstream end. Two water samples were collected from each synoptic sample site in 250 mL high-density polyethylene Nalgene bottles.

Sampling of the tributaries, especially on the north bank of Coal Creek, was often complicated by diversion along ditches next to County Road 12 and dispersal of flow from culverts under the road. Many north-bank tributaries flowed down the hillside and into ditches along the side of the road. They were then diverted along the north side of the road before reaching a culvert (Figure 6). To ensure that all hillside flow was being collected in tributary samples, tributaries entering from the north side of the creek were sampled from the southern end of their respective culverts as they crossed under County Highway 12. Furthermore, many tributary flows became too marshy or dispersed to collect samples nearer to Coal Creek. Some tributary flows even seeped into the ground without visually running into Coal Creek. For these tributaries, the culverts were the easiest accessible points and the points with the most consolidated flows. Tributaries entering from the south side of the creek were accessed by wading across the creek and sampling the tributary approximately 5 m upstream of the confluence of the tributary with Coal Creek.

In addition to the samples collected along Coal Creek during the synoptic tracer studies, samples were collected in 250 mL high-density polyethylene Nalgene bottles from sites at the Standard Mine (Figure 7) and along the iron gossan and fen (Figure 8). The samples collected at the Standard Mine included a sample from Elk Creek approximately 50 m upstream of the Level 1 adit. This sample was presumed to be unaffected by the Standard Mine drainage, although metals could have been present from other mine levels upstream. A second sample was collected from the Level 1 adit. A third sample was taken from the tailings pond effluent at the edge of the tailings pond dam. A fourth sample was collected from Elk Creek approximately 20 m downstream of the tailings pond effluent confluence. No GPS data points were collected for these sites, although detailed site descriptions were made.

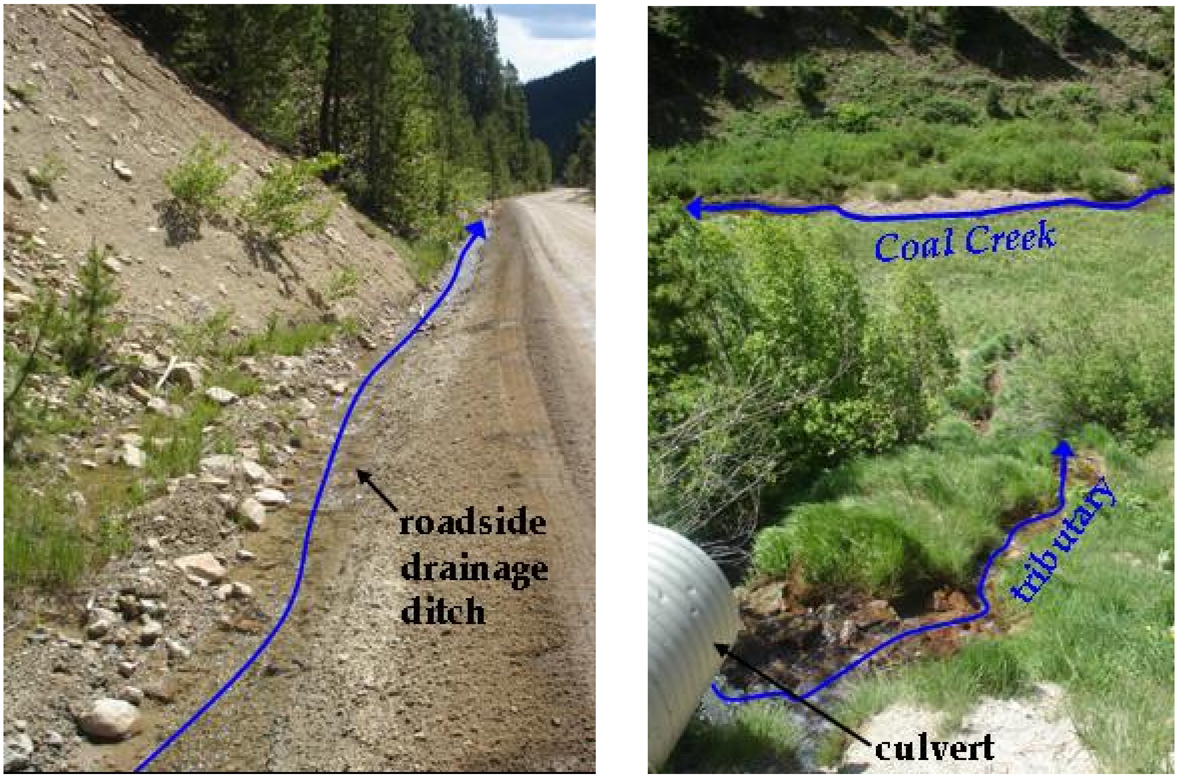

Figure 6. Water seeping from a hillside along County Road 12 on the north bank of Coal Creek (which is located to the right of the road) is diverted to a ditch which carries the water to a culvert crossing under the road further downstream (left). Water exiting a culvert under County Road 12 is dispersed into a marshy area on the north bank of Coal Creek (right). In these cases, samples were taken directly from the culvert.

Six water samples were collected along the western edge of the iron gossan and from the iron fen (Figure 8). The first was collected from a small spring-fed stream above the gossan. At this site, there was no reddish color in the rock indicative of the iron gossan. The second and third gossan samples were collected from stream flow between wetland areas along the western edge of the gossan. At both of these sites, reddish-colored soil and seeping groundwater were prevalent. The fourth sample was taken from stream flow near a white pipe labeled “Well #2.” The fifth and sixth samples were collected from water flowing west out of the large pond that constituted the iron fen. This water channel was the primary iron fen drainage. Two other hillside tributaries joined the primary iron fen drainage before it met Coal Creek as UT-3.212. UT-3.212 was the first Coal Creek tributary containing effluent from the iron gossan and fen. Visual investigation indicated that the tributaries at distances 3.212 km through 4.186 km likely contained groundwater and surface runoff from the iron gossan and fen.

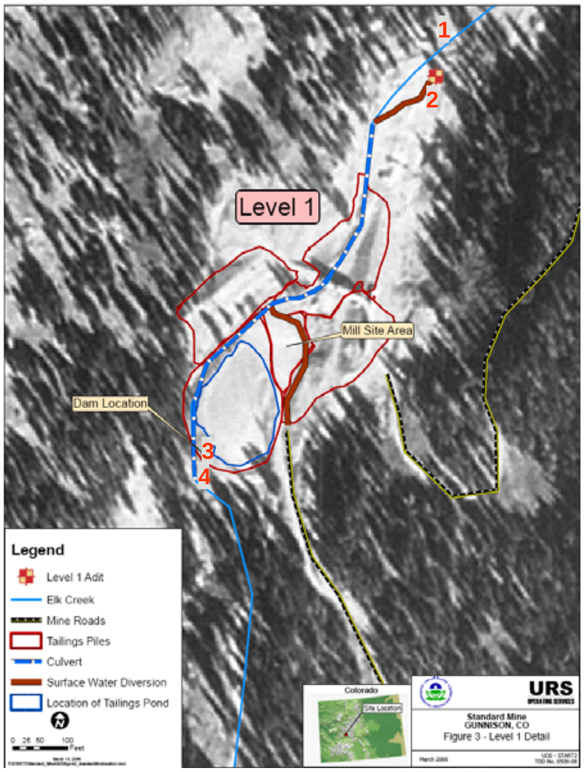

Figure 7. Approximate sample site locations near the Standard Mine. Sample sites are labeled as red numbers 1 through 4. Elk Creek (the blue curve) flows from north to south. The site map was obtained from EPA (2007).

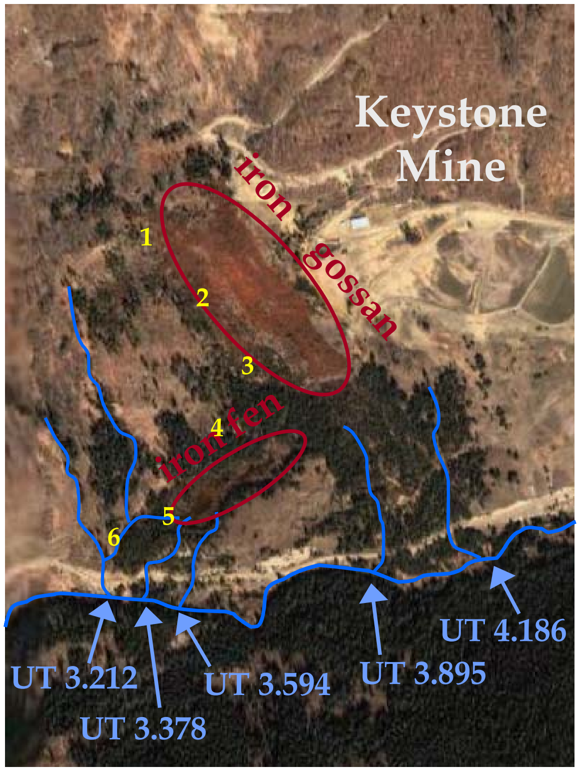

Figure 8. Approximate sample site locations near the iron gossan and fen. Sample sites are labeled as yellow numbers 1 through 6. Unnamed tributaries emanating from the iron gossan and fen are shown as "UT " with the distance downstream from the September 2005 injection in units of kilometers. The aerial photograph (Google Earth™, http://earth.google.com) is oriented with north upward. Coal Creek flows from west to east.

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 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 24 °C. The pH measurements were made with water temperatures at an average 16 °C.

Specific conductance was measured with an Orion 105A+ meter and Orion 010510 Conductivity Cell calibrated with Traceable One-Shot™ 1409 µS cm^{-1} conductivity calibration standard with an ambient temperature of approximately 24 °C. Following pH and specific conductance measurement, the sample was divided into three 60 mL samples. Two of these three samples were filtered using a syringe (30 mL BD Luer-Lok syringes) and a membrane filter (Fisherbrand nylon, 0.45 µm pore diameter, 25 mm diameter). The first 60 mL sample was filtered for measurement of chloride and other anions by ion chromatography (IC). The second 60 mL sample was filtered for measurement of dissolved major cations and metals by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The third 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 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 12 h of collecting the samples.

For every tenth sample, the "backup" sample was processed as described above to provide duplicate samples for IC, 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 chloride 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 chloride samples stored on ice or refrigerated until analysis.

The 60 mL injection tank and downstream end samples as well as the 250 mL upstream samples remained unfiltered and not acidified for measurement of chloride by IC. These were stored on ice and in the refrigerator until chloride analysis could be conducted. No cation or metals measurements were made for these samples.

The samples collected from the Standard Mine site and the iron gossan and fen were filtered and acidified as described above for dissolved and total metals measurements on the ICP-AES and ICP-MS. They were not analyzed for chloride concentrations.

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 are listed in Table 3.

Aluminum, barium, cadmium, chromium, copper, lead, manganese, 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 µg L^{-1} standard were run between every ten samples. Each sample was spiked (1:9) with an internal standard consisting of 160 µg L^{-1} of gallium, scandium, and indium and 80 µg L^{-1} bismuth in 2% nitric acid (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 are listed in Table 3.

Chloride, sulfate, and nitrate were measured by ion chromatography (Dionex ICS-2000) in the Institute for Alpine and Arctic Research (INSTAAR) at the University of Colorado at Boulder. Samples were treated to remove metals using a cation exchange resin in the protonated form (Alltech Maxi-Clean IC-H 0.5 mL cartridges). Four standards were used to calibrate the IC. The standards were run at the beginning and end of each sample run. Blanks (high-purity water) were run every fifteen samples. The detection limits for the IC are given in Table 3.

Table 3. Detection limits for inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and ion chromatography (IC) analyses. For the ICP-MS measurement of metals, two runs were made.

Analyte	**ICP-MS (µg L^{-1})**		**ICP-AES (µg L^{-1})**	**IC (µg L^{-1})**
	1st Run	2nd Run		
Aluminum	0.061	0.053		
Barium	0.025	0.015		
Cadmium	0.036	0.018		
Calcium			0.024	
Chloride				0.036
Chromium	0.085	0.179		
Copper	0.035	0.035		
Iron			0.003	
Lead	0.185	0.246		
Magnesium			0.010	
Manganese	0.040	0.051		
Nitrate				0.042
Sulfate				0.023
Zinc	0.111	0.077		

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 4.

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.

Table 4. Equations used to calculate flow rates and mass loading rates (Kimball et al., 2002) for the Coal Creek tracer dilution study.

Calculated Variable	Equation	Variable Definition
Mass balance downstream from injection site	$M_{down} = Q_{down}C_{down}$ (1) $M_{down} = Q_{up}C_{up} + Q_{inj}C_{inj}$ (2) $Q_{down} = Q_{up} + Q_{inj}$ (3)	C_{up}, tracer concentration upstream of injection site C_{down}, tracer concentration downstream of injection site C_{inj}, injectate tracer concentration 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 first site downstream of injection site with uniform background concentration	$Q_{down} = Q_{inj}\dfrac{C_{inj} - C_{up}}{C_{down} - C_{up}}$ (4)	Variables defined above
Flow rate at subsequent downstream sites with uniform background concentration and upstream surface inflow contribution	$Q_{down} = Q_{up}\dfrac{C_{up} - C_{in}}{C_{down} - C_{in}}$ (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
Flow rate at sites downstream of inflow with tracer concentration above background tracer concentration	$Q_{down} = \dfrac{Q_{down}C_{down} + Q_{in,est}C_{in,non}}{C_{down}}$ (6)	$C_{in,non}$, tracer concentration of inflow with non-uniform background concentration $Q_{in,est}$, visually estimated inflow rate
Metal loading rates	$M_i = Q_iC_i$ (7)	M_i, metal loading rate of site *i* Q_i, flow rate of site *i* C_i, metal concentration of site *i*
Tributary load rate (%)	$tributary\ load\ (\%) = \dfrac{load_i}{\sum_i load} \times 100$ (8)	$load_i$ (kg d^{-1}), loading rate at a specific tributary $\sum load$, cumulative total of all tributary inputs (kg d^{-1})

Metal Loading Calculations

Stream flow rate and metal concentration at each synoptic sample site were multiplied to obtain a metal loading rate (kg d^{-1}) for each site (Table 4, Equation 7). 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 load rate (Table 4, Equation 8) reflects the percentage of the cumulative metal loading for each metal. The calculation of tributary loading rates allows the prioritization of major sources of metal contamination.

Water Quality Standards and Hardness

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 ^{o}C and as a “Domestic Water Supply” because Coal Creek supplies the Town of Crested Butte’s drinking water (CDPHE, 2005). 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, 2005).

Many of the CDPHE metal standards are based on hardness measured in units of mg L^{-1} $CaCO_3$. Hardness was calculated as the sum of the dissolved calcium and magnesium ion concentrations:

$$Hardness = 50.05\ \left(\left[\mathrm{Ca}\right]+\left[\mathrm{Mg}\right]\right) \qquad (9)$$

where [Ca] and [Mg] are the dissolved concentrations of the calcium and magnesium ions in units of milliequivalents per liter (meq L^{-1}).

Calcium and magnesium concentrations were measured for each synoptic sample site and allowed for hardness calculations at each site. A hardness profile for the entire length of the stream was developed. 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 5). 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 5. Hardness-based equations for calculating acute and chronic aquatic life toxicity standards (CDPHE, 2007).

Metal	**Acute Aquatic Life Toxicity Standard (µg L^{-1})**
Cadmium	$(1.136672 - [\ln(hardness) \times 0.041838]) \times e^{0.9151[\ln(hardness)]-3.1485}$
(trout)	$(1.136672 - [\ln(hardness) \times 0.041838]) \times e^{0.9151[\ln(hardness)]-3.6236}$
Copper	$e^{0.9422[\ln(hardness)]-1.7408}$
Lead	$(1.46203 - [\ln(hardness) \times 0.145712]) \times e^{1.273[\ln(hardness)]-1.46}$
Manganese	$e^{0.3331[\ln(hardness)]+6.4676}$
Zinc	$0.978 \times e^{0.8525[\ln(hardness)]+1.0617}$

Metal	**Chronic Aquatic Life Toxicity Standard (µg L^{-1})**
Cadmium	$(1.101672 - [\ln(hardness) \times 0.041838]) \times e^{0.7998[\ln(hardness)]-4.4451}$
Copper	$e^{0.8545[\ln(hardness)]-1.7428}$
Lead	$(1.46203 - [\ln(hardness) \times 0.145712]) \times e^{1.273[\ln(hardness)]-4.705}$
Manganese	$e^{0.3331[\ln(hardness)]+5.8743}$
Zinc	$0.986 \times e^{0.8525[\ln(hardness)]+0.9109}$

The Mount Emmons Treatment Plant adds lime during the treatment process to raise the pH of Keystone Mine drainage to between 10 and 10.5. Cadmium and manganese require this pH increase for precipitation and removal. The addition of calcium results in a significant increase in the hardness of Coal Creek downstream of the treatment plant effluent. 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 Details

The results of the metal loading tracer dilution tests that we conducted over two reaches of Coal Creek in June 2006 are presented in this section. These tests measured metal loading rates during the historical peak of high flow in Coal Creek. These results can be compared to similar metal loading tracer dilution tests conducted during historical low flow in September 2005 (Shanklin and Ryan, 2006) and during snow melt in the watershed in April 2007 (Ryan et al., 2009).

The metal loading tracer tests were conducted on two reaches of Coal Creek on June 11 and June 13, 2006. Because the tests were conducted only two days apart and the synoptic sampling occurred at approximately the same time of each day, we assume that the metal loading results can be considered as a single test.

All distances presented in the following graphs 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. For this study, the locations of the sampling sites were measured at the creek. In the previous study, the locations were measured on County Road 12 (Shanklin and Ryan, 2006).

Two major natural Coal Creek tributaries are Splains Gulch and Elk Creek, which are located at 1.008 km and 1.425 km respectively. The main iron gossan and iron fen drainages are the unnamed tributaries located at 3.212 km, 3.378 km, 3.594 km, and 3.895 km. An unnamed tributary at 4.186 km drains the iron gossan (to the west) and the Keystone Mine (to the east). The sources and contributing waters of this tributary are ambiguous. The Town of Crested Butte drinking water supply intake is located at 5.296 km. It is immediately followed by the Mount Emmons tributary entering Coal Creek at 5.340 km. The treatment plant effluent is joined by water running in a ditch along the road prior to entering Coal Creek. The source of this water is also ambiguous as to its origination from the iron gossan, the Keystone Mine, or as seepage from the treatment plant effluent. In addition to the drinking water supply intake, the Spann-Nettic and Halazon ditches divert water from Coal Creek and are located at 8.047 km and 8.177 km respectively. Entering Coal Creek intermediate to these diversions is the drinking water reservoir return, located at 8.097 km.

Wetlands surround Coal Creek between 2.115 and 2.467 km and between 2.763 and 3.077 km. The unnamed tributary at 3.037 km flowed into this marshy area and may not have effectively diluted the Coal Creek tracer during the synoptic sampling. All samples in the wetland areas were collected from what could best be identified as the main channels to ensure proper monitoring of the tracer.

The metal loading tracer tests were conducted over a total distance of 9.4 km in two reaches, but sampling errors and an over-abundance of tributaries entering Coal Creek from both sides with insufficient spacing for proper monitoring of tracer dilution led us to conclude that flow rates, metal concentrations, and metal loading analyses were accurate only up to a distance of 5.940 km. The following graphs only include data up to 5.940 km, which includes all tributaries apparently emanating from the Mount Emmons drainages including and east of the Keystone Mine. The final tributary included in the analyses is at 5.885 km and flows from the southern flank of the peak east of Mount Emmons.

pH in Coal Creek

The pH in Coal Creek varied by a range of 0.79 pH units. The minimum Coal Creek pH was 6.26 at the distance 2.691 km; the maximum was pH 7.05 at 4.323 km (Figure 9). This maximum occurred at the upper-most synoptic sampling site of the lower tracer dilution study. The Coal Creek pH at CC-5.177, the synoptic sampling site just upstream of the drinking water intake (D.W. intake), was 6.93, 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 (CDPHE, 2005).

The pH range established for cold water aquatic life is 6.5 to 9.0 (CDPHE, 2005); thus, the first four sites of the upper Coal Creek synoptic sampling stretch fell below the lower aquatic life toxicity standard. These sites are located at 0.519 km, 0.620 km, 0.783 km, and 0.977 km. An additional site at 2.691 km also fell below the lower aquatic life toxicity standard. More than half of the tributaries flowing into Coal Creek had pH below the lower aquatic life toxicity standard. These included Splains Gulch and Elk Creek. UT-3.106 had a pH below the toxicity standard, as did all of the tributaries flowing from the iron gossan and fen region (Figure 3). The lowest measured pH was 3.27 from UT-4.186. The Mount Emmons tributary had a pH of 5.82. Other tributaries below the toxicity standard were located at 3.835 km (a south bank tributary), 4.521 km, 4.585 km, 4.627 km, 5.094 km, 5.517 km, 5.766 km, and 5.885 km. Note that UT-5.517, UT-5.766, and UT-5.885 all originate from drainages on Mount Emmons.

