Report 04-01 August 25, 2004

Characterization and Prioritization of Mining-Related Metal Sources in the Streams and Streambed Sediments of the Lefthand Creek Watershed, Northwestern Boulder County, Colorado, 2002--2003

Alice R. Wood, Roshan Cholas, Laura Harrington, Lily Isenhart, Ned Turner, and Joseph N. Ryan

Department of Civil, Environmental, and Architectural Engineering University of Colorado at Boulder

## Report 04-01

Department of Civil, Environmental, and Architectural Engineering University of Colorado at Boulder

August 25, 2004



Characterization and Prioritization of Mining-Related Metal Sources in the Streams and Streambed Sediments of the Lefthand Creek Watershed, Northwestern Boulder County, Colorado

Alice R. Wood, Roshan Cholas, Laura Harrington, Lily Isenhart, Ned Turner, and Joseph N. Ryan

Department of Civil, Environmental, and Architectural Engineering University of Colorado at Boulder

**Contact Information:** 

University of Colorado 428 UCB Boulder, CO 80309-0428

phone: 303 492 0772 fax: 303 492 7317 email: joseph.ryan@colorado.edu

#### **EXECUTIVE SUMMARY**

Metal-mining associated wastes in the Lefthand Creek watershed in Boulder County, Colorado have been implicated as a major source of stream water contamination due to acid generation and toxic metal solubility. This watershed hosts hundreds of now inactive mine openings and dozens of sites of former ore milling. No complete analysis of mine sites or their environmental impacts exists to date. State of Colorado and Environmental Protection Agency officials, as well as a local stakeholder organization, the Lefthand Watershed Oversight Group (LWOG), require site specific contaminant source information in order to develop efficient and effective To this end, graduate and cleanup and management decisions. undergraduate student researchers, under the oversight of Dr. Joseph Ryan of the Department of Civil, Environmental, and Architectural Engineering at the University of Colorado, performed the research during varying stream flow conditions during the summer of 2002 and the spring, summer, and fall of 2003.

This report documents research and analysis of the sources, transport, and fate of aluminum, copper, iron, lead, manganese, uranium, and zinc in the Lefthand Creek watershed. Total, dissolved, and colloidal metal concentrations and loads were determined with lithium chloride and sodium chloride tracer tests and synoptic sampling. Streambed sediment metal concentrations were analyzed with by a partial digestion designed to dissolve metals associated with oxyhydroxide coatings on sediment grains. A simple prioritization system based on metal load contributions and exceedances of aquatic life criteria set by the Colorado Department of Public Health and Environment was developed to rank mining-related sites according to their impact on stream system health.

Based on the data collected in this study, eleven sites in the watershed received high priority ranking for reclamation. These sites include the Big Five Tunnel on Lefthand Creek, the Fairday Mine and Bueno Mountain on James Creek, and numerous sources including the Burlington Mine site on Little James Creek. Physical properties, including local mineralization and stream flow, and chemical properties, including stream acidity, hardness, and intrinsic properties of the metals studied, influenced the speciation, transport, and fate of metals in the stream of the Lefthand Creek watershed.

#### **ACKNOWLEDGEMENTS**

The authors would like to express appreciation for financial and technical support from organizations: Honeywell, International; the Lefthand Watershed Oversight Group; the Ohana Scholarship Fund; the University of Colorado Department of Civil, Environmental, and Architectural Engineering; the University of Colorado Environmental Studies Department; the University of Colorado United Government of Graduate Students travel granting program; the University of Colorado Laboratory for Environmental and Geological Studies; and the University of Colorado Outreach Program. Additional gratitude goes to Yumiko Abe, Rula Abu-Dalo, Mark Citone, Mike Costanzo, Tracy Kirkland, David Mixon, Kim Raby, and Emily Schneider for laboratory and field support, and to Victor Ketellapper and Dr. Jason Neff for editing and advising.

# TABLE OF CONTENTS

Introduction	1
Materials and Methods	3
Field site	3
Tracer tests and synoptic sampling	5
Stream flow rate calculations	10
Metal loading calculations	10
Stream bed sediments	11
Hardness and standards	12
Results	13
Lefthand Creek	
Stream flow	13
pН	13
Hardness	15
Iron	15
Aluminum	17
Manganese	17
Zinc	20
Copper	20
Lead	23
California Gulch Segment of Lefthand Creek	
Stream flow	26
pH and Hardness	26
Metal concentrations and loads	26
Stream bed sediments	29
Summary of Lefthand Creek sources	39
James Creek	
Stream flow	41
pH and hardness	41
Iron, aluminum, and manganese	41
Uranium	44
Zinc	44
Copper	49
Lead	49
Summary of James Creek sources	52
Little James Creek	
Stream flow	55
pH and hardness	55
Iron	56
Aluminum	57

Manganese	65
Zinc	65
Copper	68
Lead	68
Streambed sediments	73
Summary of Little James Creek sources	79
Discussion	81
Stream flow	81
Metal loadings and contaminant sources	82
Metal speciation and partitioning	84
Stream pH and metal partitioning	88
Stream hardness and metal partitioning	91
Stream bed sediment metals	93
Site Ranking and Remediation Prioritization	96
The Hazard Ranking System	97
Priority ranking under Clean Water Act §303(d)	97
Metal standards- and loadings-based ranking system	98
Summary and Conclusions	104
References	105
Appendix	111

## LIST OF TABLES

1.	Tracer injection and synoptic sampling parameters	7
2.	Analytes, detection limits, and reproducibility	10
3.	Mass and flow balance equations	11
4.	Cumulative stream flow and total metal loading contributions to Lefthand Creek	40
5.	Cumulative stream flow and total metal loading contributions to James Creek	54
6.	Cumulative stream flow contributions to Little James Creek	56
7.	Cumulative stream flow and total metal loading contributions to Little James Creek	80
8.	Intrinsic acidity constants for manganese, zinc, copper, and lead	85
9.	Standards- and loadings-based priority scoring system	100
10.	Priority ranking of Lefthand Creek sites	101
11.	Priority ranking of James Creek sites	102
12.	Priority ranking of Little James Creek sites	103

## **LIST OF FIGURES**

1.	Location of the Lefthand Creek watershed	1
2.	Map of the Lefthand Creek watershed including streams, mines, and other important features	4
3.	Lefthand Creek and tributary stream flow	14
4a.	Lefthand Creek and tributary pH	16
4b.	Lefthand Creek and tributary hardness	16
5.	Lefthand Creek and tributary total and dissolved iron concentrations and loads	18
6.	Lefthand Creek and tributary total and dissolved aluminum concentrations and loads	19
7.	Lefthand Creek and tributary total and dissolved manganese concentrations and loads	21
8.	Lefthand Creek and tributary total and dissolved zinc concentrations and loads	22
9.	Lefthand Creek and tributary total and dissolved copper concentrations and loads	24
10.	Lefthand Creek and tributary total and dissolved lead concentrations and loads	25
11.	The California Gulch segment of Lefthand Creek and tributary stream flow, high and low flow results	27
12a.	The California Gulch segment of Lefthand Creek and tributary pH, high and low flow results	28
12b.	The California Gulch segment of Lefthand Creek and tributary hardness, low flow results	28

13.	The California Gulch segment of Lefthand Creek and tributary iron concentrations and loads, high and low flow results	30
14.	The California Gulch segment of Lefthand Creek and tributary aluminum concentrations and loads, high and low flow results	31
15.	The California Gulch segment of Lefthand Creek and tributary manganese concentrations and loads, high and low flow results	32
16.	The California Gulch segment of Lefthand Creek and tributary zinc concentrations and loads, high and low flow results	33
17.	The California Gulch segment of Lefthand Creek and tributary copper concentrations and loads, high and low flow results	34
18.	The California Gulch segment of Lefthand Creek and tributary lead concentrations and loads, high and low flow results	35
19a.	The California Gulch segment of Lefthand Creek and tributary bed sediment iron concentrations	36
19b.	The California Gulch segment of Lefthand Creek and tributary bed sediment aluminum concentrations	36
20a.	The California Gulch segment of Lefthand Creek and tributary bed sediment manganese concentrations	37
20b.	The California Gulch segment of Lefthand Creek and tributary bed sediment zinc concentrations	37
21a.	The California Gulch segment of Lefthand Creek and tributary bed sediment copper concentrations	38
21b.	The California Gulch segment of Lefthand Creek and tributary bed sediment lead concentrations	38
22.	James Creek and tributary stream flow	42

23.	James Creek pH	43
24.	James Creek and tributary total and dissolved iron concentrations and loads	45
25.	James Creek and tributary total and dissolved aluminum concentrations and loads	46
26.	James Creek and tributary total and dissolved manganese concentrations and loads	47
27.	James Creek and tributary total uranium concentrations and loads	48
28.	James Creek and tributary total and dissolved zinc concentrations and loads	50
29.	James Creek and tributary total and dissolved copper concentrations and loads	51
30.	James Creek and tributary total and dissolved lead concentrations and loads	53
31.	Little James Creek and tributary stream flow, high and low flow results	58
32.	Little James Creek stream flow and lithium concentrations, low flow results	59
33a.	Little James Creek and tributary pH, high flow results	60
33b.	Little James Creek and tributary hardness, high and low flow results	60
34.	Little James Creek and tributary iron concentrations and loads, high flow results	61
35.	Little James Creek and tributary iron concentrations and loads, low flow results	62
36.	Little James Creek and tributary aluminum concentrations and loads, high flow results	63

37.	Little James Creek and tributary aluminum concentrations and loads, low flow results	64
38.	Little James Creek and tributary manganese concentrations and loads, high flow results	66
39.	Little James Creek and tributary manganese concentrations and loads, low flow results	67
40.	Little James Creek and tributary zinc concentrations and loads, high flow results	69
41.	Little James Creek and tributary zinc concentrations and loads, low flow results	70
42.	Little James Creek and tributary copper concentrations and loads, high flow results	71
43.	Little James Creek and tributary copper concentrations and loads, low flow results	72
44.	Little James Creek and tributary lead concentrations and loads, high flow results	74
45.	Little James Creek and tributary lead concentrations and loads, low flow results	75
46a.	Little James Creek and tributary bed sediment iron concentrations	76
46b.	Little James Creek and tributary bed sediment aluminum concentrations	76
47a.	Little James Creek and tributary bed sediment manganese concentrations	77
47b.	Little James Creek and tributary bed sediment zinc concentrations	77
48a.	Little James Creek and tributary bed sediment copper concentrations	78