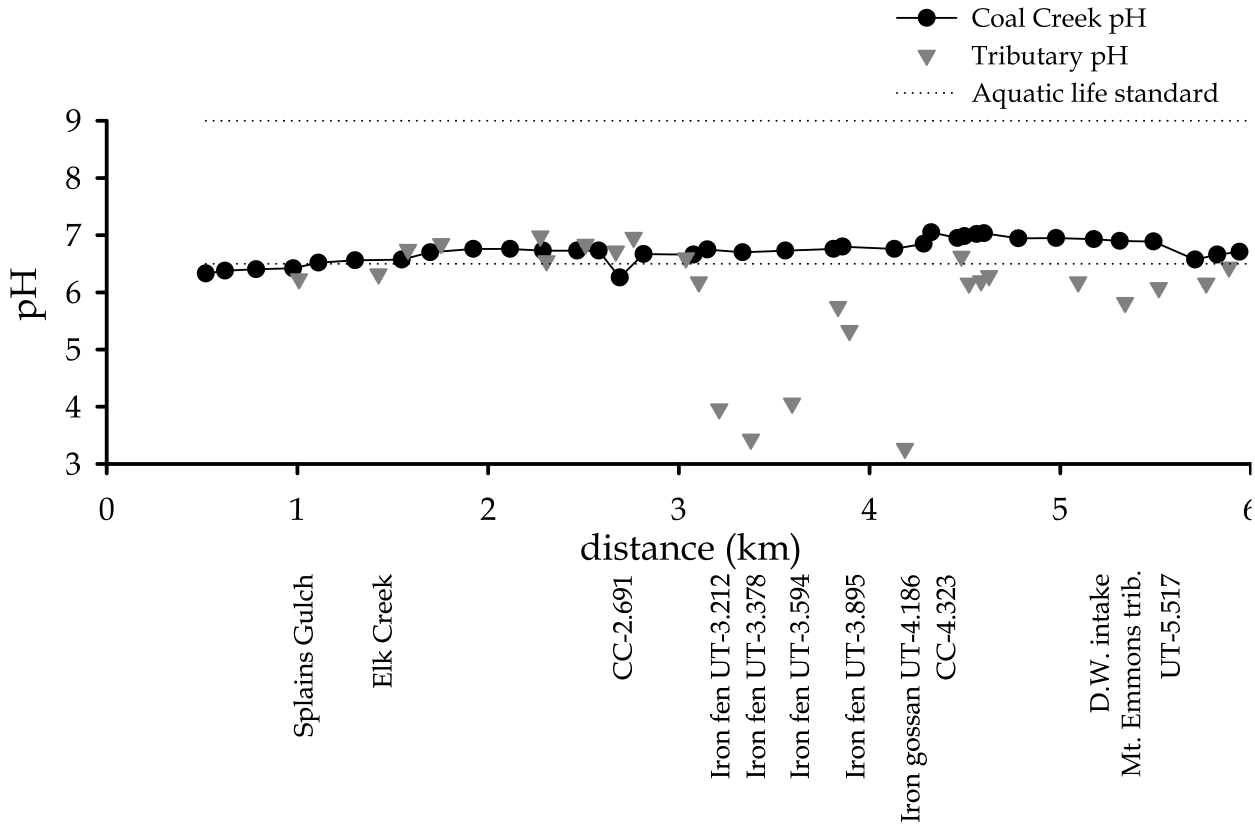

Figure 9. Coal Creek and tributary pH. All pH measurements were made within 12 h of sample collection. The aquatic life standards for pH were established by the CDPHE (CDPHE, 2007). The Town of Crested Butte drinking water intake is denoted as "D.W. intake".

Calcium and Magnesium Concentrations and Hardness in Coal Creek

Hardness was calculated from the dissolved calcium and magnesium concentrations along Coal Creek and presented in units of mg $CaCO_3$ L^{-1} (Figure 10). Magnesium concentrations remained nearly constant with a small and fairly steady increase along the length of the two tracer dilution studies. The dissolved magnesium concentration in Coal Creek ranged from 0.68 mg L^{-1} at the uppermost sample site to 1.02 mg L^{-1} at CC-4.130 km. A number of tributaries exceeded the Coal Creek magnesium concentrations, including UT-2.274, UT-3.594, and UT-4.186. UT-3.594 and UT-4.186 are major iron gossan and fen drainages.

The dissolved calcium concentrations ranged from a minimum of 5.5 mg L^{-1} at CC-1.302 to a maximum of 15.5 mg L^{-1} at CC-5.940 (Figure 10). While numerous tributaries exceeded the Coal Creek calcium concentrations, Elk Creek (14.4 mg L^{-1}) and the Mount Emmons tributary (161 mg L^{-1}) were the only two to significantly affect the calcium concentration in Coal Creek concentration.

The Coal Creek hardness ranged from 17 mg $CaCO_3$ L^{-1} at CC-1.302 to 43 mg $CaCO_3$ L^{-1} at CC-5.940 (Figure 10). Coal Creek hardness was fairly constant with two significant increases following the inflows of Elk Creek and the Mount Emmons tributary. The Coal Creek hardness increased by approximately 7.9 mg $CaCO_3$ L^{-1}

downstream of Elk Creek, whose hardness was 40 mg $CaCO_3$ L^{-1}. Hardness was again fairly constant until a small dip downstream of CC-4.978. Hardness then promptly increased by 17.5 mg $CaCO_3$ L^{-1} downstream of the treatment plant effluent, which had a hardness of 410 mg $CaCO_3$ L^{-1}. A decrease in hardness followed the sudden increase downstream of the treatment plant effluent, and then another increase in Coal Creek hardness was observed downstream of UT-5.885. The decrease was likely due to sampling Coal Creek at places not thoroughly mixed downstream of the tributaries UT-5.517 and UT-5.766.

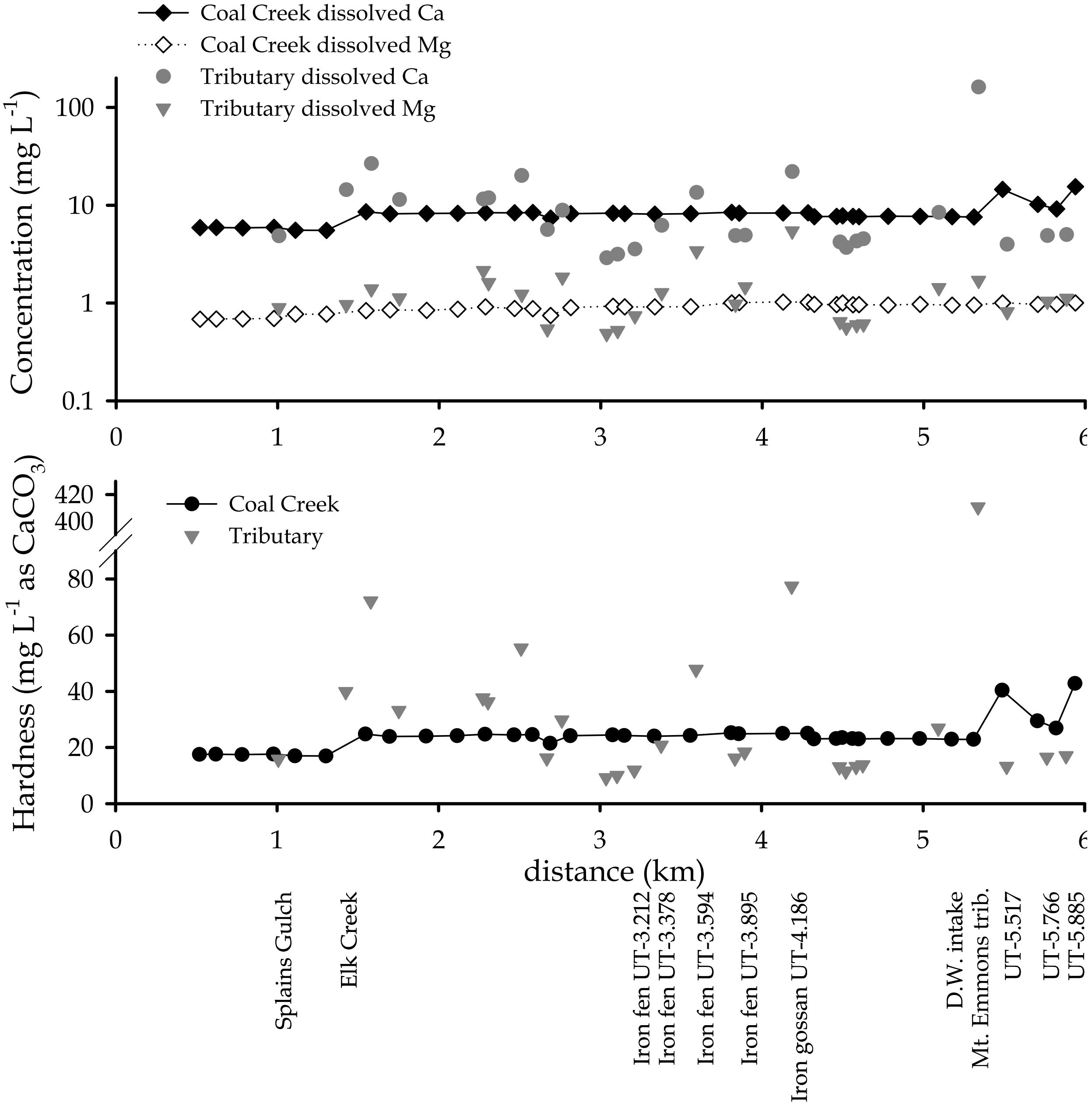

Figure 10. Magnesium and calcium concentrations and hardness along Coal Creek and its tributaries. Hardness is presented with units of mg L^{-1} as $CaCO_3$.

Chloride Concentration in Injection Solution

The average chloride concentration for the upper Coal Creek tracer injection was 48,700 mg L^{-1}, or 1.37 M. Concentrations ranged from 47,200 to 50,000 mg L^{-1} after dropping one apparent outlier at 406 mg L^{-1} (Table 6). The injection solution was replenished once at 15:10, and the conductivities of the first and second injection solutions were measured in the field to be equal. The IC results show that the concentrations in the two tanks were nearly equal.

The average chloride concentration for the lower Coal Creek tracer injection was 28,100 mg L^{-1} with a range from 21,800 to 49,500 mg L^{-1} (Table 7). The apparent outlier at 49,500 mg L^{-1} was dropped and the average concentration was time-weighted. The injection solution was replenished twice during the study. The second injection solution was started at 12:25. A third injection solution was started at 16:05.

Table 6. Chloride (Cl^-) concentration measured by IC in the injection for the metal loading tracer dilution test conducted on the upper reach of Coal Creek.

sample time (h:min)	Cl^- (mg L^{-1})
08:00	47,200
09:00	48,100
10:00	50,000
11:00	48,900
12:00	48,100
13:03	49,100
14:00	49,400
15:00	406
15:30	48,900
16:00	48,400

Table 7. Chloride (Cl^-) concentration measured by IC in the injection for the metal loading tracer dilution test conducted on the lower reach of Coal Creek.

sample time (h:min)	Cl^- (mg L^{-1})
08:42	25,600
09:42	21,800
10:35	21,900
11:37	49,500
12:33	25,200
13:33	25,400
14:37	30,500
15:37	37,800
16:07	29,900
16:35	29,800

Chloride Concentration at the Downstream Ends of the Coal Creek Reaches

Samples were collected from sites at the downstream ends of the tracer dilution study reaches every 15 min throughout the tracer dilution studies (Tables 8 and 9). The upper Coal Creek downstream site was located at CC-4.284. The minimum downstream end chloride concentration for the upper Coal Creek tracer dilution study was 0.32 mg L^{-1} measured at 09:00 (Table 8). An increase in the downstream end chloride concentration was observed beginning at 09:30. The increase continued until about 13:00, where the downstream end chloride concentration began to hold steady at an average chloride concentration of 1.28 mg L^{-1}. The marked increase indicated that the injection chloride pulse had reached the downstream end of the study reach.

The lower Coal Creek downstream end was located at CC-9.387 km. The minimum chloride concentration at the lower Coal Creek downstream end was 0.51 mg L^{-1}

measured at 08:30 (Table 9). A small increase was observed from 08:30 until 12:45, after which the concentration held steady at an average 1.27 mg L^{-1} from 12:45 until 14:15. From 14:30 until the end of the synoptic sampling at 17:00, the chloride concentration held steady at an average of 0.83 mg L^{-1} with the exception of one increase at 14:45.

Table 8. Chloride (Cl^-) concentration measured by IC at the downstream end of the metal loading tracer dilution test conducted on the upper reach of Coal Creek.

sample time (h:min)	Cl^- (mg L^{-1})
08:30	0.32
08:45	0.32
09:00	0.32
09:15	0.32
09:30	0.48
09:45	0.74
10:00	0.92
10:15	1.02
10:30	1.06
10:45	1.10
11:00	1.13
11:15	1.13
11:30	1.19
11:45	1.17
12:00	1.17
12:15	1.18
12:30	1.21
12:45	1.19
13:00	1.23
13:15	1.23
13:30	1.25
13:45	1.23
14:00	1.22
14:15	1.24
14:30	1.26
14:45	1.31
15:00	1.25
15:15	1.26
15:30	1.25
15:45	1.23
16:00	1.30
16:15	1.37
16:30	1.40

Table 9. Chloride (Cl^-) concentration measured by IC at the downstream end of the metal loading tracer dilution test conducted on the lower reach of Coal Creek.

sample time (h:min)	Cl^- (mg L^{-1})
08:30	0.51
08:45	0.62
09:00	0.70
09:15	0.74
09:30	0.85
09:45	0.63
10:00	0.76
10:30	0.90
10:45	0.86
11:00	1.01
11:15	0.82
11:30	0.87
11:45	0.87
12:00	0.80
12:15	0.93
12:30	0.91
12:45	1.17
13:00	1.12
13:15	1.43
13:30	1.18
13:45	1.38
14:00	1.33
14:15	1.15
14:30	0.87
14:45	2.28
15:00	0.76
15:15	0.79
15:30	0.86
15:45	0.83
16:00	0.81
16:15	0.80
16:30	0.79
16:45	0.84
17:00	0.98

Chloride Concentrations in Coal Creek and Tributaries

For the injection on the upper reach of Coal Creek, the "background" chloride concentration sampled at CC-0.519 was 0.45 mg L^{-1} and the chloride concentration at the first site downstream of the injection, CC-0.620, was 4.05 mg L^{-1} during the synoptic sampling. The chloride injection increased the Coal Creek chloride concentration by a factor of 9.0 (Figure 10).

For the injection on the lower reach of Coal Creek, the "background" chloride concentration sampled at CC-4.323 was 0.39 mg L^{-1} and the chloride concentration at the first site downstream of the injection, CC-4.461, was only 0.780 mg L^{-1} during the synoptic sampling. The chloride injection increased the Coal Creek chloride concentration by a factor of only 2 owing to the higher flow in lower Coal Creek (Figure 12).

Tributary chloride concentrations ranged from 0.141 mg L^{-1} to 2.74 mg L^{-1}. The upper reach injection exceeded the tributary chloride concentration through the reach, but two tributaries in the lower reach exceeded the chloride concentration in Coal Creek, which led to problems calculating the flow for these tributaries.

Flow Rate in Coal Creek

Flow rates in Coal Creek were calculated using the chloride concentrations measured during the synoptic samplings on the upper and lower reaches of Coal Creek and the equations presented in Table 4. At some locations, assumptions and estimations were required. First, the flow rate at the town drinking water supply intake located at 5.296 km was estimated at 79.3 L s^{-1} based on communications with the Town of Crested Butte. This diverted flow was subtracted from the Coal Creek flow rate.

Second, sampling sites were not always located far enough downstream from tributaries to ensure that a sample taken from one point clearly captured a mixture of the tributary and stream flow. At high flow in June 2006, separate tributaries often entered Coal Creek in close proximity. We attempted to capture the flow and metal loading of each tributary by placing stream sampling sites between tributaries. When tributaries were separated by about 25 m or less, the samples, which were usually collected from one bank (typically, the north bank), may represent the composition of the upstream tributary or the stream more than a complete mixture of the two (Figure 11). Such situations probably led to unreasonably low or high chloride concentrations at these sampling sites that did not properly reflect Coal Creek dilution by the tributary. If we determined that accurate sampling may have been compromised by tributaries in close proximity, we estimated and bracketed between a reliable upstream and downstream concentration. This type of estimation was used at the following sites:

- CC-1.547, to account for inadequate mixing just downstream of Elk Creek,
- CC-2.287, to account for inadequate mixing between the very closely spaced tributaries UT-2.274 and UT-2.306,

- CC-2.580, CC-2.691, and CC-2.815, to account for inadequate mixing between the very closely spaced tributaries UT-2.511, UT-2.670 (which drains Evans Basin), and UT-2.763,
- CC-4.461, to account for inadequate mixing of the lower reach injection at 4.324 km; and
- CC-4.600, CC-4.780, and CC-5.823, to account for inadequate mixing between very closely spaced tributaries.

The flow rate of tributary UT-2.670, which drains Evans Basin, was estimated as 25% of the Splains Gulch flow rate. This estimation was made concurrently with the chloride concentration estimations of CC-2.580, CC-2.691, and CC-2.815 in order to accurately estimate the flow rate and chloride contribution of the three closely spaced tributaries. To this end, Equation 6 (Table 4) was used to calculate the Coal Creek flow rate using the estimated tributary flow.

Figure 11. A muddy tributary flows into Coal Creek from the north bank (on the left) and gradually mixes with the stream. If a sample was collected from the north bank in this unmixed region, the measured chloride concentrations would have been more representative of the low chloride concentration in the tributary rather than the higher chloride concentration in the stream.

Third, downstream concentrations of chloride were sometimes higher than upstream concentrations, which results in invalid calculations using Equation 5 (Table 4). For example, the chloride concentration at CC-3.558 was higher than the Coal Creek concentration at the site upstream. This anomaly was likely due to the very small variation in chloride concentration at subsequent sites (less than 0.02 mg L^{-1} for some stretches) and overlapping IC error. Therefore, the chloride concentration was estimated and bracketed between the next upstream and downstream concentrations. Furthermore, UT-3.594 had a chloride concentration 1.8 times higher than that of CC-3.558, the Coal Creek site immediately upstream. When a tributary concentration is greater than the background Coal Creek concentration, Equation 5 (Table 4) breaks down and must be modified. In these cases, Equation 6 was used with the estimated chloride concentration at CC-3.558 and a tributary flow rate estimated at 0.2% of the Coal Creek flow rate. A similar situation occurred at CC-5.177, CC-5.312, and CC-5.489, which are located directly downstream of UT-5.094 and the Mount Emmons tributary (5.340 km). The chloride concentrations of UT-5.094 and the treatment plant effluent were nearly equal to the background Coal Creek concentration.

The Coal Creek flow rates calculated based on the dilution of chloride generally increased from the upstream to downstream ends of the studies. This corresponded to a decreasing trend in chloride concentration (Figure 12). All flow rate calculations were made using Equations 4, 5, and 6 (Table 4). The initial flow rate at the first site of the upper synoptic sampling stretch, CC-0.620, was 542 L s^{-1}, while the flow rate at the last sampling site of the lower synoptic sampling stretch, CC-5.940, was 2,040 L s^{-1}

(2.04 m^3 s^{-1}, or 72.0 ft^3 s^{-1}). Flow rates increased with distance at all sites except between CC-5.177 and CC-5.312 due to the decrease in flow by 79.3 L s^{-1} from the town drinking water intake. Tributary flow rates ranged from a minimum of 4.9 L s^{-1} at the unnamed tributary UT-3.594 that flowed from the iron gossan and fen to a maximum of 460 L s^{-1} at Splains Gulch. Table 10 gives the site distances, brief descriptions, and final flow rate calculations based on the chloride dilution equations and necessary estimations.

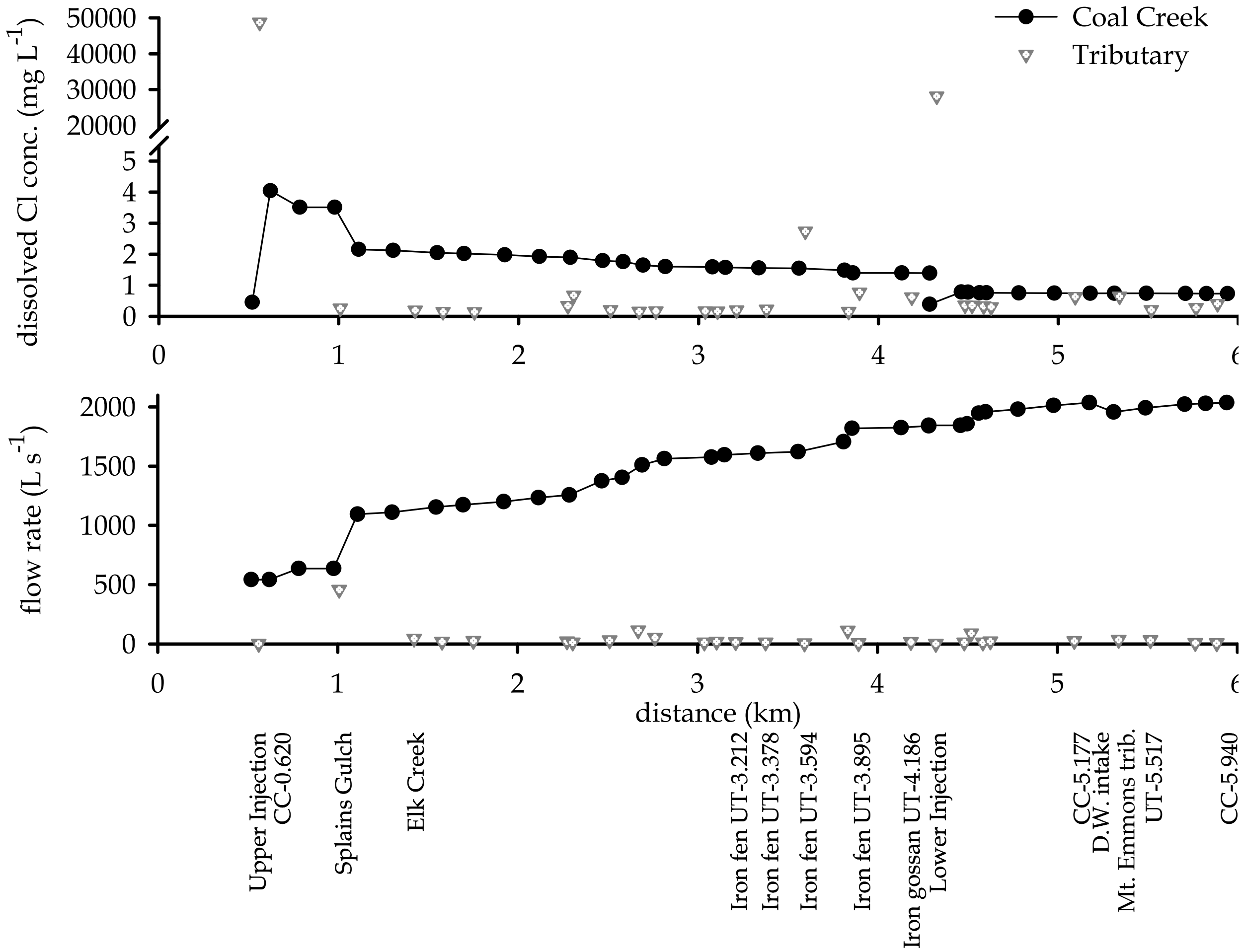

Figure 12. Dissolved chloride concentrations and flow rates along Coal Creek and its tributaries. Flow rates were calculated based on the dilution of the chloride concentration with distance downstream of the injection sites. The calculated flow rates were used to find metal loading rates.