48b.	Little James Creek and tributary bed sediment lead concentrations	78
49.	The average instream colloidal fraction of metals in Lefthand, James, and Little James Creek	86
50.	The average colloidal fractions of Mn, Zn, Cu, and Pb compared to the intrinsic surface complexation constants	87
51.	The colloidal fractions of Mn, Zn, Cu, and Pb as related to stream acidity in Lefthand, James Creeks, and Little James Creeks	89
52.	The colloidal fraction of Mn, Zn, Cu, and Pb as related to stream acidity measured in the California Gulch segment of Lefthand Creek, high and low stream flow conditions	90
53.	Colloidal fraction of Mn, Zn, Cu, and Pb in Lefthand Creek, Little James Creek, and the California Gulch segment of Lefthand Creek	92
54.	The relationship of stream bed sediment metal concentrations to dissolved and colloidal water concentrations in Little James Creek	94
55.	The relationship of stream bed sediment metal concentrations to dissolved and colloidal water concentrations in the California Gulch segment of Lefthand Creek	95

#### **INTRODUCTION**

Acidic, metal-laden water emanating from inactive mines and waste rock piles threatens aquatic life and drinking water quality in the streams of the Lefthand Creek watershed in northwest Boulder County, Colorado (Figure 1). The metals introduced to the streams from the mines pose acute and chronic risks for aquatic organisms. For example, a fish kill occurred in April 2003, in James Creek just downstream of the confluence with the Little James Creek as a result of the rapid release of snowmelt water that was temporarily stored in the subsidence pits at an inactive mine. The metals in the streams, and in the stream bed sediments, also threaten human health. Lefthand Creek serves as a key water supply—and the only winter water source—for the 14,000 customers of the Left Hand Water District. The potential exists for a catastrophic flood or mine collapse to mobilize toxic metals and contaminate the water supply (EPA, 2002).

Currently, cooperative efforts are underway to improve the water quality of the Lefthand Creek watershed. The U.S. Environmental Protection Agency (EPA) added the Captain Jack Mine and Mill site (including the Big Five Mine Tunnel) in California Gulch segment of Lefthand Creek to the National Priority List ("Superfund") in September 2003, and the Colorado



**Figure 1.** The Lefthand Creek watershed is located along the front range of the Rocky Mountains in northwestern Boulder County, Colorado.

Department of Public Health and Environment (CDPHE) is now heading up remediation planning for that site. A voluntary cleanup funded by Honeywell International, Inc. is underway at the Burlington Mine located along the Little James and Balarat Creeks west of Jamestown. The U.S. Forest Service (USFS) is planning reclamation activities at the Fairday Mine site on James Creek west of Jamestown, and at the Loder Smelter site on Lefthand Creek near Ward. The Lefthand Watershed Oversight Group (LWOG), a stakeholder consortium, has received funding through the Clean Water Act §319 granting program to develop a watershed plan that characterizes the watershed, identifies remediation targets, and chooses best management practices (BMPs) for these targets (LWTF, 2002). The experiments described in this report are part an outreach effort by the University of Colorado to assist the LWOG in characterization and prioritization of toxic metal sources and their impacts to the streams of the Lefthand Creek watershed.

Accurate characterization of metal loads carried by the streams plays a crucial role in the development of effective and efficient remediation. Thorough understanding of the location of the metal sources will foster the efforts of the LWOG in prioritizing sites for remediation. In addition, characterization of metal behavior in the streams will make possible predictions of the effectiveness of alternative remediation strategies (Runkel and Kimball, 2002). Important characteristics of metal behavior include partitioning between dissolved and colloidal phases and the mechanisms of metal removal to the stream bed, or hyporheic zone (Bencala *et al.*, 1990; Kimball *et al.*, 1995; Apodaca *et al.*, 2000).

The primary objectives of this study were to (1) locate and quantify potential sources of metals to Lefthand Creek, James Creek, and Little James Creek, (2) examine the partitioning of metals between dissolved and colloidal phases in the stream water, (3) assess the role of the stream bed sediments as a sink for metals entering the streams, and (4) apply this empirical field data to compare and prioritize sites for reclamation.

## MATERIAL S AND METHODS

#### Field site

The Lefthand Creek watershed (Figures 1 and 2) drains an area of approximately 220 km<sup>2</sup>. Located at the northern tip of the Colorado Mineral Belt, the watershed drains mainly Precambrian metamorphic and igneous formations and glacial and alluvial deposits. The watershed terrain is about one-half alpine and sub-alpine forest and one-half agricultural and urban on the high plains east of the front range of the Rocky Mountains. Lefthand Creek, James Creek, and Little James Creek are the primary streams in the Lefthand Creek watershed.

Beginning in the late 1850s, mineral extraction and processing occurred at hundreds of sites in the watershed (Cobb, 1988; EPA, 2003a). The United States Forest Service (USFS), which owns approximately 65% of the land area in the watershed, records 230 mining openings and 186 mine tailings piles, spoils, or dumps on USFS land alone (LWTF, 2002). A complete inventory of mining and milling sites in the entire watershed land area has not been conducted. The most recent mining activity ceased in the mid-1990s, and no mines or mill s currently operate in the watershed. The EPA has identified elevated concentrations of metals including aluminum, arsenic, barium, cadmium, chromium, copper, lead, manganese, mercury, nickel, silver, and zinc, within the watershed (LWTF, 2002).

Lefthand Creek originates in glacial and snow melt waters at elevations up to 4,200 m in the Indian Peaks Wilderness area near the Continental Divide approximately 5 km west of Highway 72 and the town of Ward, Colorado. Average Lefthand Creek stream flows from 1929 to 1980, recorded at a United States Geological survey staff gage at 40°07'32" north latitude and 105°18'12" west longitude, range from 97 L s<sup>-1</sup> to 4,700 L s<sup>-1</sup>. The peak flows occur in May and June (USGS, 2004). About 5 km below its headwaters, in an area locally known as California Gulch, Lefthand Creek flows through portions the Ward mining district, including a newly designated Superfund site, the Captain Jack Mine and Mill. Downstream of California Gulch, Lefthand Creek flows past mine waste rock piles and receives water from tributaries draining mine sites up the steep mountain slopes of Lefthand Canyon. The Lefthand Creek empties onto the plains at an elevation of about 1,400 m nearly 40 km downstream of the headwaters. Ultimately, Lefthand Creek drains into St. Vrain Creek, which feeds the South Platte River.

James Creek, a major tributary to Lefthand Creek, drains an area of approximately 48 km<sup>2</sup>. The sub-watershed is covered entirely by alpine and sub-alpine forest. Elevations in the James Creek watershed range from approximately 3,000 m at the headwaters in the Indian Peaks Wilderness Area to 2,000 m at the confluence with Lefthand Creek approximately 5 km



**Figure 2.** The Lefthand Creek watershed, with key streams, mines, and other features identified.

south of Jamestown. Stream flow in the James Creek ranged from about 500 L s<sup>-1</sup> to 6000 L s<sup>-1</sup> over the past five years (Colorado River Watch, 2004). The headwaters of the James Creek watershed supply only a small fraction of the flow in the James Creek. A diversion of the South St. Vrain Creek, which drains glacial-melt lakes near the continental divide, contributes nearly all of the flow of James Creek during parts of the year (CDWR, 2002; Colorado River Watch, 2004). Snowmelt in the South St. Vrain Creek headwaters feeds high flows. James Creek and its tributaries drain heavily mined slopes, including areas known as the Jamestown and Golden Age mining districts.

A tributary to James Creek, Little James Creek drains a watershed area of approximately 15 km<sup>2</sup>. The Little James Creek is a tributary to the James Creek. Alpine and sub-alpine forests cover the sub-watershed. No stream flow data for Little James Creek was available prior to this study. Observations during the years of 2002 and 2003 indicate that peak flows occur during local snowmelt periods in early spring, and that portions of the stream flow only intermittently by late summer. Little James Creek flows near the sites of mineral processing mill s and mine workings. The Colorado Department of Public Health and Environment (CDPHE) Water Quality Control Division (WQCD) developed Total Maximum Daily Load (TMDL) guidelines for the Little James Creek for cadmium, zinc, iron, manganese, and pH (WQCD, 2002).

#### Tracer tests and synoptic sampling

Metal loading tracer dilution tests were performed along Lefthand, James, and Little James Creeks to quantify stream flows at a high spatial resolution. Metal loadings, which are defined as the product of metal concentration and stream discharge for a location, describe the mass of metal entering and flowing through a stream (Kimball, 1997). Comparison of changes in instream and tributary metal loadings reveals the sources and magnitudes of metal inputs to a stream. This technique requires accurate stream flow and metal concentrations sampled at high spatial resolutions. Discharge measurements based on dilution of a conservative tracer is an effective, efficient measurement technique that quantifies flow through both the surface and hyporheic zones of streams, and allows for data collection at high spatial detail in a short time (Zellweger et al., 1989; Bencala et al., 1990; Kimball, 1997, Kimball et al., 2001a; Kimball et al., 2001b). Bencala et al. (1990) determined that lithium behaves conservatively and serves as a reliable tracer in streams impacted by acid mine drainage. This study also found that chloride behaves conservatively and is an effective tracer in acidic streams with low background chloride concentrations. Traditional discharge measurements made with stream flow meters over a cross-section of the stream may not correctly measure flow in steep, shallow, rough-bottomed

streams common to mountainous regions such as the Lefthand Creek watershed. Furthermore, traditional flow measurement techniques fail to capture stream flow through the hyporheic zone—the gravel bed under and parallel to the stream (Zellweger *et al.*, 1989; Bencala *et al.*, 1990).