Table 10. Coal Creek flow rates at sample sites and tributaries. Site names are given as either “CC- “ or “UT- “ to reflect samples taken from Coal Creek or unnamed tributaries. The numbers following the letters indicate distances in km downstream of the September, 2005, study’s upstream sample site. Flow rates (L s^{-1}) were calculated based on chloride dilution with distance downstream.

site name	**latitude**	**longitude**	**site description**	**Coal Creek flow rate (L s^{-1})**	**tributary flow rate (L s^{-1})**
CC-0.000			September 2005 metal-loading tracer-dilution test upstream site		
CC-0.519	38° 51' 20"	107° 04' 11"	upper injection upstream sample site	542.15	
0.561	38° 51' 20"	107° 04' 10"	upper injection site		
CC-0.620	38° 51' 19"	107° 04' 07"		542.19	
CC-0.783	38° 51' 19"	107° 04' 00"		636.49	
CC-0.977	38° 51' 19"	107° 03' 52"		636.70	
1.008	38° 51' 19"	107° 03' 51"	Splains Gulch		457.22
CC-1.110	38° 51' 20"	107° 03' 47"		1,093.91	
CC-1.302	38° 51' 20"	107° 03' 39"		1,110.47	
1.425	38° 51' 22"	107° 3' 34"	Elk Creek (drainage from the Standard Mine)		44.47
CC-1.547	38° 51' 22"	107° 03' 29"		1,154.94	
UT-1.580	38° 51' 22"	107° 03' 28"			19.34
CC-1.696	38° 51' 23"	107° 03' 23"		1,174.28	
UT-1.754	38° 51' 23"	107° 03' 20"			25.78
CC-1.922	38° 51' 21"	107° 03' 15"		1,200.06	
CC-2.115	38° 51' 24"	107° 03' 09"		1,234.51	
UT-2.274	38° 51' 26"	107° 03' 04"	south bank tributary, enters wetland from avalanche path		21.40
CC-2.287	38° 51' 21"	107° 03' 15"	wetland area	1,255.92	
UT-2.306	38° 51' 28"	107° 03' 05"			12.56
CC-2.467	38° 51' 24"	107° 03' 09"	wetland area	1,375.05	
UT-2.511	38° 51' 33"	107° 03' 01"			30.12
CC-2.580	38° 51' 35"	107° 02' 59"	wetland area	1,405.17	
UT-2.670	38° 51' 35"	107° 02' 56"	flows from Evans Basin		114.30
CC-2.691	38° 51' 35"	107° 02' 54"		1,509.88	
UT-2.763	38° 51' 35"	107° 02' 52"	South bank tributary near avalanche path		52.78
CC-2.815	38° 51' 36"	107° 02' 50"		1,562.65	
UT-3.037	38° 51' 42"	107° 02' 48"	flows into wetland pond, not directly into Coal Creek		12.39
CC-3.077	38° 51' 43"	107° 02' 46"		1,575.05	
UT-3.106	38° 51' 44"	107° 02' 45"			19.57
CC-3.149	38° 51' 44"	107° 02' 44"		1,594.62	
UT-3.212	38° 51' 45"	107° 02' 41"	iron fen drainage, primary		15.20
CC-3.335	38° 51' 44"	107° 02' 36"		1,609.82	
UT-3.378	38° 51' 44"	107° 02' 35"	iron gossan and fen drainage		12.44
CC-3.558	38° 51' 44"	107° 02' 29"		1,622.26	
UT-3.594	38° 51' 44"	107° 02' 28"	iron gossan and fen drainage		4.87
CC-3.811	38° 51' 45"	107° 02' 20"		1,706.18	

Table 10 (continued). Coal Creek flow rates at sample sites and tributaries. Site names are given as either "CC- " or "UT- " to reflect samples taken from Coal Creek or unnamed tributaries. The numbers following the letters indicate distances in km downstream of the September, 2005, study's upstream sample site. Flow rates (L s^{-1}) were calculated based on chloride dilution with distance downstream.

site name	latitude	longitude	site description	Coal Creek flow Rate (L s^{-1})	tributary flow rate (L s^{-1})
UT-3.835	38° 51' 44"	107° 02' 19"	south bank tributary		113.38
CC-3.858	38° 51' 45"	107° 02' 18"		1,819.56	
UT-3.895	38° 51' 46"	107° 02' 16"	iron gossan drainage		5.61
CC-4.130	38° 51' 46"	107° 02' 08"		1,825.17	
UT-4.186	38° 51' 47"	107° 02' 07"	iron gossan drainage		15.78
CC-4.284	38° 51' 48"	107° 02' 03"		1,840.95	
CC-4.323	38° 51' 49"	107° 02' 02"	lower injection upstream sample site	1,844.96	
4.324	38° 51' 50"	107° 02' 00"	lower injection site		
CC-4.461	38° 51' 50"	107° 01' 56"		1,844.98	
UT-4.482	38° 51' 50"	107° 01' 55"	south bank tributary		12.34
CC-4.498	38° 51' 50"	107° 01' 55"		1,857.32	
UT-4.521	38° 51' 50"	107° 01' 54"	south bank tributary		89.42
CC-4.562	38° 51' 51"	107° 01' 52"		1,946.74	
UT-4.585	38° 51' 51"	107° 01' 51"	south bank tributary		11.60
CC-4.600	38° 51' 52"	107° 01' 51"		1,958.34	
UT-4.627	38° 51' 52"	107° 01' 50"	south bank tributary		21.89
CC-4.780	38° 51' 55"	107° 01' 45"		1,980.22	
CC-4.978	38° 51' 58"	107° 01' 37"		2,012.28	
UT-5.094	38° 51' 58"	107° 01' 33"	south bank tributary		24.14
CC-5.177	38° 51' 59"	107° 01' 30"		2,036.43	
5.296	38° 52' 01"	107° 01' 26"	Crested Butte drinking water intake	79.29	
CC-5.312	38° 52' 01"	107° 01' 25"		1,957.14	
5.340	38° 52' 02"	107° 01' 25"	Mount Emmons tributary (Mt. Emmons treatment plant effluent, road-side ditch, and tributary draining Keystone Mine property)		34.60
CC-5.489	38° 52' 04"	107° 01' 19"		1,991.74	
UT-5.517	38° 52' 05"	107° 01' 18"	upstream of Wildcat Trail bridge		31.15
CC-5.707	38° 52' 07"	107° 01' 12"		2,022.89	
UT-5.766	38° 52' 08"	107° 01' 09"			7.00
CC-5.823	38° 52' 08"	107° 01' 07"		2,029.89	
UT-5.885	38° 52' 08"	107° 01' 04"	upstream of road turnoff to Mt. Emmons treatment plant		6.24
CC-5.940	38° 52' 09"	107° 01' 02"	at road turnoff to Mt. Emmons treatment plant	2,036.13	

Metals in Coal Creek and Tributaries

Metals analyzed included aluminum, barium, cadmium, chromium, copper, iron, lead, manganese, and zinc. Total and dissolved (0.45 µm filtration) metal concentrations were analyzed for each metal at each sample site. All aquatic life toxicity standards apply only to the dissolved metal concentrations unless otherwise noted. 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 all the metals analyzed using Equation 8 (Tables 11 and 12).

Table 11. Total ("Tot") metal loading rates expressed as percentages of the cumulative total metal loading rate for Coal Creek as determined by Equation 8. 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.

Source / Tributary	Tot Al (%)	Tot Ba (%)	Tot Cd (%)	Tot Cr (%)	Tot Cu (%)	Tot Fe (%)	Tot Pb (%)	Tot Mn (%)	Tot Zn (%)
Splains Gulch-1.008	4.8	**33.9**		*20.0*	3.8	*21.5*		0.4	0.5
Elk Creek-1.425	0.5	3.9	4.5		*12.2*	3.0	**52.5**	2.1	4.2
UT-1.580		1.7			1.3	0.2			
UT-1.754	0.3	1.4			0.2	3.1		0.1	
UT-2.274	0.1	3.4		2.7	0.3	0.2			
UT-2.306		0.6		**37.0**		0.1	0.5		
UT-2.511	0.1	2.5		4.6	0.2	1.2		0.2	
UT-2.670, Evans Basin	0.4	5.5	0.2		0.8	1.8		0.1	0.8
UT-2.763	0.1	5.4		1.8	0.2	0.3			
UT-3.037	0.2	0.6			0.2	1.4	0.4	0.1	
UT-3.106	0.3	1.1			0.3	2.0	0.8	0.1	0.1
UT-3.212, iron fen	3.7	1.8	2.1		0.5	2.9	0.4	2.2	2.6
UT-3.378, iron fen	8.1	2.0	4.4		0.6	5.8	1.5	4.9	5.8
UT-3.594, iron fen	5.7	1.3	1.3		1.0	1.5	0.6	3.9	2.6
UT-3.835	1.9	5.9			0.6	7.6		0.3	0.1
UT-3.895, iron fen	0.9	0.5	0.5		0.1	0.3		0.7	0.9
UT-4.186, iron gossan	**55.9**	2.5	**81.9**		**52.1**	8.5	*32.0*	**64.4**	**76.5**
UT-4.482	1.0	1.7		1.5	0.1	2.8	0.2		
UT-4.521	5.9	9.6		2.6	0.9	*17.7*	0.4	0.3	0.1
UT-4.585	0.5	1.6		2.1	0.1	1.4			
UT-4.627	0.8	3.1		4.9	0.3	2.4			
UT-5.094	0.9	2.3	0.1	4.2	0.5	3.4	0.4	0.1	0.2
Mount Emmons tributary	5.9	2.8	4.6	5.6	*21.3*	8.4	9.0	*18.4*	4.1
UT-5.517	1.6	3.6	0.4	1.0	2.2	0.8	0.8	1.5	1.3
UT-5.766	0.2	0.7		1.0	0.1	1.0	0.1		
UT-5.885	0.3	0.7		10.9	0.1	0.6	0.3		

Table 12. Dissolved ("Diss") metal loading rates expressed as percentages of the cumulative dissolved metal loading rate for Coal Creek as determined by Equation 8. 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.

	Diss Al (%)	Diss Ba (%)	Diss Cd (%)	Diss Cr (%)	Diss Cu (%)	Diss Fe (%)	Diss Pb (%)	Diss Mn (%)	Diss Zn (%)
Splains Gulch-1.008	4.3	**36.4**		**70.3**	4.3	**36.7**		0.3	0.7
Elk Creek-1.425	0.3	4.0	4.3		10.8	1.6	**33.6**	1.9	4.0
UT-1.580		1.7				0.3			
UT-1.754	0.1	1.4			0.2	2.1			0.1
UT-2.274		3.6		8.6	0.3	0.3			
UT-2.306		0.8			0.1			0.1	
UT-2.511		2.5		2.8	0.1			0.2	
UT-2.670, Evans Basin		5.7	0.2		0.8			0.1	0.7
UT-2.763	0.1	5.8			0.2				0.1
UT-3.037		0.6			0.1	1.0		0.1	
UT-3.106		1.0			0.2	0.8			
UT-3.212, iron fen	0.1	1.9	2.1		0.5	5.9	0.2	1.7	2.6
UT-3.378, iron fen	4.4	2.1	4.4		0.7	8.9	2.0	4.6	5.8
UT-3.594, iron fen	9.5	1.3	1.3		0.9	0.8	0.7	3.6	2.6
UT-3.835	6.5	5.2			0.5	2.5			0.1
UT-3.895, iron fen	0.2	0.6	0.6		0.1			0.7	0.9
UT-4.186, iron gossan	**65.3**	2.6	**82.0**		**60.2**	*21.2*	**63.2**	**68.3**	**76.7**
UT-4.482	0.4	1.2		1.0	0.1	1.0			0.0
UT-4.521	0.1	7.2		2.0	1.0	8.2		0.1	0.1
UT-4.585	1.1	1.5		2.9	0.2	1.3			
UT-4.627	0.2	2.9		6.1	0.3	3.5			
UT-5.094	0.5	2.1	0.1	3.6	0.4	1.7		0.1	0.2
Mount Emmons tributary	0.1	2.9	4.6	1.5	*15.9*	0.9	0.3	*16.9*	3.9
UT-5.517	6.3	3.6	0.3		1.7	0.4		1.3	1.3
UT-5.766	0.2	0.6		0.9	0.1	0.4			
UT-5.885		0.7		0.3	0.1	0.5			

Aluminum concentrations and loading rates. Aluminum concentrations in Coal Creek ranged from a minimum of 41 µg L^{-1} total and 26 µg L^{-1} dissolved aluminum at CC-2.691 to a maximum of 117 µg L^{-1} total and 77 µg L^{-1} dissolved aluminum at CC-5.489 (Figure 13). Aluminum concentrations generally decreased with distance downstream from the upstream end of the study until the minimum at CC-2.691. Downstream of this point, the concentration generally increased, largely due to the high concentrations of the tributary inflows along the iron gossan and fen reach.

Aluminum concentrations in Coal Creek did not approach the acute aquatic life toxicity standard of 750 µg L^{-1} total recoverable aluminum; however, numerous sites exceeded the chronic toxicity standard of 87 µg L^{-1} total recoverable aluminum. The designation of "total recoverable" is similar to our "total" samples. If the pH is at least

7.0 and the water hardness at least 50 mg $CaCO_3$ L^{-1}, the 87 µg L^{-1} standard does not apply, but the 750 µg L^{-1} standard must still be met. Of the Coal Creek sites exceeding the 87 µg L^{-1} standard, only a few had pH greater than or equal to 7.0 (Figure 9). The pH ranged from 6.26 to 7.05 for the Coal Creek study area. No sites met the hardness requirement. There is no 30-day drinking water supply standard for aluminum (CDPHE, 2005).

The minimum total aluminum concentration in a tributary was 3.6 µg L^{-1} in UT-2.306. All of the iron gossan and fen tributaries, UT-3.212, UT-3.378, UT-3.594, UT-3.895, and UT-4.186, had very high aluminum concentrations ranging from 700 µg L^{-1} in UT-3.895 to the maximum of 15,100 µg L^{-1} in UT-4.186. The treatment plant effluent had the fifth highest aluminum concentration of 720 µg L^{-1}. The total aluminum concentration was much greater than the dissolved phase concentration for most of the tributaries. Only Splains Gulch, Elk Creek, UT-2.306, UT-3.594, and the treatment plant effluent had more than 50% of the aluminum in the dissolved phase. All other sites had greater than 50% colloidal aluminum (where "colloidal" is defined as the difference between the total and dissolved metal). The tributaries UT-5.517 and UT-5.885, both Mount Emmons drainages located downstream of the treatment plant effluent, had the greatest colloidal fractions of 89.9% and 92.8% respectively.

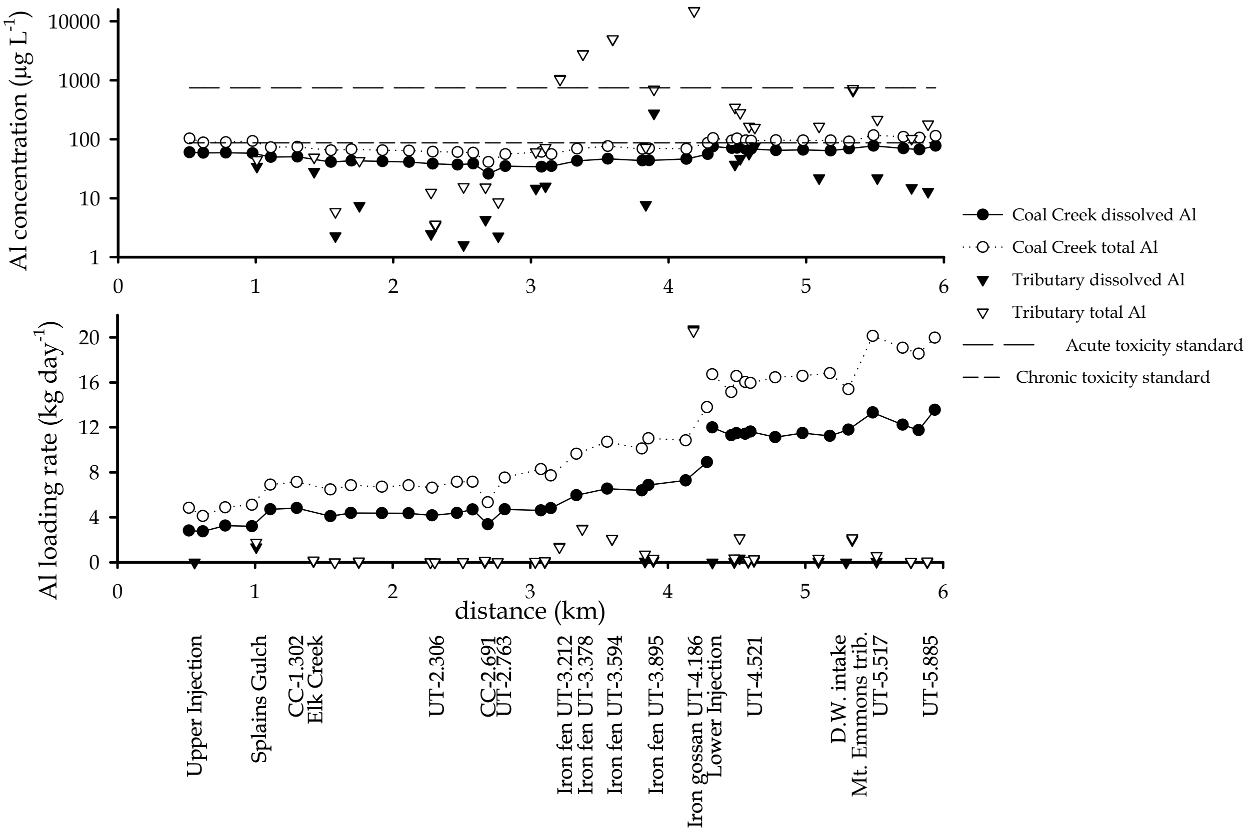

Figure 13. Total and dissolved aluminum concentrations, loading rates, and acute and chronic toxicity standards along Coal Creek and its tributaries.

Aluminum loading rates in Coal Creek steadily increased with distance downstream. There was a small jump in loading rate at CC-1.110 just downstream of the Splains Gulch inflow. A small decrease in loading rate occurred at CC-2.691 just downstream of UT-2.670, which drains Evans Basin. There was a significant loading rate spike following the inflow of UT-4.186. A second smaller spike occurred at CC-5.489 just downstream of the treatment plant effluent. The greatest loading source was UT-4.186, the tributary draining the iron gossan, which contributed 55.9% of the total and 65.3% of the dissolved phase aluminum to Coal Creek (Tables 11 and 12). No other source exceeded 10% aluminum contribution, although UT-4.521 and the treatment plant both had the next highest contributions of 5.9% total aluminum. UT-3.378 contributed 9.5% of the dissolved aluminum.

Barium concentrations and loading rates. Barium concentrations in Coal Creek did not vary much from the average of 14.7 µg L^{-1} total barium (Figure 14). The majority of barium was present in the dissolved phase, with a maximum colloidal fraction of only 6%. No aquatic life toxicity standards exist for barium. The 1-day drinking water supply toxicity standard is 1,000 µg L^{-1} dissolved barium, and the 30-day drinking water supply standard is 490 µg L^{-1} dissolved barium (CDPHE, 2007). Neither of these values was approached by the Coal Creek barium concentrations.