Table 1 details the individual tracer and stream reach information for each experiment conducted in the Lefthand Creek watershed. The James Creek water samples were collected during low flow in the summer of 2002. Lefthand Creek and Little James Creek samples were collected during high flows in the spring of 2003. Low flow experiments were conducted along the Little James Creek and the California Gulch segment of Lefthand Creek during the fall of 2003. Each test was conducted over a period of 3 to 7 h, and over a stream reach of 2 to 7 km. The James Creek experiments were conducted using a sodium chloride (NaCl) tracer. For all other tests, lithium chloride (LiCl) was used.

For both James Creek tests, tracer injection solutions were prepared in two 170 L polyethylene barrels. In each barrel, approximately 170 L of water was pumped from the stream and mixed with 36 kg sodium chloride. The tracer solutions were mixed with a plastic paddle for 30 min to dissolve the sodium chloride. Excess sodium chloride was removed from the barrels with plastic scoops. Chloride concentrations in the two barrels varied by 6.3%; therefore, a calibration curve was developed to correct the chloride concentrations of samples taken when the solution from the second barrel was in the stream were corrected to the concentration of the first barrel. For all Lefthand Creek and Little James Creek tracer dilution tests, lithium chloride tracer solutions were prepared by mixing lithium chloride and stream water in a single 380 L polyethylene tank with a plastic paddle until all lithium chloride had dissolved. The concentration of the tracer solutions for each test are provided in Table 1.

The tracer solution was injected into the stream at a constant rate with a pump (Fluid Metering Instruments, model PM6014 pump and model V200 stroke rate controller). Injection rates were measured using a graduated cylinder and stopwatch before, during, and at the conclusion of the injection to evaluate the constancy of the injection rate. Additionally, multiple samples of the tracer solution were collected during each test to evaluate the constancy of tracer concentration.

Tracer dilution studies require that the only changes in tracer concentrations result from inflows to the stream reach undergoing sampling; if the injected tracer solution has not thoroughly mixed with surface and hyporheic flows through the entire study reach, stream flows may be overestimated. Therefore, tracer solution is pumped continuously for the duration of the experiment and sampling does not begin until the initial, leading edge of tracer concentrations has passed the most downstream **Table 1.** Summary of tracer injection and synoptic sampling parameters applied in metal loading tracer dilution tests of Lefthand, James, and Little James Creeks.

Date	Location	Stream reach length (km)	Tracer	Tracer concentration (M)	Tracer injection rate (L min <sup>-1</sup> )	Tracer injection duration (min)	Number of synoptic samples collected
7/18/2002	Upper James Creek	4.94	Na <b>Cl</b>	6.16	0.8	260	29
7/2/2002	Lower James Creek	5.21	Na <b>Cl</b>	3.21	1.3	195	34
4/22/2003	Little James Creek	2.87	LiCl	0.73	1.0	255	42
5/21/2003	Lefthand Creek – California Gulch	2.51	LiCl	0.68	0.5	310	36
5/27/2003	Lefthand Creek – Sawmill Rd. to park near mile marker 11	4.93	LiCl	1.25	1.1	195	26
5/29/2003	Lefthand Creek – near mile marker 11 to Rowena	7.07	LiCl	1.19	1.0	225	38
6/5/2003	Lefthand Creek – Rowena to James Creek confluence	7.08	LiCl	1.15	1.0	280	33
6/10/2003	Lefthand Creek – James Creek confluence to Buckingham Park	5.21	LiCl	1.19	1.3	226	35
6/12/2003	Lefthand Creek – Buckingham Park to Haldi intake	5.95	<b>Li</b> Cl	1.06	1.0	320	20
6/17/2003	Little James Creek	2.23	LiCl	0.49	0.4	390	34
11/15/2003	Lefthand Creek – California Gulch	1.65	LiCl	0.40	1.0	185	22

sample site in the study reach. To determine this arrival, specific conductance at the most downstream end site was monitored for an initial increase and subsequent plateau as the tracer arrived and reached a steady state in the stream. For the Lefthand Creek and Little James Creek tests, in which the lithium chloride tracer was used, low background lithium concentrations allowed for the injection of a very low concentration lithium Dilution from inflows further reduced the tracer chloride solution. concentrations, which resulted in undetectable specific conductance increases at the farthest downstream monitoring sites. In order to signal the tracer arrival at the downstream end of the stream reach, 75 to 150 L of a saturated sodium chloride solution was added as a pulse to the stream a few minutes prior to the tracer injection. This signaled the tracer arrival at the downstream monitoring sites with a clearly observable increase in specific conductance.

During the tracer injection, three sites were monitored and sampled: 10 to 20 m upstream of the injection site ("upstream"), approximately 20 to 100 m downstream of the injection site ("downstream"), and at the downstream end of the stream reach being sampled ("end"). Upstream samples were collected every 20 to 45 min for each test. They provided background lithium or chloride concentrations for the stream to detect any change in the background tracer concentration during the injection period. Downstream samples were collected approximately every minute during the initial 20 to 30 min of the injection period in order to identify the leading edge of the tracer injection curve and every 20 to 45 min to monitor tracer concentration and specific conductance changes. Specific conductance was measured in the field at the downstream site using a conductivity meter (Orion model 105). End samples were collected for lithium or chloride analysis every 5 min during the period of tracer arrival and every 15 to 45 min during the rest of the testing period. Specific conductance was also monitored in the field at the end site in order to observe the arrival of the tracer solution at the downstream end of the study reach.

For all tests, synoptic sampling of the stream reach began after the observation of the specific conductance increase and plateau at the downstream monitoring site. Synoptic sampling refers to the collection of stream water samples during a brief time period to obtain a "snapshot" profile of the tracer and metal concentrations in the stream at a given time (Kimball, 1997). Samples were collected every 10 to 300 m, and sample locations were recorded with a global positioning satellite receiver (Garmin model GPS 12). Sample sites were selected to bracket known and observed inflows and mine sites. In areas with no known or observed inflows or mine workings, samples were collected at regular intervals. Water samples from mine waters, tributaries, and other contributing surface flows were also collected during the synoptic sampling period.

All water samples were collected in nitric acid-washed 60 ml polyethylene bottles that were rinsed three times with water to be collected at the sample site. Samples were stored in coolers at ambient temperature and transported to the laboratory within 8 h of sample collection.

In the laboratory, the pH of samples was measured with a pH meter (either a Thermo Orion model 250A+ meter and model 9157BN electrode or an Accumet model 20 meter and a Thermo Orion 8012BN electrode) within 24 h of collection. The pH meters were calibrated with pH 4 and 7 standards at room temperature.

Portions of all of the synoptic stream samples were filtered to determined total and dissolved metal concentrations. Unfiltered samples were analyzed to provide total concentrations. Filtered samples were analyzed to provide dissolved concentrations. The difference between the total and dissolved concentration was defined as the colloidal concentration. The tracer injection solution, upstream, downstream, and end samplers were not filtered; only total concentrations were measured in these samples. Approximately 30 ml of each synoptic sample was filtered using polyethylene syringes and nylon membrane filters. Samples from both James Creek experiments, and from the April 22, 2003, Little James Creek experiment, were filtered with 0.2 µm nylon filters of 25mm diameter (Fisherbrand, disposable). Samples from all other tests were filtered with 0.45 µm nylon filters (Fisherbrand, disposable) to comply with U.S. Environmental Protection Agency water sampling protocols. All samples were acidified to pH < 2 with trace metal-grade nitric acid (Fisher Chemical).

Chloride concentrations in James Creek upstream, tracer tank, downstream, end and synoptic samples were determined with an ion-specific electrode (Thermo Orion model 720A meter and Thermo Orion 94-17B combination chloride electrode and model 90-02 double-junction reference electrode). Lefthand and James Creek upstream, tracer tank, downstream, end and synoptic sample lithium concentrations were measured with by inductively coupled plasma mass spectrometry (ICP-MS; Varian model X) in the Laboratory for Environmental and Geological Studies (LEGS), Department of Geological Sciences, University of Colorado at Boulder. For all tests, copper and lead concentrations were also measured by ICP-MS. Iron, aluminum, manganese, zinc, calcium, magnesium, and uranium concentrations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-AES; ARL model 3410+) in LEGS. Table 2 lists ICP-MS and ICP-AES detection limits.

Analyte Instrument		Detection limit (mg L <sup>-1</sup> )	Reproducibility (%)
chloride Ion-specific chloride electrode		1.8	± 2
lithium	ICP-MS	0.00005	± 7
copper	ICP-MS	0.0003	± 4
lead ICP-MS		0.0001	± 6
iron ICP-AES		0.005	± 9
aluminum ICP-AES		0.02	± 4
manganese	ICP-AES	0.002	± 5
zinc	ICP-AES	0.005	± 14
calcium	ICP-AES	0.01	± 1
magnesium	ICP-AES	0.009	± 1
uranium	ICP-AES	0.0002	± 10

Table 2. Analytes, instrumentation, detection limits, and reproducibility.

#### Stream flow rate

Stream flow rates were determined for each synoptic sampling location by a mass balance of background, tracer solution, and synoptic sample lithium or chloride concentrations (Kimball *et al.*, 2001a). Table 3 lists the mass and flow balance equations used to determine flows. Tributary flow rates were estimated as the difference between the discharge values calculated for the synoptic sample sites located immediately upstream and downstream from the tributary.

## Metal loading calculations

The product of metal concentration and discharge gives a metal loading rate (kg day<sup>-1</sup>) for each synoptic sample location. Total and dissolved metal loading rates were calculated for each synoptic sampling location. For each metal and each synoptic sampling location, the net load change is calculated as the difference between metal loads two successive synoptic sample sites. Cumulative loads are the sum of all net load increases along a stream reach. The fraction of total metal loads contributed by each source was determined by the sum of cumulative total loads in the synoptic sample sites adjacent to the source divided by the sum of all cumulative total loads for the stream reach. This provides a minimum estimate of the total metal load added to the stream along the length of the stream reach (Kimball *et al.*, 2001a).