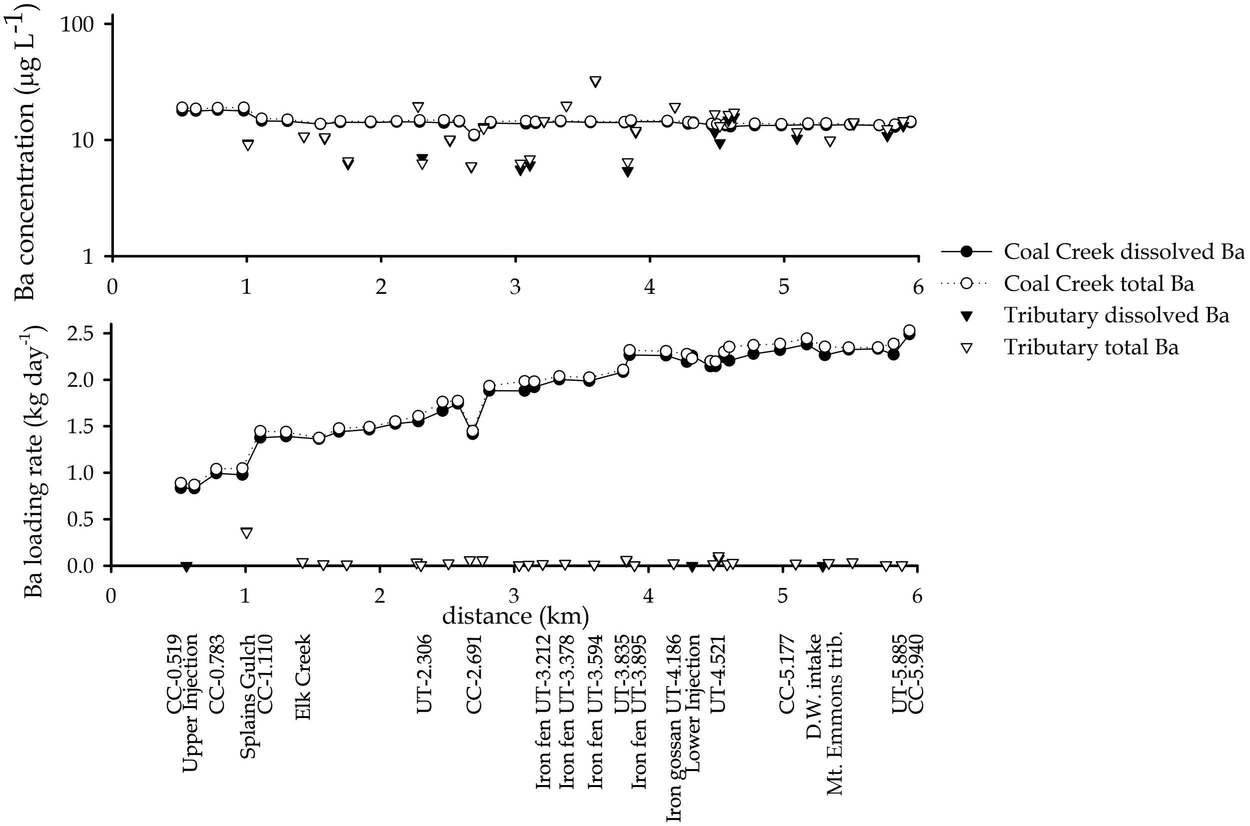

Figure 14. Total and dissolved barium concentrations and loading rates along Coal Creek and its tributaries.

Tributary barium concentrations ranged from a minimum of 6.0 µg L^{-1} total barium at UT-2.670 (Evans Basin) to a maximum of 32.9 µg L^{-1} total barium at UT-3.594. Dissolved barium concentrations were similar in the tributaries. The maximum colloidal fraction in a tributary was 31%, with the majority of tributaries less than 15% colloidal.

In a few Coal Creek and tributary samples, dissolved concentrations exceeded the total concentrations by a few percent. The probable cause for this kind of anomaly is a difference in the sample matrix between the dissolved (filtered) and total sample.

Barium loading rates steadily increased with only a small spike at CC-1.110, the first sample site downstream of Splains Gulch, and a small dip at CC-2.691. The maximum Coal Creek loading rate was 2.53 kg d^{-1} total and 2.49 kg d^{-1} dissolved barium occurring at CC-5.940. Splains Gulch contributed the most barium to Coal Creek (33.9% of the cumulative total barium loading and 36.4% of the dissolved barium loading). UT-4.521, a south bank tributary just downstream of the lower Coal Creek injection site, contributed 9.6% of total and 7.2% of dissolved barium, while UT-3.835, also a south bank tributary entering Coal Creek across from the iron gossan and fen tributaries, contributed 5.9% of total and 5.2% of dissolved barium.

Cadmium concentrations and loading rates. The Coal Creek cadmium concentration remained fairly constant except for the concentration spike at CC-1.547, immediately downstream of the Elk Creek inflow (Figure 15). Cadmium concentrations were below the detection limit in Coal Creek until its confluence with Elk Creek. The detection limits for the upper and lower Coal Creek metal loading tracer dilution tests were 0.018 µg L^{-1} and 0.036 µg L^{-1}, respectively. The detection limits were different because the trace metals were measured in two separate ICP-MS runs.

The maximum Coal Creek cadmium concentrations were 0.90 µg L^{-1} total cadmium and 0.88 µg L^{-1} dissolved cadmium. The maximum concentrations occurred at sample site CC-1.547, the first sample site downstream of Elk Creek. The majority of cadmium in Coal Creek was in the dissolved phase. The maximum colloidal fraction was 18% and occurred at CC-3.149. Dissolved cadmium concentrations exceeded total concentrations at CC-2.287 and CC-5.707.

The acute aquatic life toxicity standard was hardness-based for dissolved cadmium concentrations and was only exceeded at CC-1.547. A separate acute toxicity standard specified for trout is also hardness-based for dissolved cadmium concentrations. The trout standard was exceeded at multiple sites along Coal Creek, including CC-1.547, CC-1.696, and CC-1.922, which are the three sample sites downstream of Elk Creek, and every sample site between CC-4.284 and CC-5.177, all of which occur downstream of the iron gossan and fen tributaries. CC-5.177 was the sample site immediately upstream of the drinking water intake. The inflow of the Mount Emmons tributary added calcium, which increased hardness and the cadmium toxicity standard. Sites downstream of the treatment plant effluent have dissolved cadmium concentrations that fall back below the toxicity standard at times when the effluent is being discharged. The chronic aquatic life toxicity standard is hardness-based for dissolved cadmium concentrations and was exceeded at every Coal Creek sample site downstream of the

Elk Creek confluence. The 1-day drinking water supply standard of 5.0 µg L^{-1} cadmium (CDPHE, 2007) was never approached in Coal Creek.

Tributary concentrations ranged from below detection limit to a maximum of 142 µg L^{-1} total cadmium and 143 µg L^{-1} dissolved cadmium in UT-4.186. The maximum measured colloidal fraction was 38% in UT-5.094.

Coal Creek cadmium loading rates were reported as zero for all sites with cadmium concentrations below the detection limits. The maximum loading rates were 0.11 kg d^{-1} total cadmium at CC-5.489, the first sample site downstream of the treatment plant effluent, and 0.11 kg d^{-1} dissolved cadmium at CC-4.323, just downstream of the iron gossan and fen tributaries. Cadmium loading rates had three spikes, the first and largest occurring at CC-1.547, the first site downstream of Elk Creek. The second spike occurred downstream of UT-4.186, and the third spike occurred at CC-5.489. The iron gossan tributary UT-4.186 was the single largest source of cadmium along Coal Creek, contributing 81.9% of total and 82.0% of dissolved cadmium (Tables 11 and 12). No other source contributed more than 5%. Elk Creek contributed 4.5% of total and 4.3% of dissolved cadmium, while the Mount Emmons tributary contributed 4.6% of both total and dissolved cadmium. UT-3.378, the second iron fen tributary, contributed 4.4% of both total and dissolved cadmium.

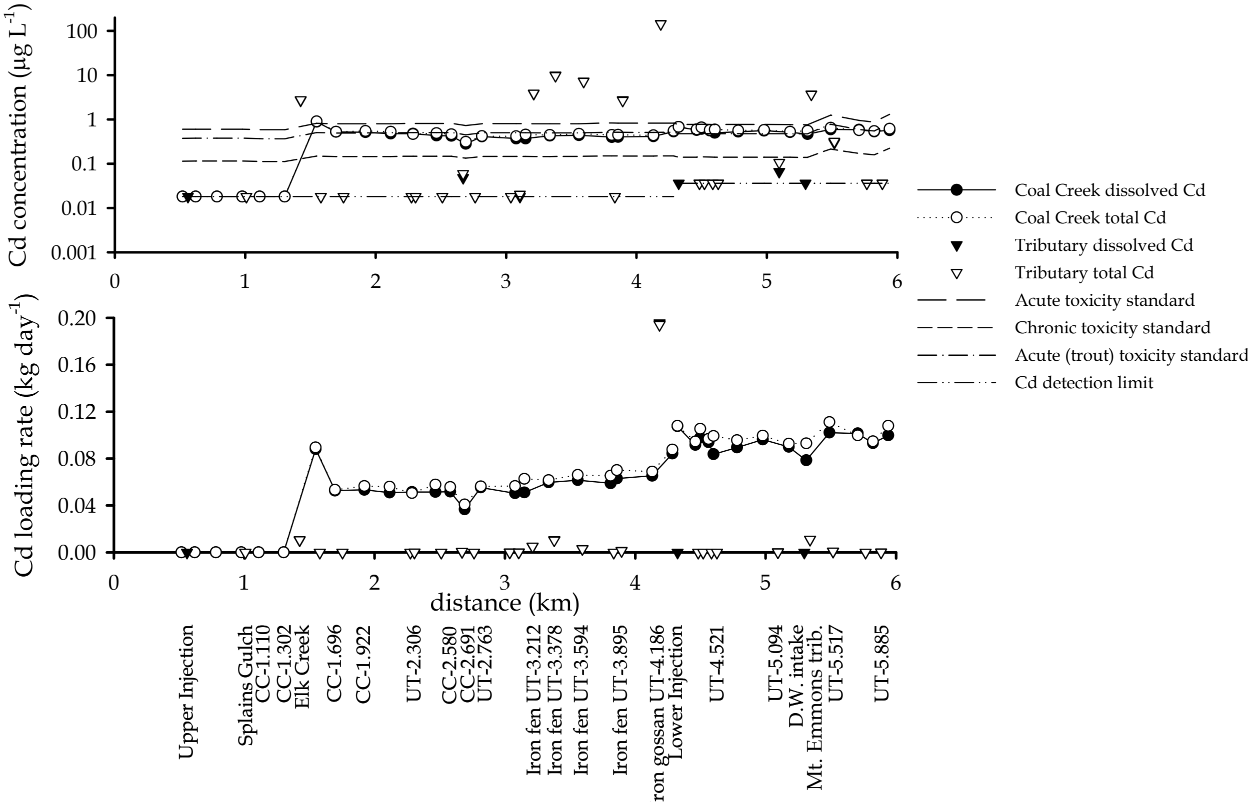

Figure 15. Total and dissolved cadmium concentrations, loading rates, acute and chronic toxicity standards, and detection limits along Coal Creek and its tributaries.

Chromium concentrations and loading rates. Chromium was nearly undetectable for most of the length of Coal Creek (Figure 16). Of the sample sites along the upper Coal Creek synoptic study stretch, only CC-0.519, CC-0.977, and CC-2.287 had total chromium concentrations greater than the detection limit of 0.18 μg L^{-1}. All samples with concentrations measured below the detection limits were reported as having the detection limit value. The detection limit for the lower Coal Creek synoptic study stretch was significantly lower, 0.085 μg L^{-1}, and yielded more variable results. The maximum Coal Creek total chromium concentration was 0.274 μg L^{-1} at CC-0.977, while the maximum dissolved chromium concentration was 0.186 μg L^{-1} at CC-5.177. Because ICP-MS analysis does not differentiate between chromium(III) and chromium(VI), CDPHE specifies that toxicity standards used should be those for chromium(VI). The acute and chronic aquatic life toxicity standards for chromium(VI) are 16 μg L^{-1} and 11 μg L^{-1} dissolved chromium respectively. No Coal Creek chromium concentrations approached these values, so the standards do not appear in Figure 16. The 1-day drinking water supply standard is 50 μg L^{-1} dissolved chromium and also does not appear in Figure 16 (CDPHE, 2007). The Coal Creek chromium speciation varied greatly from only a 4% colloid fraction at CC-2.287 to a 64% colloid fraction at CC-4.600. The dissolved chromium concentrations exceeded the total concentrations at CC-4.498, CC-4.562, and CC-4.978, indicating very small colloidal fractions.

The only measurable tributary chromium concentration along the upper Coal Creek synoptic stretch was UT-2.306, which had the maximum tributary concentrations of 2.00 μg L^{-1} total and 0.18 μg L^{-1} dissolved chromium. UT-2.306 flows from the north bank into the Coal Creek wetland almost directly across from UT-2.274, a heavily vegetated tributary flowing out of a large avalanche path. Several tributaries had measurable chromium concentrations along the lower Coal Creek synoptic stretch, including UT-5.885, which had the second highest total chromium concentration of 1.19 μg L^{-1}.

Coal Creek chromium loading was fairly constant along the upper Coal Creek synoptic stretch. A small loading rate jump occurred at CC-0.977, although the source of this increase is not clear. The inflow of Splains Gulch caused an increase in the dissolved chromium loading rate at the next downstream sample site CC-1.110. The lower Coal Creek synoptic sampling stretch loading rates jumped around considerably, with a sharp decrease in total chromium loading at CC-4.498, then a sharp increase at CC-4.600 and a second decrease at CC-4.978. A second sharp increase occurred at CC-5.177, the first downstream sample site from UT-5.094. This increase yielded the maximum total chromium loading rate of 0.048 kg d^{-1}. A third small increase in the total loading rate occurred at CC-5.823, followed by a sharp increase in the dissolved loading rate at CC-5.940. Splains Gulch was the prominent chromium source for Coal Creek, contributing 35.8% of total and 41.6% of dissolved chromium (Tables 11 and 12). UT-2.306 contributed 11.0% of total but only 1.1% of dissolved chromium, while UT-2.670 (Evans Basin) contributed 9.0% of total and 10.4% of dissolved chromium. UT-3.835, a south bank tributary, contributed 8.9% of total and 10.3% of dissolved chromium. The Mount Emmons tributary was not a significant source of chromium.

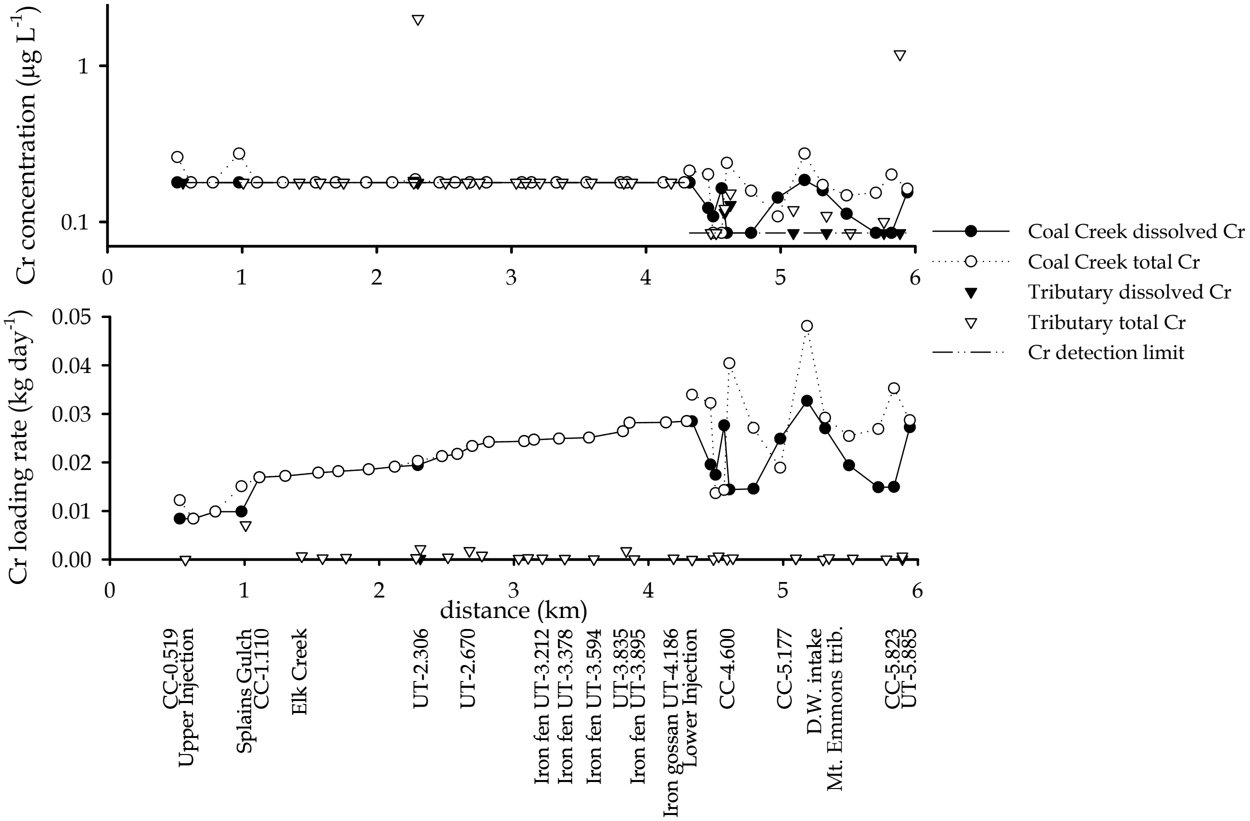

Figure 16. Total and dissolved chromium concentrations, loading rates, and detection limits along Coal Creek and its tributaries.

Copper concentrations and loading rates. The Coal Creek copper concentration was fairly constant for the first kilometer of sampling (Figure 17). A drop in copper concentration followed the input of Splains Gulch, which had a low copper concentration. The inflow of Elk Creek significantly increased the Coal Creek concentration, which remained fairly constant downstream of Elk Creek. The minimum Coal Creek copper concentration was 0.41 µg L^{-1} total copper at CC-1.302 and 0.31 µg L^{-1} at CC-1.110. The maximum copper concentration was 3.3 µg L^{-1} total and 2.8 µg L^{-1} dissolved copper occurring at CC-1.547, the first sample site downstream of Elk Creek. The acute aquatic life toxicity standard was hardness-based for dissolved copper concentrations and was never exceeded along Coal Creek. The chronic aquatic life toxicity standard was also hardness-based for dissolved copper concentrations and was exceeded only at the site CC-1.547. The 30-day drinking water supply standard of 1,000 µg L^{-1} was never approached (CDPHE, 2007). Coal Creek copper was primarily present in the dissolved phase, with the maximum colloidal fraction of 22% occurring at CC-2.580.

Tributary copper concentrations ranged from a minimum total copper concentration of 0.12 µg L^{-1} at UT-2.306 and a minimum dissolved copper concentration of 0.05 µg L^{-1}

at UT-1.580 to a maximum total copper concentration of 101 µg L^{-1} and dissolved concentration of 102 µg L^{-1} at UT-4.186, the iron gossan tributary. Dissolved copper concentrations exceeded total copper concentrations in a few tributaries. No Coal Creek sample sites had dissolved copper concentrations greater than total concentrations. Most tributaries contributed predominantly dissolved phase copper with colloidal fractions less than 35%. The colloidal fraction was 97.3% for UT-1.580, the first tributary downstream of Elk Creek.

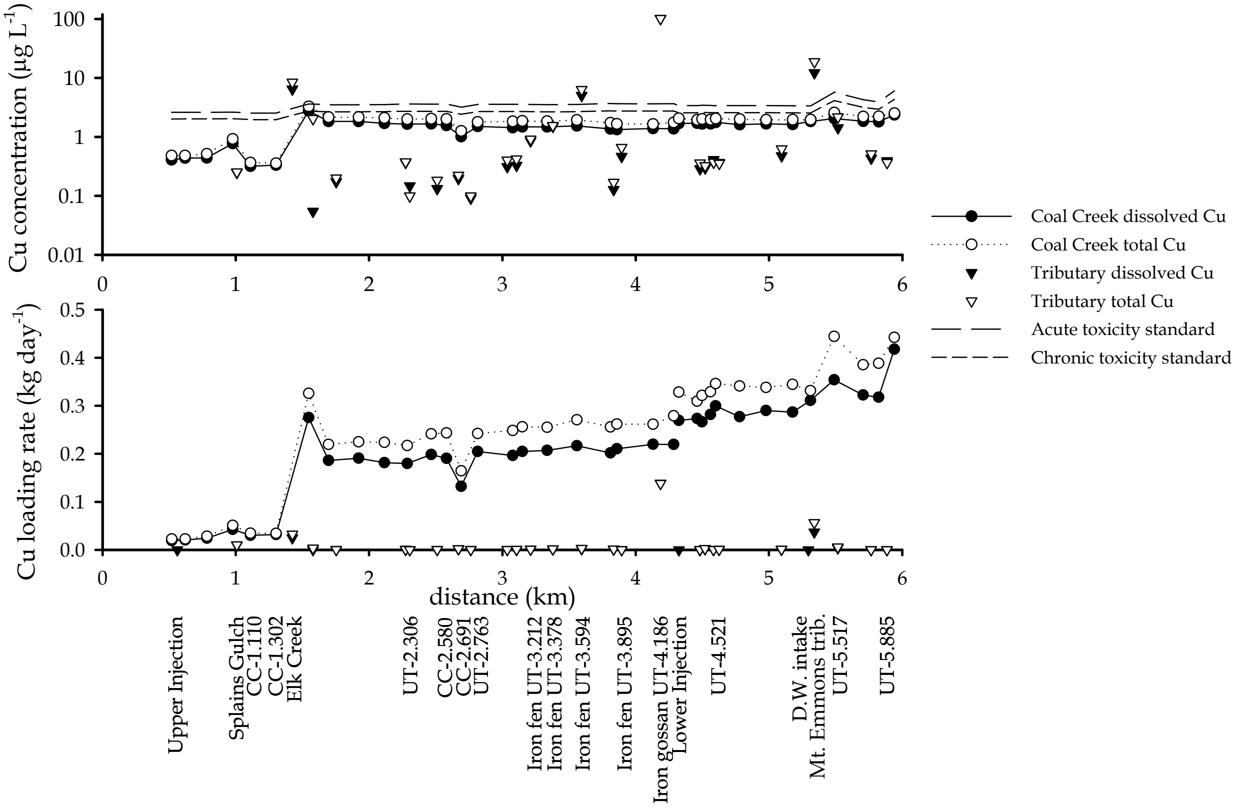

Figure 17. Total and dissolved copper concentrations, loading rates, and acute and chronic toxicity standards along Coal Creek and its tributaries.