	Equation	Variables
flow rate at first site downstream from tracer injection	$egin{aligned} egin{aligned} egi$	$Q_B$ , stream flow rate at site B $Q_{Inj}$ , tracer injection rate $C_{Inj}$ , tracer injection concentration $C_B$ , tracer concentration at site B $C_A$ , tracer background concentration
flow rate at subsequent downstream sites with uniform background concentrations	$Q_{C} = Q_{inj} \frac{\left(C_{inj} - C_{A}\right)}{\left(C_{C} - C_{A}\right)}$	$Q_{C}$ , stream flow rate at site $C$ $Q_{Inj}$ , tracer injection rate $C_{Inj}$ , tracer injection concentration $C_{C}$ , tracer concentration at site $C$ $C_{A}$ , tracer background concentration
flow rate at subsequent downstream sites with uniform background concentrations	$Q_{B} = Q_{B} \frac{(C_{B} - C_{I})}{(C_{C} - C_{I})}$	$Q_C$ , stream flow rate at site C $Q_B$ , stream flow rate at site B $C_B$ , tracer concentration at site B $C_I$ , tracer concentration in inflow $C_C$ , tracer concentration at site C

**Table 3.** Mass and flow balance equations (Kimball *et al.*, 2001a) used to calculate Lefthand, James, and Little James Creeks stream flows based on tracer dilution data.

## Streambed sediments

Stream bed sediments were collected from the California Gulch segment of Lefthand Creek on June 16, 2003 and from the Little James Creek on June 2 and 3, 2003. The sample collection and partial digestion methods outlined by Church *et al.* (1993) provided the model for the sediment collection and metal extraction techniques applied here.

Approximately 1 L of sediment was collected at each site, compositing five to ten sub-samples collected within a 10 m area. Sediment was collected only in depositional areas expected to be covered by water even at base flow, and only from the upper 5 cm of the stream bed. The composited sediment was wet-sieved with native stream water through a 4.75 mm (No. 4) brass sieve in the field, and stored in capped polyethylene bottles for transport. All samples were oven-dried at 100 °C within 48 h of collection and dry-sieved for 20 min with a Roto-tap through a nest of brass sieves to segregate the <63  $\mu$ m size fraction.

A partial digestion was employed to extract leachable metals associated with mineral coatings and (Church, 1993; Church *et al.*, 1997). Nitric acid-washed centrifuge tubes were filled with 1.0 g ( $\pm$ 0.2 g) of sediment. To each tube, 20 ml of 1.5 M trace metal-grade HCl (Mallinckrodt) and 0.2 ml 30% H<sub>2</sub>O<sub>2</sub> (Fisherbrand) were added. The tubes were capped, briefly hand-shaken to mix, placed in angled racks (approximately 45°), and agitated at

120 rpm in a reciprocating hot water bath (Sheldon Manufacturing model 1227) at 55 to 60 °C. The samples were centrifuged at 800 rpm for 10 minutes to segregate remaining sediment from the digestion solution, and the supernatant was removed from the centrifuge tubes to nitric acid-washed sample bottles with a syringe. Sediment metal concentrations for iron, aluminum, manganese, zinc, copper, and lead were determined by ICP-MS and ICP-AES analyses of the digestion solutions.

## Hardness and standards

In order to take into account variations in metal toxicity due to differences in the complexation capacity of natural waters, the Colorado Department of Public Health and Environment (CDPHE) calculates water quality standards according to stream water hardness (CDPHE, 2001). Stream water hardness, reported in mg L<sup>-1</sup> CaCO<sub>3</sub>, was determined by summing total calcium and magnesium concentrations (CDPHE, 2001):

## Hardness = 50.05([Ca] + [Mg])

where [Ca] and [Mg] are the total concentrations of calcium and magnesium ions in units of meq L<sup>-1</sup>. Hardness was calculated for approximately five sites along each sample reach of Lefthand and Little James Creek. Hardness was not measured in James Creek. According to calculated hardness values, appropriate CDPHE chronic (thirty day exposure) and acute (one day exposure) aquatic life Table Value Standards (TVS) for manganese, zinc, copper, lead, and uranium were selected for comparison to synoptic sample metal concentrations. CDPHE aquatic life parameters for iron, aluminum, and pH, which are not hardness-based, were also compared to water quality results (CDPHE, 2001).

#### RESULTS

The figures presented in this section show metal concentration, metal loading, hardness, and pH data for synoptic samples collected from Lefthand Creek in 2003 (Figures 3 to 10), James Creek in 2002 (Figures 22 to 30), and Little James Creek in 2003 (Figures 31 to 45). Data from sampling events conducted during high and low stream flow conditions are presented for the California Gulch segment of Lefthand Creek and for Little James Creek (Figures 11 to 18 and 31 to 45, respectively). Stream bed sediment metal concentrations for the California Gulch portion of Lefthand Creek (Figures 19 to 21) and for Little James Creek (Figures 46 to 48) are also included.

#### Lefthand Creek stream flow

The six tracer tests performed in geographical sequence along Lefthand Creek from May 21, 2003 to June 12, 2003 showed a discharge range from 45.0 L s<sup>-1</sup> at the most upstream sample site (0 km) to 2500 L s<sup>-1</sup> at 26.39 km (Figure 3). Tracer dilution stream flow results at overlapping synoptic sample sites varied over a short period. The flow rate in Lefthand Creek decreased by 10% from May 29 to June 5, 2003, at the sample site located at 14.37 km. From June 10 to June 12, 2003, Lefthand Creek stream flow decreased by nearly 30% at the sample site located at 26.39 km.

James Creek contributed the largest volume of water to Lefthand Creek. However, the flow of James Creek was severely overestimated as a result of sampling unmixed water downstream of this confluence; therefore, the flow of James Creek at the confluence was estimated at

550 L s<sup>-1</sup> based on stream flows observed at a meter in the town of Jamestown approximately 4.8 km upstream. Table 4 lists the tributary stream flow contributions to Lefthand Creek. Background concentrations of lithium Lefthand Creek ranged from 0.1  $\mu$ g L<sup>-1</sup> to 21  $\mu$ g L<sup>-1</sup>. Instream lithium concentrations were 5 to 130 times greater than background concentrations during the tracer injection period.

## Lefthand Creek pH

Instream pH values ranged from pH 5.2 immediately downstream of the Big Five Mine Tunnel discharge to pH 7.6 at 23.9 km (Figure 4a). The Big Five Mine Tunnel contributed the most acidic water to Lefthand Creek, with a pH of 3.7. The pH of the unnamed tributary at 0.16 km was also low, at pH 4.9. All other tributaries were above a pH of 5, with the highest pH value, 7.9, sampled from the unnamed tributary at 24.2 km. Generally, both instream and tributary pH values increased with downstream distance. Eighty-seven sites, located from the most upstream sample location to 14.37 km, fell below the CDPHE low pH parameter of pH 6.5.



**Figure 3.** Lefthand Creek stream flow as determined by LiCl tracer tests on multiple dates. Tributary flows were calculated as the difference between known flow values for sites immediately upstream and downstream of the tributary inflow.

#### Lefthand Creek hardness

Hardness values increase from a background average of 20 mg L<sup>-1</sup> CaCO<sub>3</sub> to an average of 42 mg L<sup>-1</sup> CaCO<sub>3</sub> downstream of the confluence of the Big Five Mine Tunnel discharge, and decrease to an average of 21 mg L<sup>1</sup> CaCO<sub>3</sub> downstream of Puzzler Gulch (Figure 4b). The highest instream hardness, 53 mg L<sup>-1</sup> CaCO<sub>3</sub>, was sampled just below the Big Five Mine Tunnel discharge. The lowest hardness, 8.9 mg L<sup>-1</sup> CaCO<sub>3</sub>, was collected at 17.3 km near the town of Rowena. Tributary hardness values were collected only for the Big Five Mine Tunnel discharge, Puzzler Gulch, and Indiana Gulch. These data show the highest hardness from the Big Five Mine Tunnel discharge, 200 mg L<sup>-1</sup> CaCO<sub>3</sub>, and Indiana Gulch, 96 mg L<sup>-1</sup> CaCO<sub>3</sub>, while Puzzler Gulch is only slightly higher than background levels with a hardness of 30 mg l<sup>-1</sup> CaCO<sub>3</sub>. Based on these hardness values, CDPHE TVS standards for a hardness of 50 mg L<sup>-1</sup> CaCO<sub>3</sub> were used for comparison to dissolved metal values for sites from 0–1.2 km, and for a hardness equal to 25 mg L<sup>-1</sup> CaCO<sub>3</sub> for samples collected from 1.3–31.3 km.

#### Lefthand Creek iron

Total iron concentrations measured in Lefthand Creek ranged from a low of 129  $\mu$ g L<sup>-1</sup>, measured at 1.06 km, to a peak of 1163  $\mu$ g L<sup>-1</sup> at 14.26 km (Figure 5). Dissolved iron concentrations show little variance over the entire Lefthand Creek stream reach sampled, indicating that most iron is contributed to the stream in colloidal form. Examination of inflow iron concentrations supports this, showing that more than 70%, and frequently more than 90%, of iron carried by tributaries was colloidal. A notable exception to this is the Big Five Mine Tunnel drainage, in which 80% of total iron exists as dissolved species. The unnamed tributary at 7.1 km also carries a high percentage of dissolved metal, at 71%; however, the total iron concentration of this stream is only 7.0 µg L<sup>-1</sup>. Significant spikes in total iron concentrations occur at 14.26 km near the town of Rowena, and at 26.39 km at the confluence of Sixmile Creek. The highest tributary total iron concentration was collected from Sixmile Creek, at 1,400.0 µg L<sup>-1</sup>. Iron loading follows a similar pattern to iron concentrations, with low dissolved iron loads along the entire stream reach. A small total iron load spike occurs following Indiana Gulch, with more significant spikes in loading occurring at 14.26 km and near the Sixmile Creek confluence. Tributary loads were all lower than instream loads, reflecting the relatively low stream flow rates of the tributaries. Extremely low total iron concentrations from 14.37–21.37 km, collected on June 5, do not compare with iron concentrations collected from sites at 14.37 km and 21.37 km on different dates; an analysis error is suspected and these values have been excluded from discussion here. Total iron concentrations exceeded the CDPHE total recoverable iron parameter of 1,000  $\mu$ g L<sup>-1</sup> for chronic impacts on aquatic life at only one site, 14.26 km.



**Figure 4.** (a) Lefthand Creek and tributary pH as measured in the laboratory within 24 hours of sample collection. (b) Lefthand Creek and tributary hardness values. Hardness was calculated as the sum of total calcium and magnesium ion concentrations.

#### Lefthand Creek aluminum

Total aluminum concentrations ranged from 70 µg L<sup>1</sup>, measured at 0.46 km, to 12.01 μg L<sup>-1</sup> at 19.48 km (Figure 6). Like iron, dissolved aluminum concentrations remain considerably lower than total, with an average of 16%of total aluminum present as dissolved species. Major concentration increases occur in only total aluminum, indicating that colloidal inputs are the primary sources of aluminum to the stream. With 98% of total aluminum in the dissolved form, the Big Five Mine Tunnel discharge was found to be the only tributary carrying mostly dissolved aluminum. Several tributaries showed total aluminum values significantly higher than instream values; these streams were all in the California Gulch reach from 0 to 2.51 km and from 24.23—26.39 km. A small spike in instream total aluminum concentration occurred at 0.6 km, following the contribution of an unnamed tributary, other spikes occur just downstream of the Big Five Mine Tunnel discharge, at 2.0 km near an unnamed mine opening, at the inflow of "Lee Hill" gulch, and at the inflow of Sixmile Creek. Total aluminum loads follow concentration trends, with the largest load increases corresponding to the largest concentration increases. This data shows a sharp drop in aluminum concentrations at 14.37 km from May 29 to June 5; however, aluminum concentrations measured at 21.37 km were similar when sampled on June 5 and June 10. Dissolved aluminum concentrations did not exceed CDPHE chronic or acute aquatic life parameters at any point along the stream reach.

## Lefthand Creek manganese

Total manganese concentrations ranged from 4.0 µg L<sup>-1</sup>, measured at 0 km and 0.46 km, to a maximum value of 460  $\mu$ g L<sup>1</sup> at 1.29 km (Figure 7). Averaging 32% of total instream manganese, dissolved concentrations show little variation and were generally lower than total concentrations. A notable exception to this occurs following the Big Five Mine Tunnel inflow at 1.23 km, where total and dissolved manganese concentrations and loads spike together. This data again shows the Big Five Mine Tunnel drainage as a major contributor of dissolved metals to Lefthand Creek. The dissolved manganese fraction makes up 92% of the total in the Big Five Mine Tunnel discharge waters. A smaller increase in total manganese concentrations and loads occurs at 1.99 km, downstream of the White Raven mine and mill site and near an unnamed mine opening, suggesting a colloidal input in this area. Some dilution occurs following the Puzzler Gulch confluence, causing a decrease in total and dissolved concentrations, although loads increase due to the flow inputs from Puzzler and Indiana Gulch. The largest manganese load increase was observed following the "Lee Hill" gulch inflow. Total manganese follows a generally increasing trend from 0.0–14.33 km, and a generally decreasing trend from 14.33—31.27 km. This data shows a small drop in manganese concentrations at 14.37 km from May 29 to June 5;



**Figure 5.** Lefthand Creek and tributary total and dissolved iron concentrations and loads. The CDPHE chronic aquatic life parameter for total recoverable iron is shown for comparison to observed concentrations. The CDPHE does not list an acute aquatic life standard for iron.



**Figure 6.** Lefthand Creek and tributary total and dissolved aluminum concentrations and loads.

however, manganese concentrations measured at 21.37 km were similar when sampled on June 5 and June 10. Dissolved manganese concentrations were far below CDPHE chronic or acute aquatic life criteria along the entire Lefthand Creek study reach.

### Lefthand Creek zinc

Differing from the metals discussed previously, dissolved zinc concentrations are the major fraction of the total, averaging 64% of total concentrations in instream samples (Figure 8). Total zinc concentrations range from below the detection limit at the most upstream sites from 0-0.46 km to 320 µg L<sup>1</sup> at 1.99 km. Total and dissolved zinc concentrations and loads increase following the inflow of the tributary that flows past the Dew Drop mine workings ("Dew Drop mine" tributary). Total and dissolved concentrations and loads also show a major spike downstream of the Big Five Mine Tunnel inflow, and remain high until the confluence of Puzzler Gulch. Dilution of zinc concentrations occurs following Puzzler Gulch, Indiana Gulch, and James Creek. Total and dissolved zinc concentrations gradually decrease over the remainder of the study area, with spikes in total concentrations and loads, and corresponding decreases in dissolved concentrations and loads, at the "Lee Hill" gulch and Sixmile Creek inflows. Zinc loads continue to increase until 14.33 km, after which point a generally decreasing trend is observed. Tributaries were carrying primarily dissolved zinc, with the highest total zinc concentrations found at the unnamed tributary at 0.5 km and at the Big Five Mine Tunnel discharge, with concentrations of 870  $\mu$ g L<sup>1</sup> and 330  $\mu$ g L<sup>1</sup>, respectively. Due to its larger discharge, the Big Five Mine Tunnel discharge contributed the highest total and dissolved zinc load to Lefthand Creek. Zinc concentrations measured at 14.37 km decreased from May 29 to June 5; zinc concentrations measured at 21.37 also decreased from June 5 to June 10 sampling. At a hardness of 25 mg L<sup>-1</sup> CaCO<sub>3</sub> and 50 mg L<sup>-1</sup> CaCO<sub>3</sub>, chronic and acute zinc criteria are nearly equal. Along the Lefthand Creek study area, dissolved concentrations violated chronic and acute standards at 38 sites, with 21 of those sites located in the California Gulch segment of the creek from 0.68-2.51 km.

## Lefthand Creek copper

Instream total copper concentrations ranged from 1.2  $\mu$ g L<sup>-1</sup> at 0.25 km to 150  $\mu$ g L<sup>-1</sup> at 1.29 km, just downstream of the Big Five Mine Tunnel inflow (Figure 9). Total and dissolved copper concentration and load data patterns compare closely to zinc, with an average of 48% of total copper present as dissolved species. Total and dissolved concentrations and loads spike together following the Big Five Mine Tunnel input, and total concentrations and loads again spike at 1.99 km near the unnamed mine opening, at 5.12 km, and at 9.66 km. Similar to zinc, total copper concentrations and loads



Figure 7. Lefthand Creek and tributary total and dissolved manganese concentrations and loads.



**Figure 8.** Lefthand Creek and tributary total and dissolved zinc concentrations and loads. CDPHE acute and chronic aquatic life standards are equal at the hardness values measured.

increased at the inflows of "Lee Hill" gulch and Sixmile Creek, while dissolved concentrations and loads decreased at these sites. Measured as the highest concentration in the study area with a total copper concentration of 280 mg l, 100% of which was dissolved, the Big Five Mine Tunnel drainage carried the largest tributary copper load. Copper concentrations measured at 14.37 km decreased from May 29 to June 5; copper concentrations measured at 21.37 km also decreased from June 5 to June 10 sampling. Instream dissolved copper concentrations exceeded CDPHE chronic aquatic life criteria at 129 sites, 103 of which exceeded acute standards. Acute standard violations occurred from 2.51 km to 20.95 km; following the confluence with James Creek only chronic standards were exceeded.

#### Lefthand Creek lead

Dissolved lead concentrations and loads remain low throughout most of the study area, with total lead concentrations consisting of an average of 48% dissolved species upstream of the Big Five Mine Tunnel inflow (Figure 10). For all sites downstream of this inflow, dissolved species average only 6% of total lead concentration, suggesting a large colloidal input from the Big Five Mine Tunnel discharge and downstream sources. Total lead concentrations and loads increase immediately downstream of the Big Five Mine Tunnel inflow, followed by a larger spike in total concentration and load at 1.99 km near the unnamed mine opening, at 3.97 km and 4.35 km, and at 9.66 km. The largest total lead concentration and load peak was observed at the "Lee Hill" gulch inflow. Total lead concentrations and loads generally increase until 14.37 km, with a general decrease following this point. The Carnage Canyon tributary at 24.23 km exhibited the highest total lead concentration, at 13.3 µg L<sup>-1</sup> (6% dissolved). Indiana Gulch and the Big Five Mine Tunnel discharge also carried relatively high lead concentrations, at 3.5  $\mu$ g L<sup>-1</sup> (4% dissolved) and 2.4  $\mu$ g L<sup>-1</sup> (100% dissolved), respectively. Lead concentrations measured at 14.37 km decreased from May 29 to June 5; lead concentrations measured at 21.37 also decreased from June 5 to June 10 sampling. Dissolved lead concentrations exceeded CDPHE chronic aquatic life criteria at four sites located at 1.29 km, 7.30 km, 9.11 km, and 12.76 km.



Figure 9. Lefthand Creek and tributary total and dissolved copper concentrations and loads.


Figure 10. Lefthand Creek and tributary dissolved and total lead concentrations and loads.

### California Gulch segment of Lefthand Creek stream flow

To examine the effects of varying stream flow conditions, Lefthand Creek discharge rates were calculated for metal loading tracer dilution tests performed in the California Gulch segment of the creek on May 21, 2003 and November 15, 2003 (Figure 11). Along the sites sampled for stream flow during both tests, from 0.84 to1.85 km, average discharge decreased by 85% from the 150 L s<sup>-1</sup> in May to 22 L s<sup>-1</sup> in November. Similarly, flow from the Big Five Mine Tunnel drainage, the only tributary sampled for discharge during both tests, decreased by 89% from 24 L s<sup>-1</sup> to 3.3 L s<sup>-1</sup>. The low flow conditions observed in November lead to a longer tracer transport time than predicted; synoptic sample sites located downstream of 1.85 km had not received the full pulse of lithium chloride tracer when sampled. Therefore, these sites were not included in stream flow or metal loading results.