Coal Creek copper loading rates followed a gradually increasing trend except for a very large loading rate spike at CC-1.547 just downstream of Elk Creek. A marked shift in the copper loading rate was observed at the breaking point between the upper and lower Coal Creek synoptic study reaches. This was apparently due to decreased loading rates the day of the upper Coal Creek synoptic study. A second loading rate spike occurred at CC-5.489 just downstream of the treatment plant effluent. A third loading rate spike was observed at CC-5.940 just downstream of UT-5.885. The minimum Coal Creek loading rate was 0.022 kg d^{-1} total and 0.019 kg d^{-1} dissolved copper at the most upstream sample site CC-0.519. The maximum Coal Creek loading rate was 0.44 kg d^{-1} total copper at the site CC-5.489 and 0.42 kg d^{-1} dissolved copper at the site CC-5.940. The sharp increase in dissolved copper loading at CC-5.940 indicates a small colloidal fraction at that site. The maximum tributary loading rate was 0.14 kg d^{-1} total and dissolved copper at UT-4.186, the iron gossan tributary. UT-4.186 was the primary copper source for Coal Creek, contributing 52.1% of total and 60.2% of dissolved copper (Tables 11 and 12). The Mount Emmons tributary contributed 21.3% of total and 15.9% of dissolved copper. Elk Creek contributed 12.2% of total and 10.8% of dissolved copper. No other source contributed more than 5% of Coal Creek's copper.

Iron concentrations and loading rates. Iron concentrations in Coal Creek ranged from a minimum of 55 µg L^{-1} total iron and 30 µg L^{-1} dissolved iron at CC-2.691 to a maximum of 150 µg L^{-1} total iron at the upper Coal Creek upstream end CC-0.519 and 71 µg L^{-1} dissolved iron at the first upper Coal Creek synoptic sampling site CC-0.620 (Figure 18).

The chronic toxicity standard for aquatic life is 1,000 µg L^{-1} dissolved iron. This standard was never exceeded along Coal Creek. There is no acute aquatic life toxicity standard. The 30-day drinking water supply standard for dissolved iron is 300 µg L^{-1} and was never exceeded along Coal Creek (CDPHE, 2007).

The tributary total iron concentrations ranged from 4.2 µg L^{-1} at UT-2.306 to 450 µg L^{-1} at the most downstream iron gossan drainage, UT-4.186. Dissolved tributary iron concentrations ranged from below the detection limit to 430 µg L^{-1} at UT-4.186. Tributary concentrations measured below the ICP-AES detection limits were plotted at the detection limit value of 3.0 µg L^{-1}. Total iron concentrations were much greater than dissolved iron concentrations for the tributaries UT-3.378, UT-3.594, UT-4.482, UT-4.521,

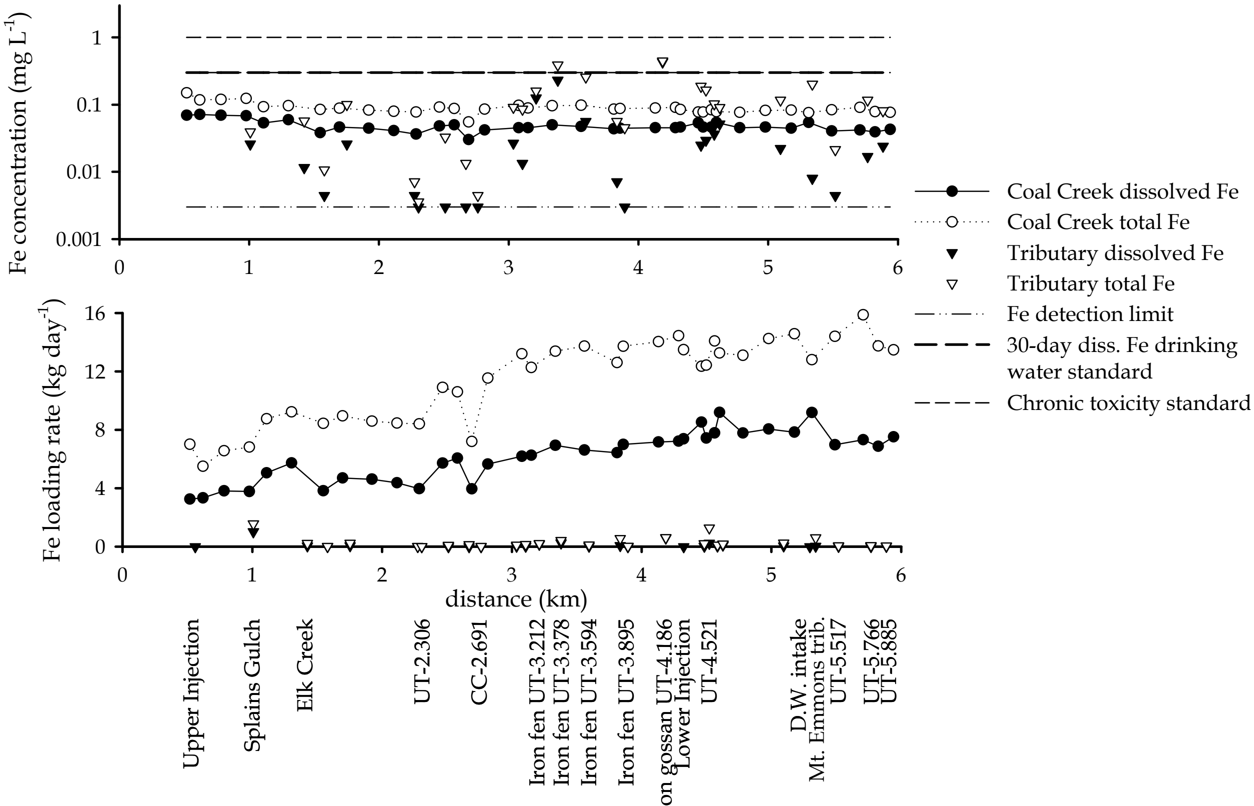

Figure 18. Total and dissolved iron concentrations and loading rates, detection limits, chronic aquatic life toxicity standard, and 30-day drinking water standard along Coal Creek and its tributaries.

the Mount Emmons tributary, and UT-5.766.

Iron loading rates generally increased with distance downstream. The Coal Creek minimum iron loading rate was 5.5 kg d^{-1} at CC-0.620 and the maximum loading rate was 15.8 kg d^{-1} at CC-5.707.

Splains Gulch and the tributary UT-4.521, a south bank tributary, were the primary sources of total iron loading in Coal Creek, contributing 21.5% and 17.7% respectively (Tables 11 and 12). Splains Gulch and UT-4.186, the iron gossan tributary, were the primary sources of dissolved iron loading, contributing 36.7% and 21.2% respectively. UT-4.186 had a relatively low flow rate, but very high iron concentrations (as well as other metals). UT-4.186 primarily contributed dissolved iron to Coal Creek, whereas Splains Gulch contributed both colloidal and dissolved iron and UT-4.521 contributed predominantly colloidal iron.

Lead concentrations and loading rates. Upstream of Elk Creek, lead was nearly undetectable, while downstream of Elk Creek the concentrations jumped to an average of 1.3 µg L^{-1} (Figure 19). CC-1.110 and CC-1.302 had total lead concentrations below the detection limits and were reported at the detection limit value of 0.2 µg L^{-1} for the upper Coal Creek synoptic samples. The maximum Coal Creek concentrations were 3.1 µg L^{-1} total lead and 1.5 µg L^{-1} dissolved lead occurring at CC-1.547, the first sample site downstream of Elk Creek.

Coal Creek lead concentrations never approached the acute aquatic life toxicity standard, which was hardness-based for dissolved lead and averaged 13.3 µg L^{-1}. The chronic aquatic life toxicity standard, which is also hardness-based for dissolved lead, was exceeded at twelve sites between CC-1.547 and CC-3.558, all of which were downstream of Elk Creek. Sites CC-4.323 through CC-5.312 also exceeded the chronic toxicity standard downstream of the iron gossan and fen. The 1-day drinking water supply standard is 50 µg L^{-1} total recoverable lead (CDPHE, 2007). This standard was never approached by the Coal Creek total lead concentrations. The colloidal fraction ranged from 29% to 68%, the average being 52%.

Tributary lead concentrations ranged from undetectable to a maximum of 16 µg L^{-1} of both total and dissolved lead in UT-4.186, the iron gossan tributary. Only eleven tributaries had total lead concentrations above the detection limit of 0.2 µg L^{-1}. Elk Creek had the second highest lead concentrations with 9.4 µg L^{-1} total lead and 3.1 µg L^{-1} dissolved lead. Tributary colloidal fractions ranged from only 1% in UT-4.186 to 94% in UT-3.378, an iron fen tributary. The Elk Creek colloidal fraction was 68%.

Loading rates were nearly zero for the reach of Coal Creek upstream of the Elk Creek confluence. A large spike occurred at CC-1.547, the first sample site downstream of Elk Creek, resulting in the maximum Coal Creek loading rates of 0.31 kg d^{-1} total lead and 0.15 kg d^{-1} dissolved lead. Loading rates were then fairly constant for the remainder of the study stretch, averaging 0.19 kg d^{-1} for total lead. A distinct increase in the average loading rate was observed between the upper and lower synoptic sampling stretches, which indicates slightly lower loading rates the day of the upper Coal Creek synoptic study. The maximum tributary loading rates both occurred in Elk Creek and were 0.036 kg d^{-1} total lead and 0.022 kg d^{-1} dissolved lead. Elk Creek was the primary source of total lead in Coal Creek, contributing 53% of total and 34% of dissolved lead (Tables 11 and 12). UT-4.186, the iron gossan tributary, was the primary dissolved lead source, contributing 32% of total lead and 63% of dissolved lead. The Mount Emmons tributary contributed 9% of the total lead and a negligible amount of dissolved lead.

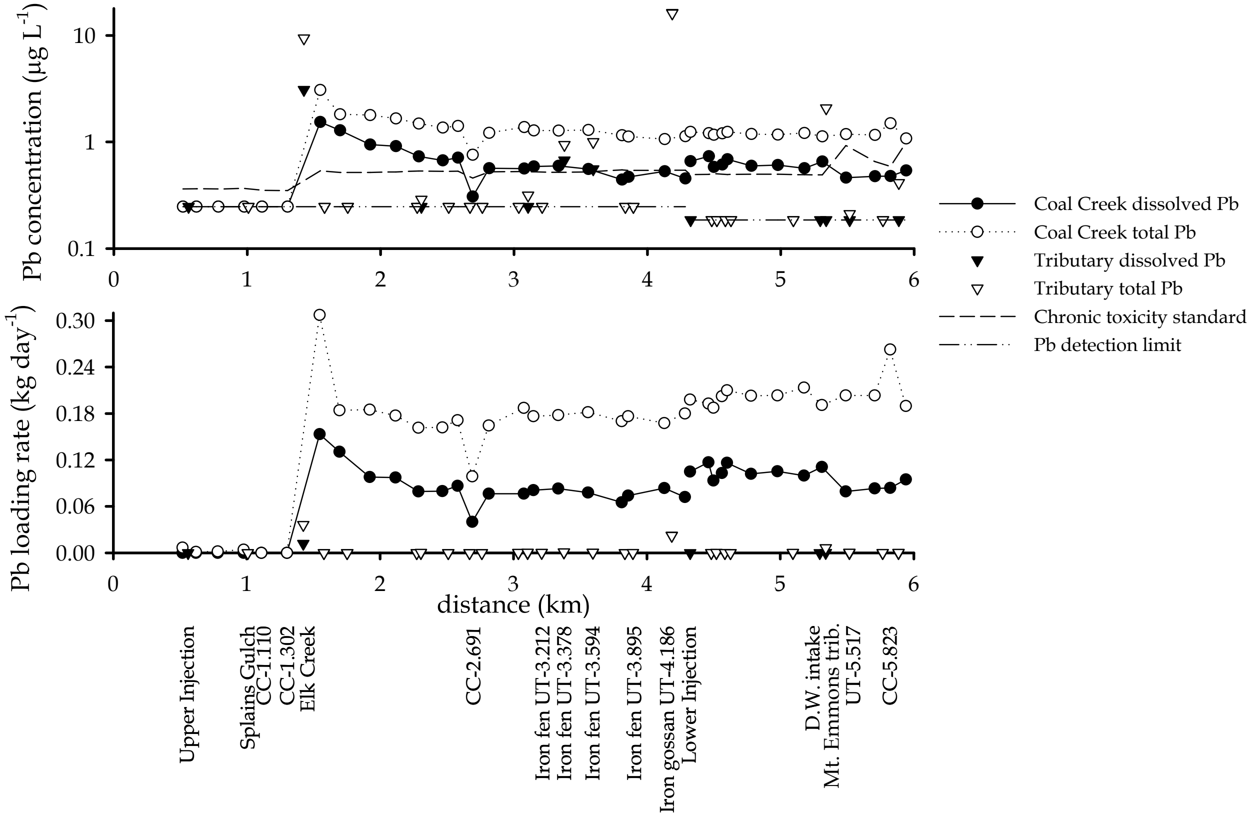

Figure 19. Total and dissolved lead concentrations, loading rates, chronic toxicity standards, and detection limits along Coal Creek and its tributaries.

Manganese concentrations and loading rates. Manganese concentration generally increased with distance downstream in Coal Creek (Figure 20); however, a significant decrease in concentration occurred downstream of Splains Gulch, which had a very high flow rate and low manganese concentration. The minimum Coal Creek total manganese concentration was 6.6 µg L^{-1} at CC-1.302. A sharp increase in Coal Creek manganese concentration followed the inflow of Elk Creek, which had a relatively high manganese concentration. The maximum Coal Creek total manganese concentration was 44 µg L^{-1} at CC-5.489, the first sample site downstream of the Mount Emmons tributary. For the entire study area, the total manganese concentrations were only slightly greater than the dissolved phase concentrations, indicating that manganese was present predominantly in the dissolved phase. The greatest colloidal-phase sample was 29% at CC-0.519.

Coal Creek manganese concentrations were significantly below both the acute and chronic aquatic life toxicity standards, which were both hardness-based and on the scale of 900 µg L^{-1} to 2,200 µg L^{-1} dissolved manganese. The 30-day drinking water supply standard is fixed at 50 µg L^{-1} for dissolved manganese (CDPHE, 2007). Coal Creek concentrations never exceeded this standard. The in-stream dissolved manganese concentration just upstream of the drinking water intake was 24.1 µg L^{-1}.

All of the iron gossan and fen tributaries (UT-3.212, UT-3.378, UT-3.594, UT-3.895, and UT-4.186), had high manganese concentrations ranging from 160 µg L^{-1} to a maximum of 5,000 µg L^{-1} in UT-4.186, the iron gossan tributary. The Mount Emmons tributary had the third-highest manganese concentration of 650 µg L^{-1}. In the tributaries, manganese was predominantly in the dissolved phase.

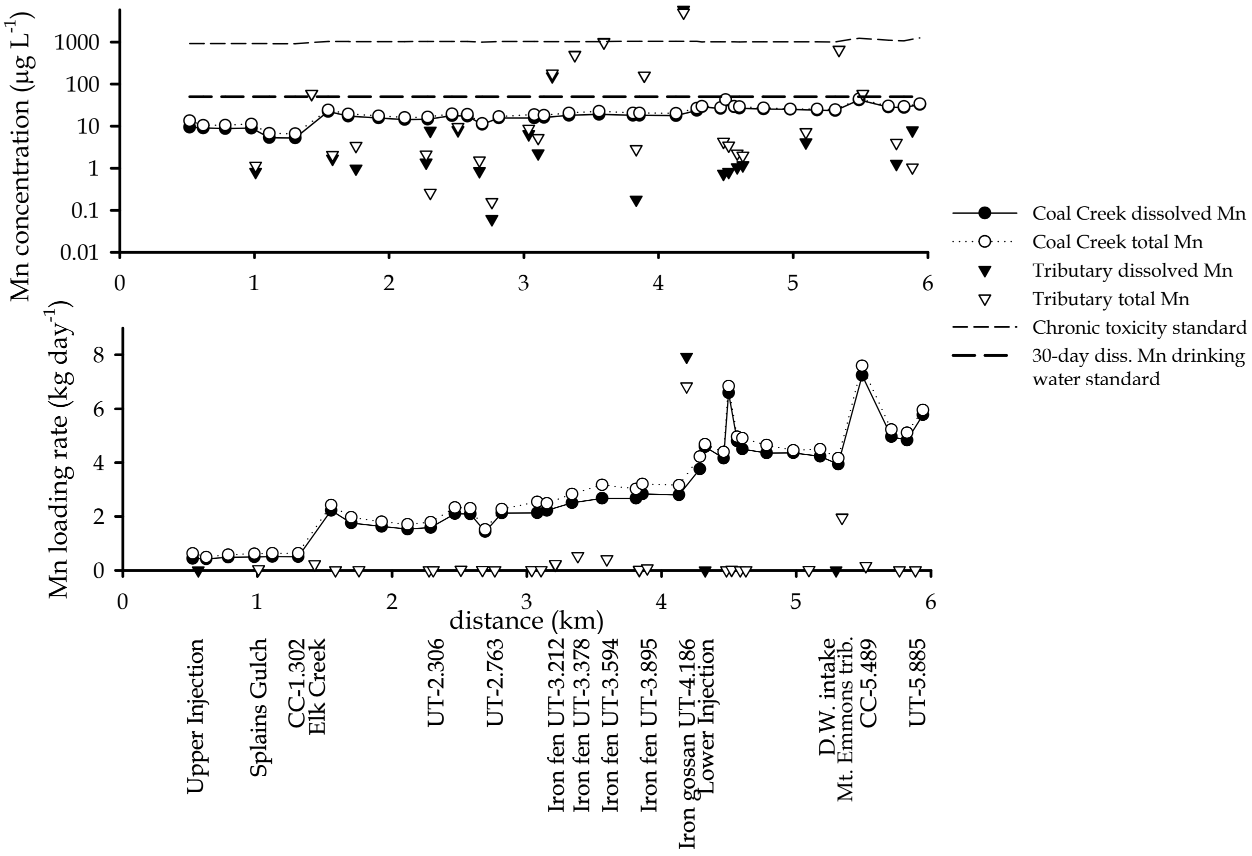

Figure 20. Total and dissolved manganese concentrations and loading rates, chronic toxicity standard, and 30-day drinking water standard along Coal Creek and its tributaries.

Coal Creek manganese loading rates generally increased with distance downstream. Three large loading rate spikes occurred at CC-1.547, CC-4.498, and CC-5.489. These spikes immediately followed the tributary inflows of Elk Creek, UT-4.482, and the Mount Emmons tributary. There was a gradual loading rate increase following the inflow of the iron gossan tributary UT-4.186, which contributed to the high loading rate at CC-4.498. The maximum total manganese loading rate was 7.6 kg d^{-1} at CC-5.489.

Total manganese loading rates were only slightly greater than dissolved loading rates, indicating that the majority of Coal Creek manganese was present in the dissolved phase. The iron gossan tributary UT-4.186 was the primary manganese loading source, contributing 64.6% of the total and 68.3% of the dissolved phase manganese (Tables 11 and 12). The Mount Emmons tributary was also a major contributor with 18.4% of the total and 16.9% of the dissolved phase manganese.

Zinc concentrations and loading rates. Coal Creek had two reaches of relatively constant zinc concentrations with a large increase in concentration occurring at CC-1.547 (Figure 21). The cause of the increase was the Elk Creek inflow, which had a high total zinc concentration of 390 µg L^{-1}. The maximum zinc concentrations in Coal Creek were 143 µg L^{-1} total zinc and 135 µg L^{-1} dissolved zinc at CC-1.547.

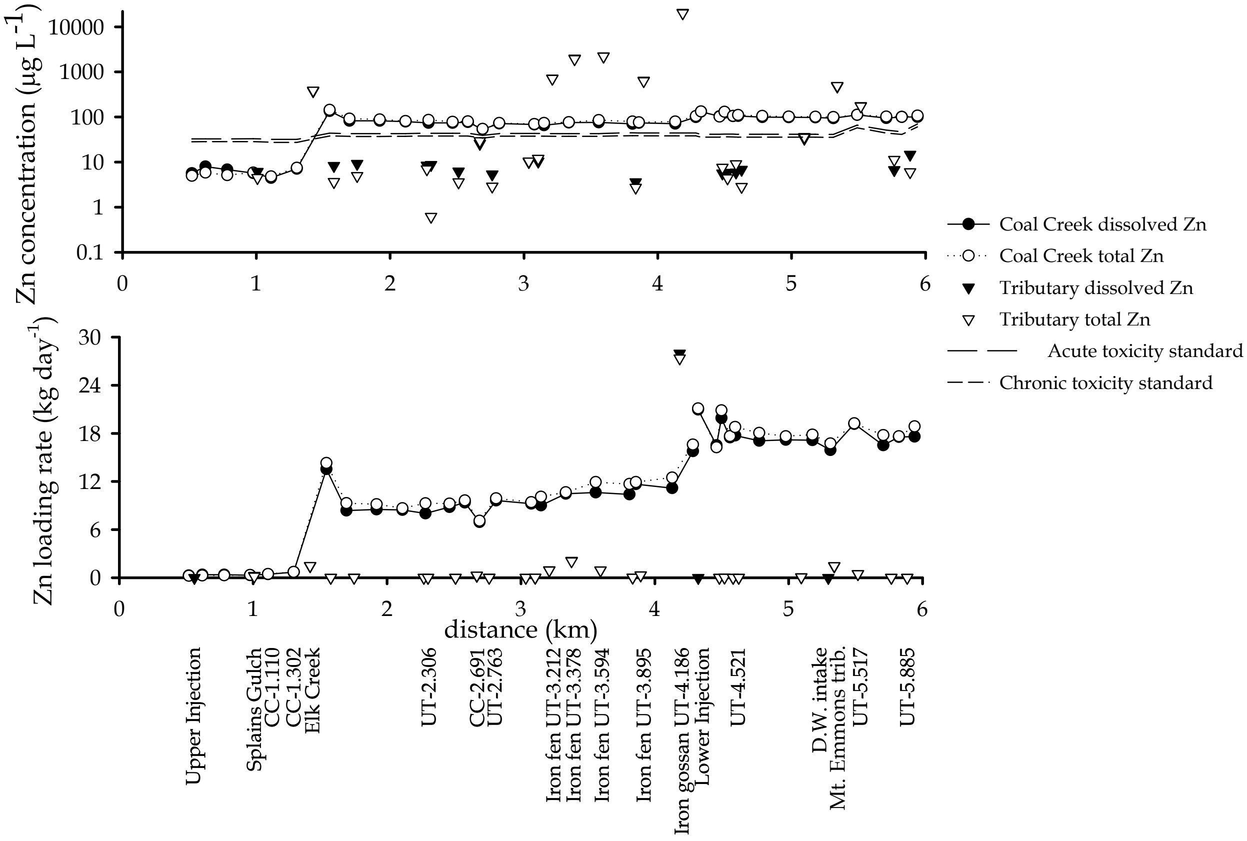

Figure 21. Total and dissolved zinc concentrations, loading rates, and acute and chronic toxicity standards along Coal Creek and its tributaries.

Downstream of the Elk Creek confluence, the Coal Creek zinc concentrations exceeded both acute and chronic aquatic life toxicity standards and never fell below them again for the remaining study reach. Both of the standards are hardness-based. The acute toxicity standard was in the 40 µg L^{-1} range, while the chronic toxicity standard was in the 30 µg L^{-1} range for Coal Creek. Coal Creek zinc concentrations did not approach the 5,000 µg L^{-1} 30-day drinking water supply standard for total recoverable zinc (CDPHE, 2007).

The maximum tributary zinc concentrations were 20,100 µg L^{-1} total zinc and 20,500 µg L^{-1} dissolved zinc, both of which occurred in UT-4.186, the iron gossan tributary. Four Coal Creek sample sites and 17 tributary samples had dissolved zinc concentrations exceeding the total concentrations.

All of the iron gossan and fen tributaries (UT-3.212, UT-3.378, UT-3.594, UT-3.895, and UT-4.186) had very high zinc concentrations ranging from 630 µg L^{-1} total zinc in UT-3.895 to the maximum of 20,100 µg L^{-1} total zinc in UT-4.186, the iron gossan tributary. The zinc from these tributaries was predominantly in the dissolved phase. The Mount Emmons tributary had concentrations of 490 µg L^{-1} total zinc and 480 µg L^{-1} dissolved zinc.

Zinc loading rates generally increased with distance downstream. Two significant increases in zinc loading rate occurred – one at CC-1.547 as a result of the Elk Creek inflow and one downstream of UT-4.186, the iron gossan tributary. A small loading rate increase occurred at CC-5.489, just downstream of the Mount Emmons tributary. The maximum loading rates were 21.1 kg d^{-1} total zinc and 20.1 kg d^{-1} dissolved zinc at CC-4.323, two sample sites downstream of the tributary UT-4.186. The maximum tributary loading rate was 27.3 kg d^{-1} total and 27.9 kg d^{-1} dissolved zinc at UT-4.186. UT-4.186 was the primary zinc source, contributing 76.5% of total zinc and 76.7% of dissolved zinc (Tables 11 and 12). No other sources exceeded 6%.

Metals in Standard Mine Samples

The four samples collected at the Standard Mine site were analyzed for pH, conductivity, and cation and metal concentrations (Figure 7). Samples SM-1 and SM-4 are Elk Creek sample sites.

Standard Mine pH. In the Standard Mine samples, the pH ranged from a minimum of 3.13 at SM-2, the Level 1 adit, to a maximum of 6.00 at SM-4, Elk Creek downstream of the tailings pond effluent (Table 13). The pH range established for cold water aquatic life is 6.5 to 9.0 (CDPHE, 2007). All of the Standard Mine samples were below the lower aquatic life toxicity standard, including both of the samples taken directly from Elk Creek.

Table 13. Values of pH measured in water samples taken from the Standard Mine site. For locations of the sample sites, refer to Figure 7.

sample site	pH
SM-1 Elk Creek upstream of the Standard Mine site	5.94
SM-2 Standard Mine Level 1 mine adit	3.13
SM-3 Standard Mine tailings pond effluent	5.27
SM-4 Elk Creek downstream of the tailings pond	6.00

Standard Mine hardness. Hardness was calculated from the dissolved calcium and magnesium concentrations measured in the Standard Mine samples. It is presented in units of mg $CaCO_3$ L^{-1} (Figure 22). Magnesium concentrations were significantly lower than calcium concentrations. The Elk Creek dissolved calcium concentration at SM-4, downstream of the tailings pond, was 12.1 mg L^{-1}, which is similar to the dissolved calcium concentration measured in Elk Creek at the confluence with Coal Creek, 14.4 mg L^{-1}. Hardness in Elk Creek ranged from 11.8 mg $CaCO_3$ L^{-1} at SM-1 to 34.5 mg $CaCO_3$ L^{-1} at SM-4. At the Elk Creek confluence with Coal Creek, we measured hardness of 39.9 mg $CaCO_3$ L^{-1}.

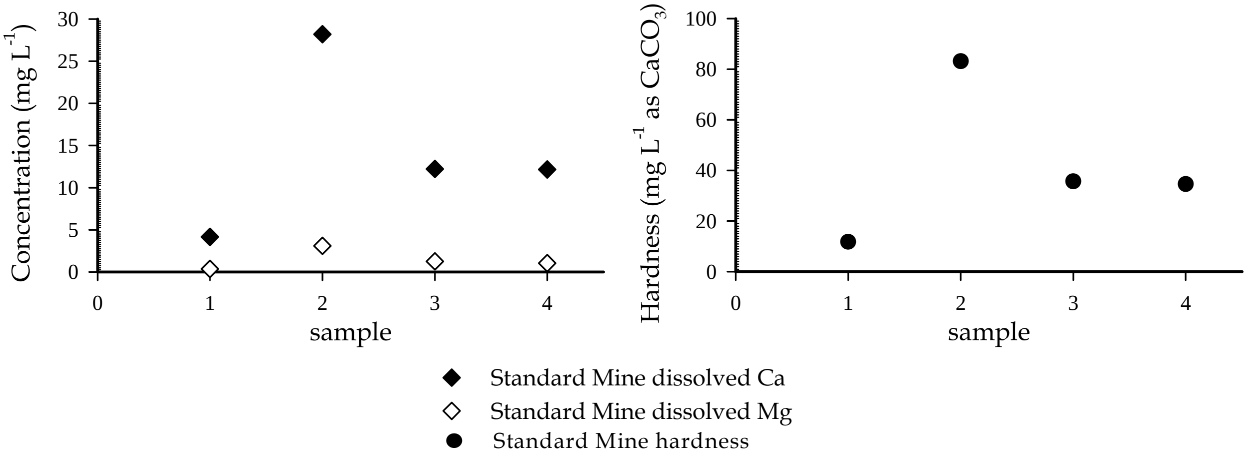

Figure 22. Magnesium and calcium concentrations and hardness of the Standard Mine samples.

Standard Mine aluminum. The aluminum concentrations at the Standard Mine site ranged from 19 µg L^{-1} total and 16 µg L^{-1} dissolved aluminum at SM-1 to 880 µg L^{-1} total aluminum and 880 µg L^{-1} dissolved aluminum at SM-2, the Level 1 adit (Figure 23). The Elk Creek concentrations at SM-4 were 140 µg L^{-1} total aluminum and 32 µg L^{-1} dissolved aluminum. These were somewhat higher than the Elk Creek concentrations found at the confluence with Coal Creek, which were 50 µg L^{-1} total aluminum and 28 µg L^{-1} dissolved aluminum. The maximum colloidal fraction was 89% at SM-3, the tailings pond effluent. The Elk Creek colloidal fraction at SM-4 was 77%.

The acute aquatic life toxicity standard is 750 µg L^{-1} total recoverable aluminum (CDPHE, 2007). This standard was exceeded only at SM-2. The chronic toxicity standard is 87 µg L^{-1} total recoverable aluminum. This standard was exceeded at sites SM-2, SM-3, and SM-4. The CDPHE maintains that if the pH is at least 7.0 and the water hardness at least 50 mg L^{-1} as $CaCO_3$, the 87 µg L^{-1} standard does not apply, but the 750 µg L^{-1} standard must still be met. Of the Standard Mine sites exceeding the 87 µg L^{-1} standard, none have pH greater than or equal to 7.0 (Table 13), and only SM-2 met the hardness requirement.

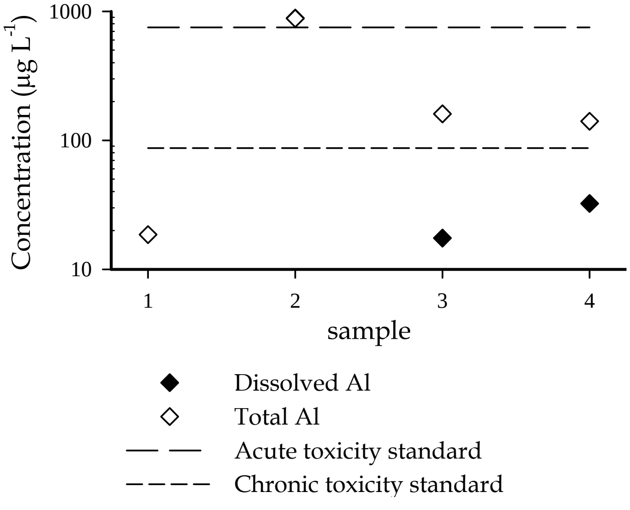

Figure 23. Total and dissolved aluminum concentrations and acute and chronic aquatic life toxicity standards of the Standard Mine samples.

Standard Mine barium. The maximum concentrations were 14 μg L^{-1} of both total and dissolved barium at SM-2, the level 1 adit (Figure 24). Elk Creek concentrations at SM-4 were 8 μg L^{-1} of both total and dissolved barium. These were lower than the Elk Creek concentrations found during the tracer dilution study, which were 11 μg L^{-1} of both total and dissolved barium. The majority of barium was in the dissolved phase. There are no aquatic life toxicity standards for barium (CDPHE, 2007).

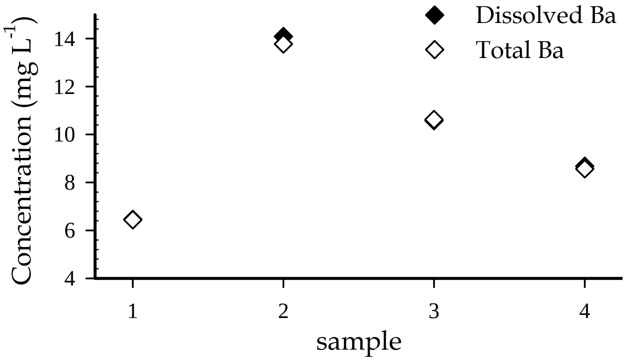

Figure 24. Total and dissolved barium concentrations of the Standard Mine samples.

Standard Mine cadmium. The cadmium concentrations at the Standard Mine sites ranged from a minimum of 0.7 μg L^{-1} total cadmium and 0.7 μg L^{-1} dissolved cadmium at SM-1 to a maximum of 77 μg L^{-1} total cadmium and 79 μg L^{-1} dissolved cadmium at SM-2, the Level 1 adit (Figure 25). The Elk Creek concentrations at SM-4 were 12 μg L^{-1} total cadmium and 12 μg L^{-1} dissolved cadmium. These were significantly higher than the Elk Creek concentrations found during the tracer dilution study, which were 2.8 μg L^{-1} total and 2.7 μg L^{-1} dissolved cadmium. The majority of cadmium was in the dissolved phase. The maximum colloidal fraction was only 5% at SM-1.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved cadmium concentrations. A separate acute toxicity standard specified for trout is also hardness-based for dissolved cadmium concentrations (CDPHE, 2007). All three standards were exceeded by every Standard Mine sample, including both of the samples taken from Elk Creek.

Standard Mine chromium. All of the Standard Mine samples had undetectable chromium concentrations. The chromium detection limit for the ICP-MS analysis was 0.1 μg L^{-1}. Elk Creek chromium concentrations during the tracer dilution study were also undetectable, although the detection limit for the tracer dilution study Elk Creek sample analysis was 0.2 μg L^{-1}.

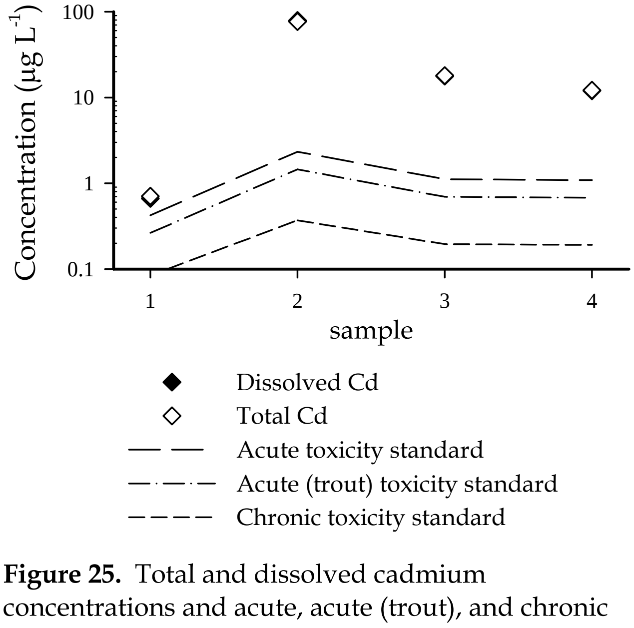

Figure 25. Total and dissolved cadmium concentrations and acute, acute (trout), and chronic aquatic life toxicity standards of the Standard Mine samples.

Standard Mine copper. The copper concentrations at the Standard Mine sites ranged from a minimum of 1.2 μg L^{-1} total copper and 1.0 μg L^{-1} dissolved copper at SM-1 to a maximum of 390 μg L^{-1} total copper and 390 μg L^{-1} dissolved copper at SM-2, the Level 1 adit

(Figure 26). The Elk Creek concentrations at SM-4 were 42 µg L^{-1} total copper and 23 µg L^{-1} dissolved copper. These were significantly higher than the Elk Creek concentrations found during the tracer dilution study, which were 8 µg L^{-1} total copper and 6 µg L^{-1} dissolved copper. The majority of copper was in the dissolved phase. The maximum colloidal fraction was 45% at SM-4.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved copper concentrations (CDPHE, 2007). Both standards were exceeded at sites SM-2, SM-3, and SM-4.

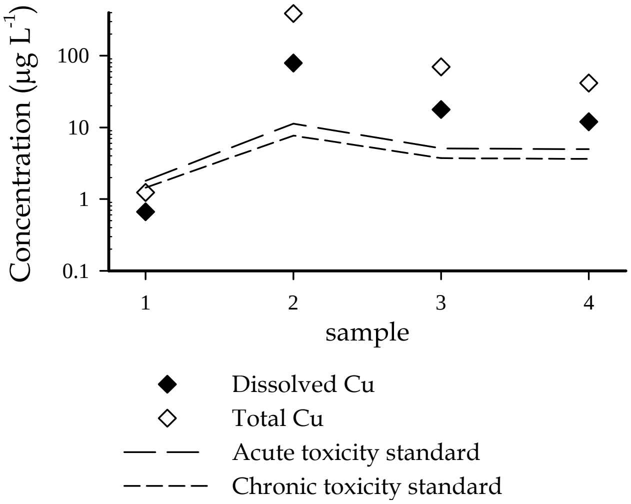

Figure 26. Total and dissolved copper concentrations and acute and chronic aquatic life toxicity standards of the Standard Mine samples.

Standard Mine iron. The minimum iron concentration at the Standard Mine sites was 0.012 mg L^{-1} total iron at SM-1. The dissolved iron concentration was undetectable at SM-4, the lower Elk Creek sample site, and was reported as the detection limit value of 0.003 mg L^{-1} (Figure 27). The maximum concentrations of 2.18 mg L^{-1} total iron and 1.51 mg L^{-1} dissolved iron were found at SM-2, the Level 1 adit. The Elk Creek total iron concentration at SM-4 was 0.15 mg L^{-1}. This was an order of magnitude greater than the Elk Creek concentrations found at the confluence with Coal Creek, which were 0.057 mg L^{-1} total and 0.012 mg L^{-1} dissolved iron. The maximum colloidal fraction was 71% at SM-3, the tailings pond effluent. The Elk Creek colloidal fraction at SM-4 was undetermined since the dissolved phase concentration was below the detection limit.

The chronic toxicity standard for aquatic life is 1.0 mg L^{-1} dissolved iron. This standard was only exceeded at SM-2, the level 1 adit. There is no acute aquatic life toxicity standard (CDPHE, 2007).

Standard Mine lead. The lead concentrations at the Standard Mine sites ranged from a minimum of 8.2 µg L^{-1} total lead and 5-3 µg L^{-1} dissolved lead at SM-1 to a maximum of 1,190 µg L^{-1} total lead and 1,170 µg L^{-1} dissolved lead at SM-2, the level 1 adit (Figure 28). The Elk Creek concentrations at SM-4 were 82 µg L^{-1} total lead and 27 µg L^{-1} dissolved lead. These were considerably higher than the Elk Creek concentrations found at the confluence with Coal Creek, which were 9.3 µg L^{-1} total lead and 3.1 µg L^{-1} dissolved lead. The maximum

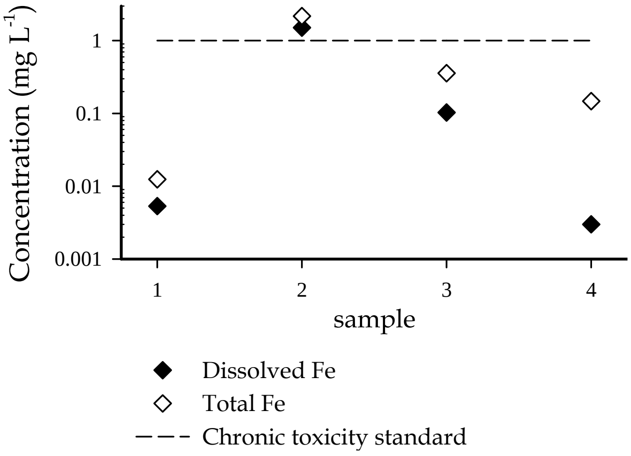

Figure 27. Total and dissolved iron concentrations and acute and chronic aquatic life toxicity standards of the Standard Mine samples.

colloidal fraction was 67% at SM-4, the lower Elk Creek site.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved lead concentrations (CDPHE, 2007). The acute toxicity standard was exceeded at sites SM-2, SM-3, and SM-4. The chronic toxicity standard was exceeded at all four Standard Mine sites.

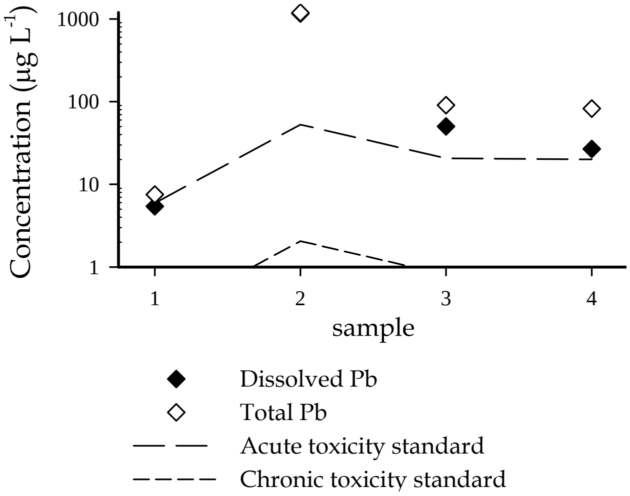

Figure 28. Total and dissolved lead concentrations and acute and chronic aquatic life toxicity standards of the Standard Mine samples.

Standard Mine manganese. The manganese concentrations at the Standard Mine sites ranged from a minimum 2.7 µg L^{-1} of both total and dissolved manganese at SM-1 to a maximum of 4,700 µg L^{-1} total manganese and 4,800 µg L^{-1} dissolved manganese at SM-2, the Level 1 adit (Figure 29). The Elk Creek concentrations at SM-4 were 600 µg L^{-1} total manganese and 600 µg L^{-1} dissolved manganese. These concentrations were significantly higher than the Elk Creek concentrations found at the confluence with Coal Creek, which were 59 µg L^{-1} total manganese and 58 µg L^{-1} dissolved manganese. Essentially all of the manganese was in the dissolved phase.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved lead concentrations (CDPHE, 2007). These standards were only exceeded by SM-2, the Level 1 mine adit.

Standard Mine zinc. The zinc concentrations at the Standard Mine sites ranged from 118 µg L^{-1} total zinc and 116 µg L^{-1} dissolved zinc at SM-1 to 12,500 µg L^{-1} total zinc and 12,500 µg L^{-1} dissolved zinc at SM-2, the Level 1 adit (Figure 30). The Elk Creek concentrations at SM-4 were 2,000 µg L^{-1} total zinc and 2,000 µg L^{-1} dissolved zinc. These were considerably higher than the Elk Creek concentrations found at the confluence with Coal Creek, which were 390 µg L^{-1} total zinc and 380 µg L^{-1} dissolved zinc. The majority of zinc was present in the dissolved phase.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved zinc concentrations (CDPHE, 2007). Both standards were exceeded at all four Standard Mine sites.

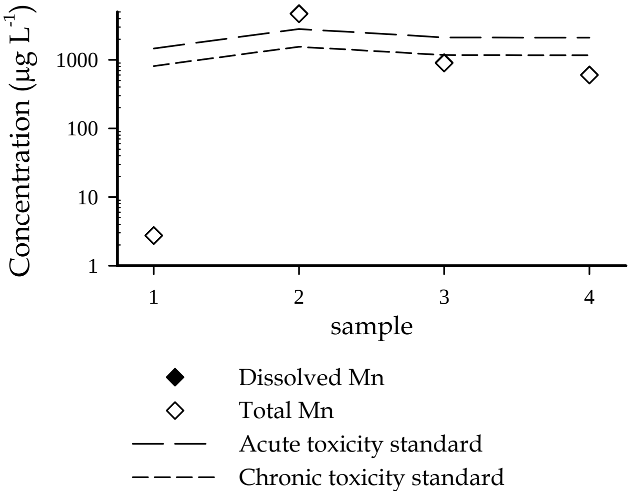

Figure 29. Total and dissolved manganese concentrations and acute and chronic aquatic life toxicity standards of the Standard Mine samples.