# California Gulch segment of Lefthand Creek pH and hardness

Stream pH and hardness also varied between the two testing dates (Figure 12a). November sampling showed lower average instream pH values, at pH 5.0, while pH measured in May averaged 5.8. Hardness showed slight variation, with a May instream average hardness of 24 mg L<sup>-1</sup> CaCO<sub>3</sub> and a November average hardness of 36 mg L<sup>-1</sup> CaCO<sub>3</sub> (Figure 12b). In both tests, sites located immediately downstream of the Big Five Mine Tunnel inflow exhibited the lowest pH and highest hardness values. Samples of the Big Five Mine Tunnel discharge had pH values of 4.0 and 3.2 and hardness values of 120 mg L<sup>-1</sup> CaCO<sub>3</sub> and 202 mg L<sup>-1</sup> CaCO<sub>3</sub> in May and November, respectively. CDPHE TVS standards for hardness equal to 25 mgL<sup>-1</sup> CaCO<sub>3</sub> were compared to instream dissolved metal concentrations from both tests for sites located upstream of the Big Five Mine Tunnel discharge confluence, while standards for hardness equal to 50 mg L<sup>-1</sup> CaCO<sub>3</sub> were used downstream of this confluence.

# California Gulch segment of Lefthand Creek metal concentrations and loads

Iron (Figure 13), aluminum (Figure 14), and lead (Figure 18), all with high concentrations of colloidal phase species, were present in highest concentrations in the May sampling event. All three of these metals exhibited increases downstream of the Big Five Mine Tunnel inflow in both May and November, and increases in total concentrations and loads near the unnamed mine opening at 1.99 km during May. Aluminum and lead concentrations also increased at the inflow of the "Dew Drop mine" tributary when sampled in May.

During both high and low flow conditions, the Big Five Mine Tunnel mine drainage added high concentrations and loads of total and dissolved manganese, zinc, and copper (Figures 15, 16, and 17, respectively). Metal inputs to Lefthand Creek near the unnamed mine opening at 1.99 km were



**Figure 11.** Stream flow in the California Gulch reach of Lefthand Creek, measured during high flow conditions on May 21, 2003 and low flow conditions on November 15, 2003.



**Figure 12.** (a) Lefthand Creek and tributary pH as measured in the laboratory within 24 hours of sample collection. (b) Lefthand Creek and tributary hardness values. Hardness was calculated as the sum of total calcium and magnesium ion concentrations.

observed in May during flow, but no significant change in metal concentrations were measured in this area in November. The Puzzler and Indiana Gulch inflows diluted metal concentrations in Lefthand Creek during both sampling events; however, the dilution was greatest during April due to the high flows of these streams at that time. These tests indicate that the Big Five Mine Tunnel mine drainage is the primary metal source to the California Gulch segment of Lefthand Creek during both high and low flow conditions. The mostly colloidal metal inputs near the unnamed mine opening at 1.99 km were found to be significant only during high flow events.

### California Gulch segment of Lefthand Creek stream bed sediments

Analysis of metals sorbed to stream bed sediment oxy-hydroxide precipitates and colloids in the partial-digestion leachable phase indicates that aluminum (Figure 19b), manganese (Figure 20a), zinc (Figure 20b), copper (Figure 21a), and lead (Figure 21b) sediment concentrations increase with downstream distance along this reach. Iron (Figure 19a) concentrations exhibited no regular spatial trends and deviated only 26% from the mean sediment concentration of 370 mol kg<sup>-1</sup>. Zinc and copper concentrations in stream bed sediments initially increase at 0.07 km, and again just upstream of the inflow from the Big Five Mine Tunnel. Aluminum, manganese, zinc, and copper sediment concentrations increase downstream of the Big Five Mine Tunnel inflow, downstream of the White Raven mine site, and downstream of the unnamed mine opening at 1.99 km. Sediment lead concentrations show the greatest increase downstream of the Big Five Mine Tunnel inflow, with a smaller spike downstream of the unnamed mine opening.



**Figure 13.** The California Gulch segment of Lefthand Creek total and dissolved iron concentrations and loads, as measured on May 21, 2003 and November 15, 2003. The CDPHE total recoverable iron concentration parameter for chronic aquatic life threats is shown.



measured on May 21, 2003 and November 15, 2003.



**Figure 15.** The California Gulch segment of Lefthand Creek total and dissolved manganese concentrations and loads, as measured on May 21, 2003 and November 15, 2003.



**Figure 16.** The California Gulch segment of Lefthand Creek total and dissolved zinc concentrations and loads, as measured on May 21, 2003 and November 15, 2003. At the hardness values measured, chronic and acute aquatic life standards for zinc are the same value.



**Figure 17.** The California Gulch segment of Lefthand Creek total and dissolved copper concentrations and loads, as measured on May 21, 2003 and November 15, 2003.



**Figure 18.** The California Gulch segment of Lefthand Creek total and dissolved lead concentrations and loads, as measured on May 21, 2003 and November 15, 2003.





Figure 20. The California Gulch segment of Lefthand Creek stream bed total manganese (a) and zinc (b) concentrations.



Figure 21. The California Gulch segment of Lefthand Creek stream bed total copper (a) and lead (b) concentrations.

#### Summary of Lefthand Creek metal and acidity sources

Sites located along the California Gulch segment of Lefthand Creek were the initial sources of metal loading increases and CDPHE water quality standard violations along the 31.27 km Lefthand Creek study reach. In particular, the Big Five Mine Tunnel mine drainage contributed the largest concentrations of dissolved aluminum, manganese, zinc, copper, and lead. The tributary that flows past the Dew Drop mine site also added dissolved and colloidal manganese, zinc, and copper as well as colloidal aluminum and lead. Colloidal increases of all metals analyzed, and particularly lead and zinc, were measured at 1.99 km near an unnamed mine opening. Inflows from Puzzler and Indiana Gulch diluted metal concentrations in Lefthand Creek for all metals except iron. Various unnamed and unidentified metal loading sources exist upstream of the village of Rowena. James Creek added somewhat to the iron and aluminum loading of Lefthand Creek, but diluted concentrations of all other metals. Finally, "Lee Hill" gulch added a high percentage of the aluminum, manganese, zinc, copper, and lead colloidal metal loads to Lefthand Creek. Table 4 lists the relative stream flow and cumulative total metal loading contributions of sites identified as potential contaminant sources to Lefthand Creek.

Stream Distance Al Mn Zn Cu Pb Fe Source flow (**km**) (%) (%) (%) (%) (%) (%) (%) "Dew Drop mine" 0.61-0.68 < 1 < 1 1.2 < 1 1.1 < 1 < 1 tributary Big Five Mine 1.18-1.29 < 1 < 1 1.6 5.5 4.7 7.7 < 1 Tunnel White Raven mine < 1 1.55-1.71 < 1 6.7 < 1 < 1 < 1 < 1 Unnamed mine 1.99-2.19 < 1 < 1 < 1 2.221.0 < 1 < 1 opening Loder smelter 2.66 - 3.21< 1 < 1 < 1 1.0 1.3 1.3 1.6 Puzzler Gulch 2.24-2.38 1.3 < 1 < 1 < 1 < 1 < 1 < 1 Indiana Gulch 2.38 - 2.422.0 < 1 < 1 < 1 < 1 < 1 < 1 Tuscarora Gulch 4.35-4.84 2.1 3.2 3.3 6.9 3.2 7.4 11.8 Unidentified 4.84 - 5.121.8 < 1 1.7 2.9 3.0 11.5 2.0 source Unnamed tributary 6.98-7.19 < 1 7.1 6.7 6.3 12.3 11.9 9.6 Unidentified 8.48-8.96 5.9 5.6 6.9 7.7 9.5 8.4 5.8 source Spring Gulch 10.64 - 11.436.5 1.8 2.31.5 1.7 2.22.8 Reedy mine and 11.90-12.07 < 1 1.6 1.0 3.12 < 1 1.4 1.3 Lick Skillet gulch Prussian mine 12.60-13.01 2.7 2.74.1 2.0 2.2 3.5 < 1 waste pile Slide mine 13.16-13.50 2.4 1.2 1.6 < 1 < 1 < 1 < 1 "Lee Hill" gulch 19.25-19.48 1.5 1.5 17.8 21.1 12.9 8.3 16.1 James Creek 21.22 - 21.3720.5 7.9 3.2 < 1 < 1 < 1 < 1 Carnage Canyon 24.14-24.31 1.7 4.3 2.9 < 1 1.0 < 1 1.4 gulch Sixmile Creek 26.09-26.39 < 1 < 1 < 1 < 1 < 1 < 1 < 1

**Table 4.** Cumulative stream flow and total metal loading contributions to Lefthand Creek. Loads were determined with metal loading tracer dilution tests and synoptic sampling from May 21 to June 12, 2003.

#### James Creek stream flow

The two tracer tests performed along Lefthand Creek on July 2 and 18, 2002, show 47% higher discharge values for the upstream sample reach, tested on July 18 (Figure 22). James Creek flow ranged from 580 L s<sup>-1</sup> at 8.55 km to 2500 L s<sup>-1</sup> at the most downstream site sampled on July 18, 2002. The only measured tributary flow was from an unnamed gully located at 0.49 km, with a flow of 106 L s<sup>-1</sup>. Little James Creek, which flows into James Creek at 4.88 km, was not a contributor of surface flow to James Creek, although flow increases on July 18 suggest a subsurface flow of 103 L s<sup>-1</sup> in the area of the Little James Creek confluence. The year 2002 was an extremely dry year; therefore, the absence of flowing tributaries in July is not extraordinary. Background chloride concentrations in James Creek ranged from 860 to 2,700  $\mu$ g L<sup>-1</sup>. Instream chloride concentrations were 2 to 5 times greater than background.

### James Creek pH and hardness

Instream pH values ranged from pH 6.2 to pH 7.6, falling below the CDPHE low pH parameter of pH 6.5 at only one site, located at 0.18 km (Figure 23). Tributary pH data were not recorded. Hardness data also were not collected during the 2002 sampling events; however, samples collected monthly at five sites along James Creek from November 1996 to September 2000 showed a hardness range from 4 to 36 mg L<sup>-1</sup> CaCO<sub>3</sub> (Colorado River Watch, 2004). Based on this data, CDPHE TVS standards for stream water hardness equal to 25 mg L<sup>-1</sup> CaCO<sub>3</sub> were compared to dissolved metal concentrations.