Metals in Iron Gossan and Fen Samples

The six samples collected along the western edge of the iron gossan and fen were analyzed for pH, conductivity, and metal content (Figure 8). Locations IG-5 and IG-6 were both located along the primary iron fen drainage, which was joined by two other tributaries before meeting Coal Creek as UT-3.212. The results for the most downstream of the primary iron fen samples, IG-6, are compared with those of UT-3.212 in the following text.

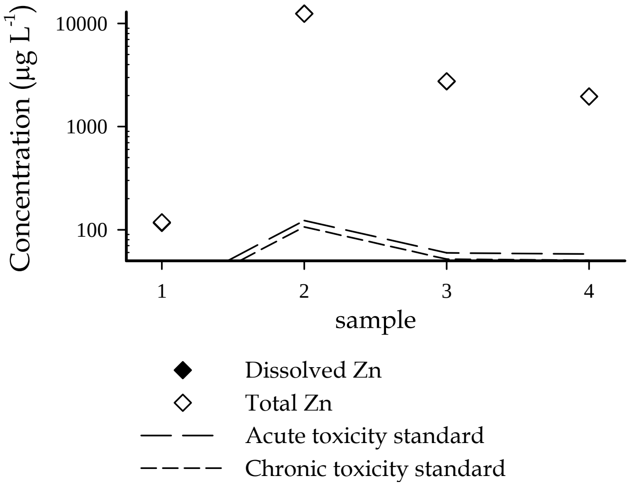

Figure 30. Total and dissolved zinc concentrations and acute and chronic aquatic life toxicity standards of the Standard Mine samples.

Iron gossan and fen pH. The iron gossan and fen pH values ranged from a minimum of 3.21 at IG-5, the first of the primary iron fen drainage samples, to a maximum of 4.72 at IG-1, the upper-most gossan sample (Table 14). The pH range established for cold water aquatic life is 6.5 to 9.0 (CDPHE, 2007). All of the iron gossan and fen samples were below the lower aquatic life toxicity standard, including both of the samples taken from the primary iron fen drainage.

Table 14. Values of pH measured in water samples taken from the iron gossan and fen. For locations of the sample sites, refer to Figure 8.

sample site	**pH**
IG-1 northwestern corner of gossan	4.72
IG-2 western edge of gossan	3.47
IG-3 southwestern corner of gossan	3.93
IG-4 iron fen drainage near "Well #2"	3.91
IG-5 iron fen drainage to UT-3.212	3.21
IG-6 iron fen drainage to UT-3.212	3.34

Iron gossan and fen hardness. Hardness was calculated from the dissolved calcium and magnesium concentrations from the iron gossan and fen samples. It is presented in units of mg $CaCO_3$ L^{-1} (Figure 31). Magnesium concentrations were significantly lower than calcium concentrations. The

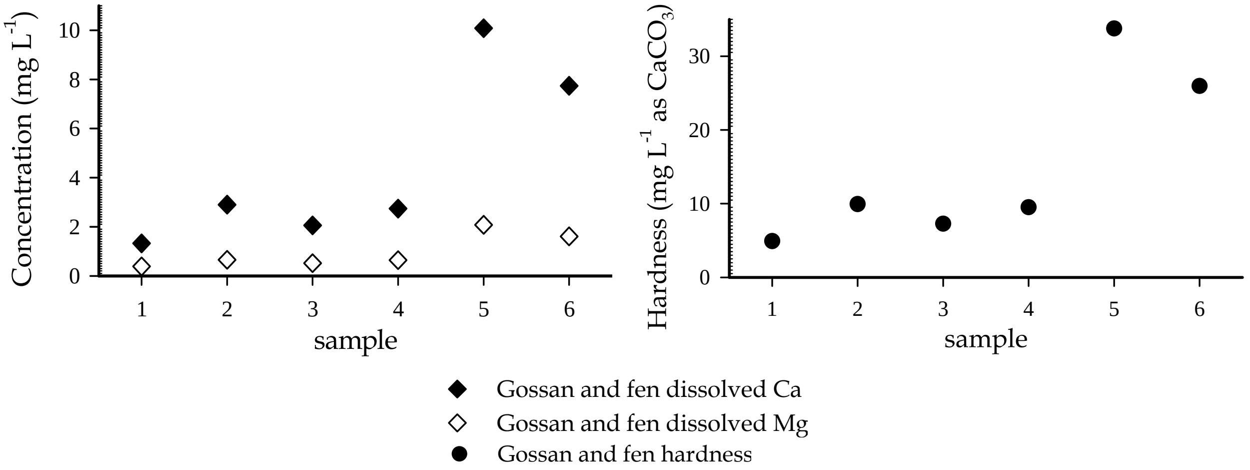

Figure 31. Magnesium and calcium concentrations and hardness of the iron gossan and fen samples. Hardness is presented with units of mg L^{-1} as $CaCO_3$.

minimum hardness was 4.9 mg $CaCO_3$ L^{-1} at IG-1 and the maximum calculated hardness was 33 mg $CaCO_3$ L^{-1} at IG-5. IG-6 had a hardness of 26 mg $CaCO_3$ L^{-1}, which was higher than the hardness measured in UT-3.212, 12 mg $CaCO_3$ L^{-1}. This indicates significant dilution from waters not affected by the iron gossan before UT-3.212 enters Coal Creek.

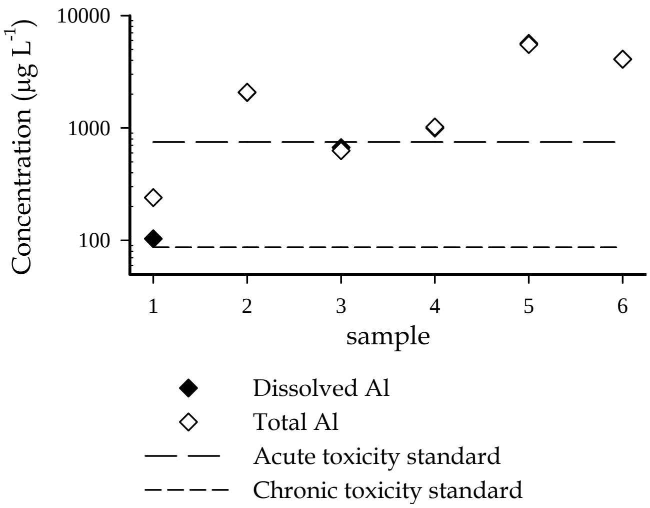

Figure 32. Total and dissolved aluminum concentrations and acute and chronic aquatic life toxicity standards of the iron gossan and fen samples.

Gossan and fen aluminum. The aluminum concentrations at the iron gossan and fen sites ranged from a minimum of 240 µg L^{-1} total aluminum and 100 µg L^{-1} dissolved aluminum at IG-1 to a maximum of 5,500 µg L^{-1} total aluminum and 5,700 µg L^{-1} dissolved aluminum at IG-5, the first of the iron fen drainage samples leading to UT-3.212 (Figure 32). The iron fen drainage concentrations at IG-6 were 4,100 µg L^{-1} total aluminum and 4,100 µg L^{-1} dissolved aluminum. These were considerably higher than the UT-3.212 concentrations, which were 1,000 µg L^{-1} total aluminum and 1,100 µg L^{-1} dissolved aluminum. The majority of aluminum was in the dissolved phase. The maximum colloidal fraction was 57% at IG-1.

The acute aquatic life toxicity standard is 750 µg L^{-1} total recoverable aluminum (CDPHE, 2007). This standard was exceeded at sites IG-2, IG-4, IG-5 and IG-6. The chronic toxicity standard is 87 µg L^{-1} total recoverable aluminum and was exceeded at all six gossan and fen sites. The CDPHE maintains that if the pH is at least 7.0 and the water hardness at least 50 mg $CaCO_3$ L^{-1}, the 87 µg L^{-1} standard does not apply but the 750 µg L^{-1} standard still must be met. None of the gossan and fen sites met these pH and hardness requirements (Table 14 and Figure 32).

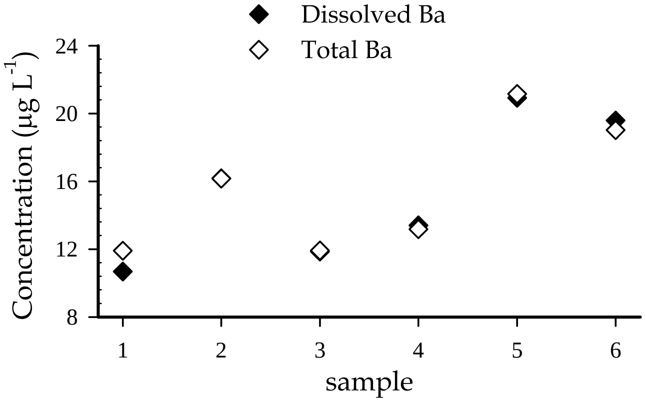

Figure 33. Total and dissolved barium concentrations of the iron gossan and fen samples.

Gossan and fen barium. The minimum barium concentrations of the iron gossan and fen samples were 12 µg L^{-1} total barium and 11 µg L^{-1} dissolved barium at IG-1 (Figure 33). The maximum concentrations were 21 µg L^{-1} total barium and 21 µg L^{-1} dissolved barium at IG-5, the first of the primary iron fen drainage samples. The IG-6 concentrations were 19 µg L^{-1} total barium and 19 µg L^{-1} dissolved barium. These were higher than the UT-3.212 concentrations found during the tracer dilution study, which were 15 µg L^{-1} total barium and 14 µg L^{-1} dissolved barium. The majority of barium was in the dissolved phase. The maximum colloidal fraction was 10% at IG-1. There are no aquatic life toxicity standards given for barium (CDPHE, 2007).

Gossan and fen cadmium. The cadmium concentrations of the iron gossan and fen samples ranged from a minimum of 0.3 µg L^{-1} total cadmium and 0.3 µg L^{-1} dissolved cadmium at IG-1 to a maximum of 21 µg L^{-1} total cadmium and 21 µg L^{-1} dissolved cadmium at IG-5, the first of the primary iron fen drainage samples (Figure 34). The IG-6 concentrations were 15 µg L^{-1} total cadmium and 15 µg L^{-1} dissolved cadmium. These were significantly higher than the UT-3.212 concentrations, which were 3.9 µg L^{-1} total cadmium and 3.8 µg L^{-1} dissolved cadmium. Essentially all of the cadmium was in the dissolved phase.

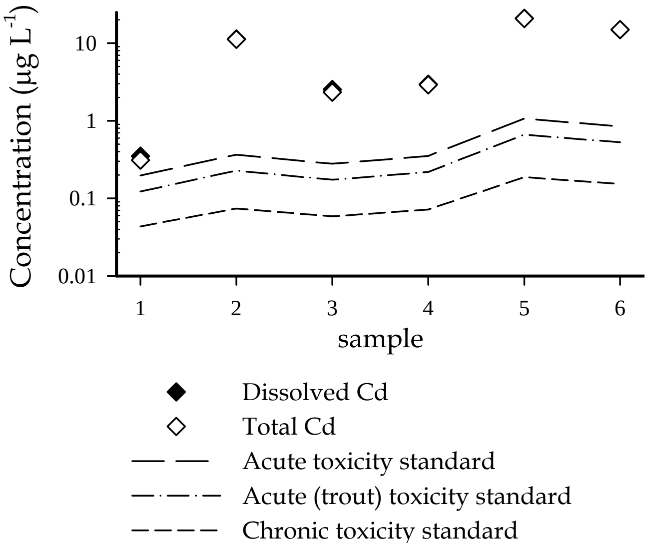

Figure 34. Total and dissolved cadmium concentrations and acute, acute (trout), and chronic aquatic life toxicity standards of the iron gossan and fen samples.

Both the acute and chronic aquatic life toxicity standards are hardness-based for dissolved cadmium concentrations. A separate acute toxicity standard specified for trout is also hardness-based for dissolved cadmium concentrations (CDPHE, 2007). All three standards were exceeded by every gossan and fen sample.

Gossan and fen chromium. All of the iron gossan and fen samples had undetectable chromium concentrations. The chromium detection limit for the ICP-MS analysis was 0.09 µg L^{-1}. UT-3.212 chromium concentrations during the tracer dilution study were also undetectable, although the detection limit for the tracer dilution study UT-3.212 sample analysis was 0.18 µg L^{-1}.

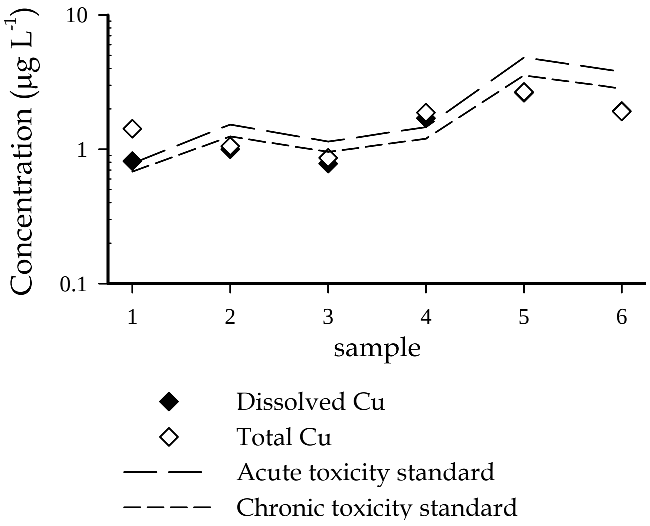

Figure 35. Total and dissolved copper concentrations and acute and chronic aquatic life toxicity standards of the iron gossan and fen samples.

Gossan and fen copper concentrations. The copper concentrations of the iron gossan and fen samples ranged from a minimum of 0.9 µg L^{-1} total copper and 0.8 µg L^{-1} dissolved copper at IG-3 to a maximum of 2.7 µg L^{-1} total copper and 2.6 µg L^{-1} dissolved copper at IG-5, the first of the primary iron fen drainage samples (Figure 35). The IG-6 concentrations were 1.9 µg L^{-1} total copper and 1.9 µg L^{-1} dissolved copper. These were nearly double the UT-3.212

copper concentrations, which were 0.9 μg L^{-1} total copper and 0.9 μg L^{-1} dissolved copper. Nearly all of the copper was in the dissolved phase. The maximum colloidal fraction was 43% at IG-1.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved copper concentrations (CDPHE, 2007). Both of the standards were exceeded at sites IG-1 and IG-4.

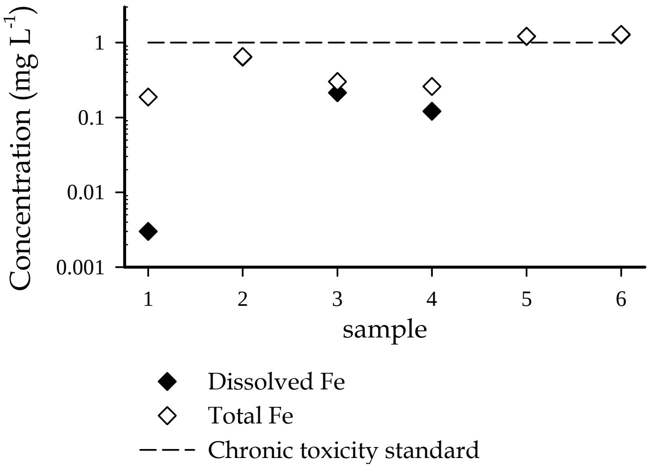

Figure 36. Total and dissolved iron concentrations and chronic aquatic life toxicity standards of the iron gossan and fen samples.

Gossan and fen iron concentrations. The minimum iron concentration of the iron gossan and fen samples was 0.19 mg L^{-1} total iron at IG-1 (Figure 36). The maximum concentrations were of 11.3 mg L^{-1} total iron and 11.3 mg L^{-1} dissolved iron at IG-6, the second of the primary iron fen drainage samples. The IG-6 iron concentrations were an order of magnitude greater than the UT-3.212 concentrations, which were 0.16 mg L^{-1} total and 0.13 mg L^{-1} dissolved iron. The colloidal fraction of iron ranged from essentially zero at IG-5 to 53% IG-4, or nearly 100% at IG-1, where the colloidal fraction was undetermined because the dissolved phase concentration was below the detection limit.

The chronic toxicity standard for aquatic life is 1.0 mg L^{-1} dissolved iron. This standard was only exceeded at sites IG-5 and IG-6 along the primary iron fen drainage. There is no acute aquatic life toxicity standard (CDPHE, 2007).

Gossan and fen lead. The minimum lead concentrations of the iron gossan and fen samples were 0.48 μg L^{-1} total lead at IG-2 and 0.47 μg L^{-1} dissolved lead at IG-3 (Figure 37). The dissolved lead concentration was undetectable at IG-1 and was reported as the detection limit value of 0.19 μg L^{-1}. The maximum concentrations were 2.3 μg L^{-1} total lead at IG-1 and 0.94 μg L^{-1} dissolved lead at IG-4. The IG-6 concentrations were 0.70 μg L^{-1} total lead and 0.69 μg L^{-1} dissolved lead. These were slightly higher than the UT-3.212 concentrations, which were 0.24 μg L^{-1} total and 0.06 μg L^{-1} dissolved lead. The colloidal fraction ranged from zero at IG-5 to 31% at IG-3, or greater at IG-1, where the colloidal fraction was undetermined because the dissolved

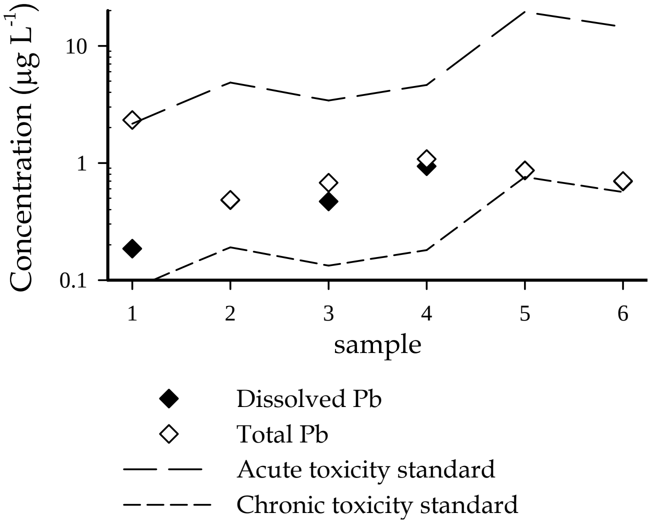

Figure 37. Total and dissolved lead concentrations and acute and chronic aquatic life toxicity standards of the iron gossan and fen samples.

phase concentration was below the detection limit.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved lead concentrations. The acute toxicity standard was never exceeded. The chronic toxicity standard was exceeded at all six sites.

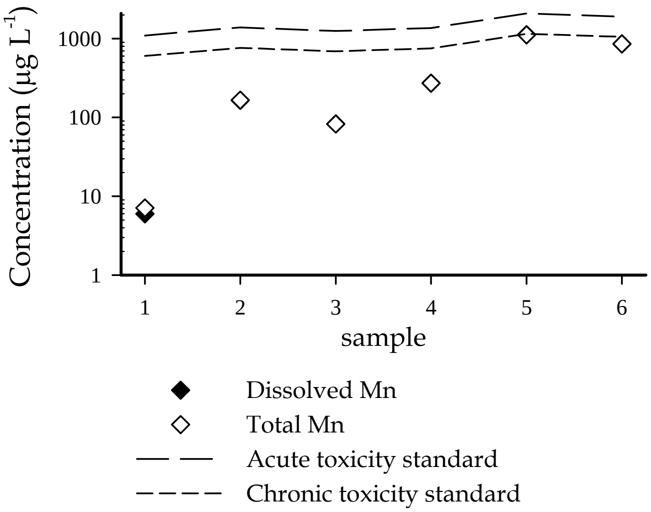

Figure 38. Total and dissolved manganese concentrations and acute and chronic aquatic life toxicity standards of the iron gossan and fen samples.

Gossan and fen manganese. The minimum manganese concentrations of the iron gossan and fen sites were 7.4 µg L^{-1} total manganese and 6.1 µg L^{-1} dissolved manganese (Figure 38). The maximum concentrations were 1,100 µg L^{-1} total manganese and 1,100 µg L^{-1} dissolved manganese at IG-5, the first of the primary iron fen drainage samples. The IG-6 concentrations were 860 µg L^{-1} total manganese and 860 µg L^{-1} dissolved manganese. These were significantly higher than the UT-3.212 concentrations, which were 180 µg L^{-1} total manganese and 150 µg L^{-1} dissolved manganese. Most of the manganese was in the dissolved phase.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved manganese concentrations (CDPHE, 2007). These standards were never exceeded, though IG-5 very nearly exceeded the chronic toxicity standard.

Gossan and fen zinc. The zinc concentrations of the iron gossan and fen samples ranged from a minimum of 76 µg L^{-1} total zinc and 68 µg L^{-1} dissolved zinc at IG-1 to a maximum of 4,700 µg L^{-1} total zinc and 4,700 µg L^{-1} dissolved zinc at IG-5, the first of the primary iron fen drainage samples (Figure 39). The IG-6 concentrations were 3,400 µg L^{-1} total zinc and 3,400 µg L^{-1} dissolved zinc. These were considerably higher than the UT-3.212 concentrations, which were 710 µg L^{-1} total zinc and 720 µg L^{-1} dissolved zinc. Most of the zinc was in the dissolved phase. The maximum colloidal fraction was 10% at IG-1.

Both the acute and chronic aquatic life toxicity standards were hardness-based for dissolved zinc concentrations (CDPHE, 2007). Both standards were exceeded by significant amounts at all six iron gossan and fen sites.