### James Creek iron, aluminum, and manganese

Iron (Figure 24), aluminum (Figure 25), and manganese (Figure 26) data suggest that these metal species occur primarily as colloids in James Creek, with dissolved metal concentrations making up less than 25% of total metal concentrations. Little variation occurs in dissolved metal concentrations for these three metals; any significant concentration and load changes occur only in total iron, aluminum, and manganese. Total iron concentrations ranged from 140  $\mu$ g L<sup>-1</sup> at 4.95 km to 560  $\mu$ g L<sup>-1</sup> at 4.66 km, while total aluminum concentrations ranged from 51  $\mu$ g L<sup>1</sup> at 4.82 km to 170  $\mu$ g L<sup>-1</sup> at 0.18 km. Finally, total manganese concentrations ranged from 6.0  $\mu$ g  $L^{-1}$  at 5.54 km to 29 µg  $L^{-1}$  at 4.66 km. Interestingly, the iron, aluminum, and manganese concentrations recorded at 4.82 km were 34%, 38%, and 51% higher, respectively, when sampled at the same location on July 18. This increase occurred almost entirely in the colloidal fraction for iron, but primarily in dissolved aluminum and manganese concentrations. A large spike in total iron, aluminum, and manganese concentrations occurred at 4.66



Figure 22. James Creek stream flow calculated with NaCl tracer dilution tests.



Figure 23. James Creek pH as measured in the laboratory immediately following sample collection.

km near an ephemeral gully that flows near the Bueno Mountain tailings pile ("Bueno Mountain gully"), and a smaller increase is observed at 4.96 km, following the inflow of Little James Creek. Aluminum also spiked at 0.18 km near the John Jay mine workings, and a spike in both aluminum and manganese total concentrations was recorded at 9.47 km, downstream of the Castle Gulch inflow. Following the pattern of metal concentrations, a major spike in the total load for all three metals occurs at 4.66 km, with a smaller spike in total aluminum load at 0.18 km. Very high total iron, aluminum, and manganese concentrations were found in the unnamed gully at 0.49 km, with the following total metal concentrations measured: iron, 14,000  $\mu$ g L<sup>-1</sup>, aluminum, 180  $\mu$ g L<sup>-1</sup>, and manganese, 12,000  $\mu$ g L<sup>-1</sup>. However, this stream added very little load to James Creek due to its low flow. No sites in the entire James Creek study reach exceeded chronic or acute aquatic water quality criteria for iron, aluminum, or manganese.

# James Creek uranium

Although was once mined at the Fairday mine site, only low uranium concentrations were observed in James Creek (Figure 27). Total uranium concentrations varied from below the 0.2  $\mu$ g L<sup>1</sup> detection limit at 13 sites, all located from 0 to 2.26 km, to 0.9  $\mu$ g L<sup>-1</sup> at 4.66 km. All dissolved uranium samples were below the detection limit. A spike in total uranium concentration was found at 1.34 km near the Fairday Mine, followed by a concentration increase beginning at 2.44 km and continuing for the remainder of the stream reach. Additional total concentration spikes were recorded at 4.66 km near the drainage from Bueno Mountain, downstream of the Little James Creek inflow at 4.96 km, and downstream of the Castle Gulch inflow at 9.47 km. Tributary total and dissolved uranium concentrations greatly exceeded instream concentrations. The highest total uranium concentration in the sub-watershed, at 72 µg L<sup>-1</sup>, was collected from the unnamed tributary at 0.49 km. This tributary showed higher metal loading than adjacent instream samples. Dissolved uranium concentrations were far below aquatic life water quality criteria for the entire stream reach.

# James Creek zinc

Dissolved zinc concentrations average 81% of total zinc over the entire study reach, demonstrating that zinc exists predominantly as dissolved species (Figure 28). Total zinc concentrations ranged from 1.4  $\mu$ g L<sup>-1</sup> at 4.82 km to 280  $\mu$ g L<sup>-1</sup> at 2.80 km. Spikes in total and dissolved zinc concentrations and loads occur throughout the upper portions of the study reach, with the largest spike occurring at 2.80 km in an area where no mining sites were observed. Other spikes were measured at 0.58 km following the unnamed gully inflow, from 1.16 to 1.71 km near the John Jay and Fairday mine sits, at



**Figure 24.** James Creek and tributary total and dissolved iron concentrations and loads. The CDPHE chronic aquatic life parameter for total recoverable iron is shown for comparison. The CDPHE does not list an acute parameter for aquatic life.



Figure 25. James Creek and tributary total and dissolved aluminum concentrations and loads.



Figure 26. James Creek and tributary total and dissolved manganese concentrations and loads.



**Figure 27.** James Creek and tributary total uranium concentrations and loads. Dissolved concentrations for all sample sites fell below the detection limit.

3.72 km (total zinc only), and at the Little James confluence at 4.82 km. The spike in total and dissolved zinc concentrations observed at 4.82 km during the July 18 sampling event was not observed in July 2 samples. Total zinc concentrations at this site increased from 1.4 µg L<sup>-1</sup> on July 2 (100% dissolved) to 95 µg L<sup>-1</sup> (69% dissolved) on July 18. Similarly, all sites sampled on July 2, located from 4.66 km to the end of the study reach, showed an average of 95% lower concentrations than the upstream sites sampled on July 18. The dissolved zinc fraction made up 100% of total concentrations in both measured tributaries. Total and dissolved zinc concentrations measured in the unnamed gully at 0.49 km fit instream concentrations, with a total concentration of 41  $\mu$ g L<sup>1</sup>. Due to their low flow conditions in July of a drought year, the load contribution of this stream was below nearby instream loads. At the hardness of 25 mg L<sup>-1</sup> CaCO<sub>3</sub>, acute and chronic aquatic life criteria are equal. James Creek stream water exceeded both criteria 13 samples sites, all of which were found in the upper portion of the study reach upstream of 4.88 km.

### James Creek copper

Approximately 50% of copper in James Creek was present as dissolved species, showing a balance between the dissolved and colloidal copper fractions (Figure 29). Significant spikes in copper concentrations and loads occur primarily in total copper, however, indicating that colloidal inputs were the primary copper sources to James Creek. Total copper concentrations ranged from 1.0  $\mu$ g L<sup>-1</sup> at 4.95 km to 9.9  $\mu$ g L<sup>-1</sup> at 1.71 km. A small spike in total and dissolved copper concentrations and loads occurred at 1.16 km near the John Jay mine site. The largest concentration and loading increase occurred at 1.71 km, just downstream of the Fairday Mine site. Another significant total concentration and load spike occurred at 4.66 km, near the "Bueno Mountain gully". Copper concentrations in the unnamed gully at 0.49 km were higher than instream concentrations, with a total copper concentration of 5.5  $\mu$ g L<sup>1</sup>, 78% of which was dissolved. The total tributary load was again less than adjacent instream loads. No sites in the entire James Creek study reach exceeded acute or chronic aquatic water quality criteria for copper.

# James Creek lead

Total lead concentrations ranged from below the detection limit of 0.2  $\mu$ g L<sup>-1</sup> at 7 sites, from 4.82—5.90 km, to a high value of 3.7  $\mu$ g L<sup>-1</sup> at 4.66 km (Figure 30). Total and dissolved concentrations measured **a**t 4.82 km varied by 94% from July 2 to July 18. Total lead was below the detection limit at this site on July 2, but was found to be nearly the highest in the stream, at 2.3  $\mu$ g L<sup>-1</sup> (15% dissolved), on July 18. Dissolved lead concentrations in James Creek fell below the detection limit of 0.2  $\mu$ g L<sup>-1</sup> for 48 sample sites, including



**Figure 28.** James Creek and tributary total and dissolved zinc concentrations and loads. At the hardness value of 100 mg  $L^{-1}$  CaCO<sub>3</sub>, CDPHE acute and chronic aquatic life standards are the same.



Figure 29. James Creek and tributary total and dissolved copper concentrations and loads.

all sites downstream of 4.82 km. An average of the remaining 15 sites showed that 53% of lead in the stream existed as dissolved species; however, this may be an overestimation of the dissolved fraction since dissolved concentrations below the detection limit were not included in the percentage calculations. Total lead concentrations and loads show the greatest increase at 4.66 km, near the "Bueno Mountain gully" ephemeral inflow, with a smaller spike at 1.71 km, near the Fairday mine site. Dissolved lead concentrations and loads begin a slight increase at 4.82 km, at the Little James inflow, although this increase was not observed at the duplicate sites sampled on July 2. Lead concentrations and loads in the unnamed gully at 0.49 km were below the detection limit, and this tributary did not contribute to instream loading. Dissolved lead concentrations exceeded chronic aquatic life criteria at two sites, located at 1.71 km and 4.94 km.

# Summary of James Creek metal and acidity sources

Table 5 lists the relative stream flow and cumulative total metal loading contributions of sites identified as potential contaminant sources to Lefthand Creek. Highest total metal loading contributions for iron, aluminum, manganese, lead, and uranium were measured at 4.66 km, near the "Bueno Mountain gully". The load increases at this site were primarily observed in the colloidal fraction. An ephemeral gully drains the Bueno Mountain area, which was dry at the time of sampling; this indicates subsurface flow and metal contributions to James Creek. Total and dissolved zinc concentrations and loads were highest at 2.80 km. It is possible that surface or groundwater interactions with the Bueno Mountain mine workings also explain this increase; however, further research is necessary to confidently identify this important zinc source. The principal input of total and dissolved copper loads was found at 1.71 km, near the Fairday Mine site. Finally, temporally varying measurements made at the 4.82 km and 4.95 km sample sites suggest that Little James Creek intermittently contributes dissolved aluminum, manganese, zinc, copper, and lead loads to James Creek.



**Figure 30.** James Creek and tributary total and dissolved lead concentrations and loads. Dissolved lead concentrations sampled from 5 km to the downstream end of the study reach fell below the xx detection limit.