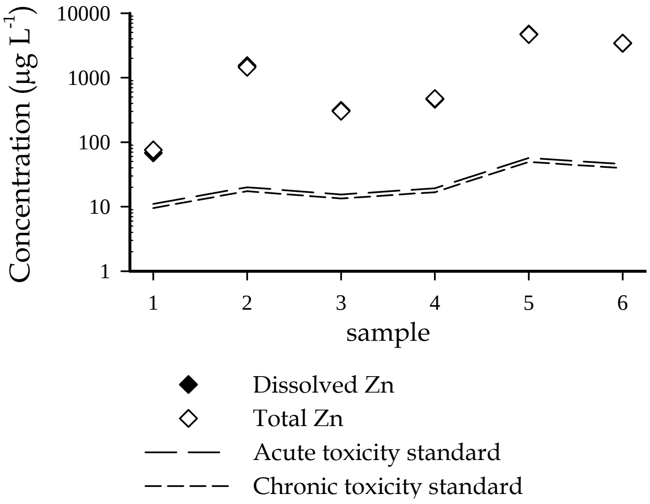

Figure 39. Total and dissolved zinc concentrations and acute and chronic aquatic life toxicity standards of the iron gossan and fen samples.

DISCUSSION

Suitability of Chloride as a Tracer in Coal Creek

An appropriate tracer must have several characteristics to qualify it for use in a tracer dilution study. The tracer must be (1) conservative, or non-reactive and not prone to sorb to solid material, (2) insensitive to variations in pH and metal chemistry that occur naturally within the study reach, (3) at concentrations several times greater than background concentrations, (4) cost-effective, and (5) it must not pose a risk to human health or aquatic life (Bencala et al., 1990). Previous studies show that chloride behaves conservatively as only physical processes such as dilution, dispersion, and transient storage influence the attenuation of chloride concentration. Biogeochemical reactions have minimal impact on chloride attenuation. Chloride is commonly referred to as the "universal tracer" because of its conservative behavior; however, it is also more likely to be present in moderate concentrations in natural waters (Bencala et al., 1990). Atmospheric deposition and weathering are sources of chloride in natural systems (Kimball et al., 2002).

Background chloride concentrations of three tributaries were sufficiently high to cause problems in calculating the chloride mass balance in Equation 5 (Table 4). If the tributary chloride concentration is greater than the chloride concentration either upstream or downstream of the inflow, the assumptions for Equation 5 are not met, and the tributary flow rate must be estimated. The estimated tributary flow rates were used to calculate the downstream flow rate with Equation 6 (Table 4).

In retrospect, it is apparent that chloride was not an entirely suitable tracer for the Coal Creek metal loading tracer dilution tests. In the first metal loading tracer dilution test conducted at low flow in September 2005, chloride provided suitable estimates of flow when it was apparent that the transport of lithium, the intended tracer, was not conservative (Shanklin and Ryan, 2006). For the high flow conditions of June 2006, chloride should have been injected at a higher rate of injection. In the third Coal Creek tracer dilution study conducted in April 2007, bromide was used as the tracer because the background concentrations were very low (Ryan et al., 2009).

Steady-State Conditions for Tracer Injections 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. Although the upper Coal Creek tracer injection had fairly constant flow rates and concentrations, the lower Coal Creek tracer injection rates and concentrations were not sufficiently consistent. In lower Coal Creek, the injected chloride reached the downstream end, but the concentration of chloride did not remain at a plateau (Table 9); therefore, we were not certain that steady-state concentrations were achieved along the reach. To avoid misinterpretations of metal loading rates based in inaccurate flow rate calculations, we restricted the analysis of the synoptic samples to the first approximately 1.5 km of the lower reach of Coal Creek. Over this reach, we were certain that the chloride injection was steady in flow and concentration and the chloride concentrations had reached steady state.

Since synoptic sampling occurred on two different days for the upper and lower Coal Creek reaches, a slight variation in stream conditions occurred. Although no major weather events or temperature changes occurred between the two synoptic sampling days, there is a noticeable increase in the Coal Creek flow rate, metal concentrations, and loading rates between the upper Coal Creek reach and the lower Coal Creek reach. This increase does not significantly affect the continuity of the results of this high flow study; however, it does affect assessment of exceedances of the toxicity standards. UT-4.186, the iron gossan tributary, was the most downstream tributary of the upper Coal Creek reach. Some of the metal loading from UT-4.186 was more evident at CC-4.323, located 137 m downstream of the confluence of UT-4.186 with Coal Creek. This indicates that flow from UT-4.186 may have been somewhat greater on June 11, the day of the lower Coal Creek synoptic sampling, than on June 13, the day of the upper Coal Creek synoptic sampling. The toxicity standards on June 11 may have extended slightly farther upstream of CC-4.323 than the results of the upper Coal Creek synoptic sampling demonstrated.

The background chloride concentration for the upper Coal Creek reach measured at CC-0.519 was 0.45 mg L^{-1}. The background concentration for the lower Coal Creek reach measured at CC-4.323 was 0.39 mg L^{-1} (Figure 12). In-stream chloride concentrations dropped to within 1.0 mg L^{-1} of these background concentrations at the last three sites of the upper Coal Creek tracer study, and all of the lower Coal Creek in-stream chloride concentrations were within 0.4 mg L^{-1} of the background concentration. One upper Coal Creek tributary had a chloride concentration exceeding the concentration in the stream, while most of the lower Coal Creek tributary chloride concentrations were similar to the concentrations in the stream. To determine consistent stream and tributary flow rates, we need to estimate flow for some tributaries.

Coal Creek Stream Flow

The U.S. Geological Survey (USGS) maintained a stream flow gauge station for Coal Creek between the years of 1941 and 1946. The gauge station was located downstream of the Coal Creek and Elk Creek confluence at a distance of 1.862 km along the study reach. The average June flow rate for 1941 to 1946 was 3,310 L s^{-1} (USGS, 2006). The U.S. EPA measured a flow rate of 2,380 L s^{-1} during a sampling event on June 14, 2005 (EPA, 2005b). The average flow rate measured by the USGS for June 13, the date of the upper Coal Creek synoptic study, was 3,200 L s^{-1}. For this study, the flow rate calculated from the chloride dilution equations at CC-1.922, the site nearest to the former USGS gauge station location, was 1,200 L s^{-1}. The average minimum June flow rate was 1,090 L s^{-1}. The annual minimum June flow rates occurred as late in the month as June 30 or as early as June 2 (USGS, 2006). This average minimum flow rate more closely resembles the study flow rate and indicates that the June 2006 synoptic sampling probably did not occur during the annual peak runoff.

The Western Regional Climate Center, administered by the National Oceanic and Atmospheric Administration (NOAA), has recorded temperature data for Crested Butte since 1909. The average June temperature for 1941 through 1946 was 10.2 ºC. The average June temperature for 2006 was nearly 1.6º greater at 11.8 ºC. The average May temperature for 1941 through 1946 was 6.4 ºC, whereas the May, 2006, average temperature was 7.8 ºC. These higher temperatures may have caused an earlier seasonal runoff in the Coal Creek drainage, resulting in lower than expected flow rates during the second week of June 2006.

The USGS operated a gauge station on the Slate River approximately 1.6 km east of Crested Butte and downstream of the Coal Creek and Slate River confluence from 1940 until October 2006 (USGS, 2006). Data from this gauge station shows that the maximum Slate River flow rate for 2006 occurred on May 23, 2006. This maximum was the peak runoff for the Slate River drainage, which includes Coal Creek and other tributaries. A second smaller peak occurred on June 8, 2006. A comparison of the 2006 peak runoff dates with the 1945 peak runoff dates (Figure 40) indicates that the annual peak runoff now occurs nearly one month earlier than it did 60 years ago. The 1945 Slate River peak runoff occurred on June 15 (USGS, 2006).

From the Town of Crested Butte temperature data and Slate River flow rate data, we conclude that this Coal Creek metal loading tracer dilution study did not occur during the peak spring runoff. The Coal Creek watershed peak runoff likely occurred during the week of May 23 and possibly one or two days prior to the Slate River peak runoff. Regional temperature variation of the Slate River drainage area was likely insignificant to cause a much earlier or later Coal Creek peak runoff.

Metal Loading Anomalies

Sample site CC-2.691 was consistently an anomaly along the upper Coal Creek synoptic study reach. Every metal concentration and loading rate showed a small but significant dip at CC-2.691. This sample site was located only 21 m downstream of the tributary UT-2.670, a north bank tributary that drains Evans Basin and flows into Coal Creek through a marshy area downstream of a wetland. Based on the consistent decrease in Coal Creek metal concentrations and loading rates at this site, we surmise that synoptic sampling occurred where mixing of the tributary and the creek was not sufficient due to the presence of the marshy brush. All Coal Creek metal concentrations and loading rates can likely be extrapolated through CC-2.691 to fit the generally decreasing metal concentrations and increasing loading rates. Extrapolation indicates that the lead concentration at CC-2.691 does exceed both chronic and acute toxicity standards despite the contrary sampling error indications. UT-2.670, which drains Evans Basin, was an insignificant source of metals.

Mount Emmons Treatment Plant Effluent and Hardness

The Mount Emmons treatment plant adds lime (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. The calcium used during the treatment process then enters Coal Creek when the effluent is released. The treatment plant discontinues effluent release by 16:00 each day. The release is not steady; it varies from 0 to 79 L s^{-1} over each day (John Perusek, personal communication, July 15, 2005).

For the synoptic sampling in lower Coal Creek, the flow rate of the Mount Emmons tributary was calculated to be 35 L s^{-1}. The synoptic samples were taken near the Mount Emmons treatment plant effluent between 13:59 and 14:16 on Sunday, June 11, 2006. It is not known if the Mount Emmons treatment plant effluent was running at that time or if the waters being sampled were strictly from the road-side ditch and the surface tributary that join the effluent before reaching Coal Creek. Calcium and hardness concentrations peaked at CC-5.489, approximately 0.149 km downstream of the treatment plant effluent. A second peak occurred at CC-5.940. This second peak was the maximum calcium concentration and hardness measured along Coal Creek.

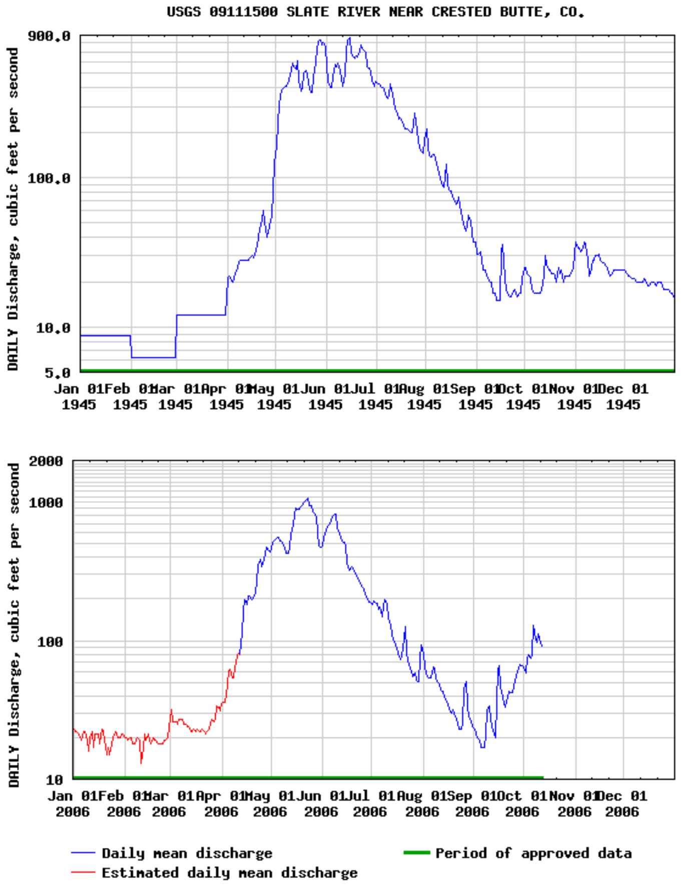

Figure 40. A comparison of the annual peak runoff of the Slate River near Crested Butte, Colorado, for 1945 and 2006. The peak runoff appears to occur more than three weeks earlier than it did 60 years ago, indicating that the June, 2006, Coal Creek tracer dilution study did not occur during peak runoff. Graphs taken from the USGS National Water Information System (USGS, 2006).

Large daily fluctuations in calcium concentration and hardness in Coal Creek are expected due to the Mount Emmons treatment plant effluent. At the time of the synoptic sampling, the downstream calcium concentration was approximately 2 times greater than the concentration upstream of the treatment plant effluent. With the input of calcium, hardness and hardness-based aquatic life toxicity standards will also show daily fluctuations. Hardness-based acute and chronic toxicity standards are not to be exceeded more than once every three years on average and should be computed using the lowest daily calcium and magnesium concentrations (CDPHE, 2007). When hardness drops, toxic metal uptake by aquatic organisms increases because less calcium and magnesium is present to compete with the toxic metals for binding sites on gills and in the digestive tract. For comparison purposes, hardness-based standards upstream of the Mount Emmons tributary can be extrapolated to sites downstream to represent conditions when elevated calcium is not present in Coal Creek.

The calcium concentrations and hardness measure in these tests at high flow were significantly lower than at low flow in September 2005. At low flow, calcium concentrations ranged from 12.5 mg L^{-1} to 154 mg L^{-1}; at high flow, the maximum calcium concentration was only 15.5 mg L^{-1}. At low flow, hardness ranged from 43.2 mg $CaCO_3$ L^{-1} to 400 mg $CaCO_3$ L^{-1}; at high flow, the maximum hardness was only 42.8 mg $CaCO_3$ L^{-1}. The Mount Emmons tributary was the dominant source of calcium and hardness at both low flow and high flow.

Standards Exceedances

At high flow in June 2006, metal concentrations exceeded the CDPHE acute and chronic aquatic life toxicity standards at multiple sample sites along the Coal Creek study reach (Table 15). For cadmium and zinc, acute toxicity standards were exceeded. Cadmium concentrations exceeded an additional acute toxicity standard for trout. Aluminum, cadmium, copper, lead, and zinc exceeded chronic toxicity standards. The CDPHE drinking water supply standards were never exceeded.

Summary of Metal Sources

The major, minor, and trace sources for the nine metals analyzed for high flow conditions for this study are presented in Table 16. “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.

The major sources of metal contamination in Coal Creek were Elk Creek, UT-4.186, and Splains Gulch. Elk Creek was a

Table 15. Coal Creek sample sites exceeding the CDPHE acute and chronic aquatic life toxicity standards (CDPHE, 2007).

metal	acute toxicity standard exceeded	chronic toxicity standard exceeded
Aluminum	None	CC-0.519 to CC-0.977 CC-4.323 to CC-5.940
Barium[1]	--	--
Cadmium	CC-1.547	CC-1.547 to CC-5.940
Cadmium (trout)	CC-1.547 to CC-1.922 CC-4.284 to CC-5.177	--
Chromium	None	None
Copper	None	CC-1.547
Iron	--	None
Lead	None	CC-1.547 to CC-3.558 (not CC-2.691) CC-4.323 to CC-5.940
Manganese	None	None
Zinc	CC-1.547 to CC-5.940	CC-1.547 to CC-5.940

[1] Standard does not exist

major source of cadmium, copper, lead, zinc, and possibly manganese. UT-4.186, the iron gossan tributary, was a major source of aluminum, cadmium, copper, lead, manganese, and zinc. Splains Gulch was a major source of barium and chromium. There are no aquatic toxicity standards for barium and chromium was consistently measured at or near the detection limit; therefore, Splains Gulch will not be further discussed as a metal loading source. One other source classified as major is an unidentified upstream source that caused the chronic toxicity standard for aluminum to be exceeded at the first four sample sites of the upper Coal Creek.

Minor sources of metal contamination in Coal Creek included Elk Creek, UT-4.521, the Mount Emmons tributary, and Splains Gulch. Trace sources included several wetland tributaries, the iron gossan and fen tributaries, the Mount Emmons tributary, and two south bank unnamed tributaries.

Recent and future EPA remediation activities at the Standard Mine site will likely reduce or possibly eliminate the metal contamination associated with Elk Creek. In the summer of 2006, following this study, the EPA channelized Elk Creek and redirected hillside surface drainages with cement blocks to protect them from mine site contamination. Water was also removed from the tailings pond. These efforts have likely minimized metal contamination coming from Elk Creek into Coal Creek. Future work at the Standard Mine site is focused on treatment of the adit drainages.

The unnamed tributary UT-4.186, referred to as the iron gossan tributary, drains the area between the iron gossan and the Keystone Mine (Figure 3). The source of the metal-contaminated water in this tributary is not entirely 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.

Several tributaries entering the wetland areas in the upper reach of Coal Creek were trace metal sources, including UT-2.306 and UT-2.670, which drains Evans Basin. Three south bank tributaries were also trace sources of some metals. All of these tributaries had relatively small flow rates and large metal concentrations (Tables 11 and 12). Only UT-2.670 (Evans Basin) had a significantly large flow rate of 114 L s^{-1}. UT-3.835 was attributed with a flow rate of 113 L s^{-1}; however, visual inspection indicated that a substantial portion of this was likely groundwater flow from the north bank amid the iron gossan and fen drainages. We observed that some of the iron gossan and fen tributaries disappeared below the surface and probably entered Coal Creek as groundwater.

Table 16. Major, minor, and trace sources of metals in the Coal Creek watershed. 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. The Mount Emmons tributary is designated "Mount Emmons."

metal	major sources	minor sources	trace sources
Aluminum	UT-4.186 (iron gossan tributary), unidentified upstream source		UT-3.378 (iron fen tributary), UT-3.594 (iron fen tributary), UT-4.521 (south bank tributary), Mount Emmons
Barium	Splains Gulch		UT-2.670 (Evans Basin tributary into wetland) UT-2.763, UT-3.835, UT-4.521 (south bank tributaries)
Cadmium	Elk Creek, UT-4.186		
Chromium	Splains Gulch		UT-2.306 (tributary into wetland), UT-2.670 (Evans Basin tributary into wetland) UT-3.835 (south bank tributary)
Copper	Elk Creek, UT-4.186 (iron gossan tributary)	Mount Emmons	
Iron		Splains Gulch, UT-4.521 (south bank tributary)	UT-3.378 (iron fen tributary), UT-3.835 (south bank tributary), UT-4.186 (iron gossan tributary), Mount Emmons
Lead	Elk Creek, UT-4.186 (iron gossan tributary)		Mount Emmons
Manganese	UT-4.186 (iron gossan tributary)	Elk Creek, Mount Emmons	
Zinc	Elk Creek, UT-4.186 (iron gossan tributary)		UT-3.378 (iron fen tributary)

The tributaries UT-3.378 and UT-3.594 appear to originate from the iron fen (Figure 3). These drainages were trace sources of aluminum, iron, and zinc. The iron fen is naturally-occurring and supports a diverse population of wildlife and vegetation, including the *Drosera rotundifolia*, an endangered carnivorous plant has not been found anywhere else in the Central or Southern Rocky Mountains.

The Coal Creek wetland downstream of the Elk Creek confluence may be effectively removing metals from solution. The methods employed in this study may underestimate the actual metal loading rates entering Coal Creek if metals are quickly attenuated by plant, sediments, or microbes in the wetland. It is likely that wetland sediments contain toxic metal concentrations. Wetland remediation or dredging may be needed in addition to the remedial activities planned for the Standard Mine.

Comparison of Metal Sources and Exceedances of Standards at Low and High Flow

The metals of primary concern in Coal Creek are cadmium, copper, lead, and zinc. At low flow in September 2005, the major sources were

- for cadmium, *UT-3.895*, an unnamed tributary draining the iron gossan (Figure 41), and *Elk Creek*,
- for copper, numerous minor and trace sources including two tributaries to the wetlands (UT-2.511 and UT-2.670, which drains Evans Basin), the Town of Crested Butte's drinking water reservoir return, and *Elk Creek*,
- for lead, the reservoir return flow, and
- for zinc, *UT-3.895* and *Elk Creek*.

Shanklin and Ryan (2006) referred to UT-3.895 as UT-3.595 owing to an error in the location measured by GPS. During the low flow metal loading tracer dilution test, the Mount Emmons treatment plant was not producing effluent; therefore, it was not a source of metals at low flow.

Drainage from the iron gossan was also a major source of cadmium, copper, lead, and zinc at high flow, but the path of the drainage was different. At high flow, the main path of metal loading was UT-4.816 (Figure 3). At low flow, the main path of metal loading was UT-3.895. At low flow, only three unnamed tributaries were draining the iron gossan and fen. At high flow, five unnamed tributaries were draining the fen.

Elk Creek was also a major source of cadmium, copper, lead, and zinc at high flow. To be a major source at both high and low flow, the loading rate for Elk Creek increases by a factor of two to ten depending on the metal (not accounting for the possible mis-estimation of the Elk Creek flow rate, which would have resulted in greater loading rates for Elk Creek at high flow). The amount of metals released by the Standard Mine must be increasing with the seasonal increase in flow in the Coal Creek watershed.

Figure 41. Aerial photograph of Coal Creek near the Keystone Mine at the base of Mount Emmons showing tributaries flowing at low flow in September 2005. Coal Creek flows from the southwest to the northeast. The aerial photo was retrieved using Google Earth™ (http://earth.google.com).

During the high flow test in June 2006, the synoptic sampling did not extend to the Town of Crested Butte's drinking water reservoir return flow, which was a major source of lead and minor source of copper at low flow in

September 2005. The unexpected result of the reservoir return flow contributing to the metal of Coal Creek was not re-tested in June 2006.

At low flow in September 2005, cadmium, chromium, and zinc exceeded acute toxicity standards and cadmium, chromium, nickel, and zinc exceeded the chronic toxicity standards (Shanklin and Ryan, 2006). In addition, chromium, iron, and manganese exceeded the drinking water supply standards. Chromium was not a metal of particular concern during the June 2006 study because the maximum chromium concentration was more than two orders of magnitude less than the toxicity standards. Nickel was not analyzed for the June 2006 study.

Exceedances of toxicity standards are thought to occur more commonly during low-flow conditions. In Coal Creek, the number of exceedances was similar for low flow in September 2005 and high flow in June 2006. Most of the exceedances occurred downstream of Elk Creek and the iron gossan tributaries.

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