**Table 5.** Cumulative metal loading contributions to James Creek. Loads were determined with metal loading tracer dilution tests and synoptic sampling on July 2 and 18, 2002.

Source	Distance (km)	Stream flow (%)	Fe (%)	Al (%)	Mn (%)	Zn (%)	Cu (%)	Pb (%)	U (%)
John Jay mine	0.40— 0.73	3.7	2.0	1.5	1.5	6.1	1.6	< 1	< 1
Fairday mine	1.34— 1.71	7.8	5.1	5.8	3.1	5.6	35.5	13.3	7.4
Unidentified source	2.62— 2.80	< 1	2.8	2.1	4.1	28.8	< 1	< 1	2.5
Unidentified source	3.7—4.1	12.5	6.4	7.1	4.9	12.8	4.4	8.3	9.2
Bueno Mountain	4.27— 4.82	11.6	56.1	26.6	42.9	16.6	22.5	53.0	45.0
Little James Creek	4.82— 4.96	12.6	28.9	12.4	11.4	< 1	3.4	< 1	14.6
Castle Gulch	8.74— 8.92	3.4	7.2	2.1	2.2	< 1	< 1	< 1	1.2
Unidentified source	9.29— 9.47	< 1	9.5	4.3	5.3	< 1	1.2	2.5	5.3

### Little James Creek stream flow

Stream flow in Little James Creek, measured April 22, 2003, increased from 110 L s<sup>-1</sup> at the most upstream site to 540 L s<sup>-1</sup> just upstream of the Little James confluence with James Creek (Figure 31). Five tributaries to the Little James were sampled, with the largest tributary input, 71 L s<sup>1</sup>, discharged from Balarat Creek at 1.28 km. Stream flow in Little James Creek at had decreased by an average of 94% when sampled on June 17, 2003. During June sampling, the stream was found to become a losing reach beginning at approximately 1.47 km, expressed on the surface as intermittent pools and channels from 1.47 km to the confluence with James Creek at 2.87 km. Due to the extremely low flows in June, stream flow and metal load calculations were carried out only for sample sites located upstream of 1.34 km. Balarat Creek added the only measurable tributary flow on June 17, with a discharge of 5.2 L s<sup>1</sup>, while the Emmett adit contributed a small trickle of flow that disappeared into the subsurface approximately 5 m before reaching Little James Creek (Table 6).

Background concentrations of lithium in Little James Creek ranged from 3.4  $\mu$ g L<sup>-1</sup> to 14  $\mu$ g L<sup>-1</sup>. Instream lithium concentrations were 20 to 1000 times greater than background concentrations during the tracer injection period. Water inflows to the streams lead to dilution of the lithium and chloride tracers, corresponding to stream flow increases (Figure 31). This relationship is the basis of stream flow calculations by means of the tracer dilution method. Where the inverse relationship exhibited in Figure 29 from 0.64 to 1.62 km was not observed, such as in the lower portion of the Little James Creek when sampled during low flow on June 17, 2003 (Figure 32, boxed section), discharge data were considered unreliable and were not used in metal load calculations.

### Little James Creek hardness and pH

Stream pH data was collected only during the June 17 sampling event (Figure 33a). Instream pH measurements ranged from pH 5.8 to pH 7.1, with a general decrease from 0—1.85 km followed by a plateau for the remainder of the stream. The Emmett adit, pH 3.4, had the highest acidity measured in the Little James Creek sub-watershed. Balarat Creek was also acidic, with pH 4.0. Twenty-four sites, all located downstream of the Emmett adit and Balarat Creek inflows, fell below the CDPHE low pH parameter of pH 6.5 in June.

Hardness data were collected at four sites along the stream reach during the April 22 sampling event and at five sites on June 17 (Figure 33b). Hardness in April ranged from 48 mg L<sup>-1</sup> CaCO<sub>3</sub> at 0.68 km to 87 mg L<sup>-1</sup> CaCO<sub>3</sub> at 2.68 km. Hardness in June ranged from 41 mg L<sup>-1</sup> CaCO<sub>3</sub> at 0.64 km to 190 mg L<sup>-1</sup> CaCO<sub>3</sub> at 2.68 km. During both tests, hardness more than doubled following the Balarat Creek confluence. Based on these measured

Source	Distance (km)	April stream flow (%)	June stream flow (%)
Undetermined source	0.37—0.64	8.4	
"Argo gully"	0.77—0.89	4.0	30.0
Emmett adit	1.18—1.23	< 1	19.2
Balarat Creek	1.23—1.34	13.3	32.8
Subsurface inflow	1.55—1.83	25.8	
Unnamed tributary	1.85—1.91	6.5	
Streamside tailings and "Bueno Mountain gully"	2.36—2.41	6.4	
Subsurface inflow	2.59—2.68	11.6	
Subsurface inflow	2.76—2.81	12.1	

**Table 6.** Cumulative stream flow additions to Little James Creek determined with tracer dilution tests and synoptic sampling on April 22, 2003 and June 17, 2003.

hardness values, CDPHE TVS standards for hardness equal to 50 mg L<sup>-1</sup> CaCO<sub>3</sub> were applied to April 22 sampling event results from sites located at 0-1.18 km, and for hardness equal to 75 mg L<sup>-1</sup> CaCO<sub>3</sub> from 1.23 km to the confluence with James Creek. For the June 17 sampling event, standards for hardness equal to 50 mgL<sup>-1</sup> CaCO<sub>3</sub> were applied to sites located at 0 to 1.18 km, and for hardness equal to 150 mg L<sup>-1</sup> CaCO<sub>3</sub> from 1.23 km to the confluence with James Creek.

### Little James Creek iron

During the April 22 sampling event, total and dissolved iron concentrations remained low and within a small range of values across the entire stream reach, with an average total concentration of 751  $\mu$ g L<sup>-1</sup>, ranging from 367  $\mu$ g L<sup>-1</sup> at the most upstream site to 1334  $\mu$ g L<sup>-1</sup> at 1.34 km (Figure 34). An average of 11% of total iron was present as dissolved species. A concentration and loading increase, primarily in total iron, was measured following the Balarat Creek inflow at 1.34 km. Additionally, a spike in

dissolved iron loads was observed at 1.83 km. The Emmett adit, Balarat Creek, and the unnamed tributary at 1.96 km all showed high total and dissolved iron concentrations, with concentrations at the Emmett adit roughly 200 times greater than instream concentrations. Average total and dissolved iron concentrations were lower during the June 22 sampling (Figure 33), ranging from 39  $\mu$ g L<sup>-1</sup> at 0.81 km to 830  $\mu$ g L<sup>-1</sup> at1.55 km; however, the percentage of dissolved iron increased to 47%. Total iron concentration spikes occurred at 1.1 km and 2.76 km, while increases in both total and dissolved concentrations and loads occurred downstream of Balarat Creek at 1.34 km and near an unnamed mine waste pile at 1.55 km.

### Little James Creek aluminum

During both April and June sampling events (Figures 36 and 37), total and dissolved aluminum concentrations and loads remain low until 1.34 km. just downstream of the Balarat Creek inflow. Total aluminum concentrations consisted of 46% and 82% dissolved aluminum species in April and June, respectively. In both tests, the percentage of dissolved aluminum increased immediately downstream of the Balarat Creek inflow. Total aluminum concentrations measured in April ranged from 520 µg L<sup>-1</sup> at 0.81 km to 5,300  $\mu$ g L<sup>-1</sup> at 2.11 km, while total concentrations in June ranged from 270  $\mu$ g L<sup>-1</sup> at 0.81 km to 10,700 µg L<sup>-1</sup> at 2.11 km. During April sampling, the Emmett adit discharge and Balarat Creek total and dissolved concentrations were much higher than instream concentrations, at 102,000  $\mu$ g L<sup>-1</sup> and 14,000  $\mu$ g L<sup>-1</sup>, respectively. All other tributary concentrations fit instream concentration and load values. During June sampling, the Emmett adit discharge concentrations decreased from April measurements, with a total aluminum concentration of 99,000  $\mu$ g L<sup>1</sup>, while the total aluminum concentration in Balarat Creek increased to 19,000 µg L<sup>-1</sup>. During both sampling events, total and dissolved loads increased downstream of the Balarat Creek confluence at 1.34 km, and again at the unnamed mine waste pile near 1.55 km. Loads continued to increase over the remainder of the stream reach. Dissolved aluminum concentrations at every sample site, and from both the April and June tests, exceeded chronic aquatic life parameter. Twenty-four of those sites also exceeded the acute parameter during both tests. All acute parameter exceedances occurred from 1.23 km to the end of the stream reach at the confluence with James Creek.



**Figure 31.** Little James Creek stream flow sampled during high and low flow conditions on April 22, 2003 (a) and June 17, 2003 (b).



**Figure 32.** Calculated stream flow and lithium concentrations measured in Little James Creek on June 17, 2003. The data in the box did not follow the expected inverse relationship of stream flow- to- tracer. Sampling error is suspected, and the data was not used in discharge calculations.



**Figure 33.** Little James Creek pH (a), as measured in the lab on June 17, 2003. Hardness (b) was calculated at the sum of total calcium and magnesium ions for samples collected on April 22, 2003 and June 17, 2003.


Figure 34. Little James Creek and tributary iron concentrations and loads sampled on April 22, 2003.



Figure 35. Little James Creek and tributary total and dissolved iron concentrations and loads sampled on June 17, 2003.



2003.



**Figure 37.** Little James Creek and tributary total and dissolved aluminum concentrations and loads sampled on June 17, 2003.

#### *Little James Creek manganese*

Both April and June sampling events show that the dissolved manganese fraction accounted for an average of 100% of total concentrations (Figures 38 and 39). Total manganese measured in April was below the detection limit at seven sites located from 0-1.10 km, increasing to a maximum value of 840  $\mu$ g L<sup>-1</sup> at 1.83 km. Total concentrations measured in June ranged from below the detection limit at 1.10 km to 2,500  $\mu$ g L<sup>-1</sup> at 1.83 km. During both tests, manganese increases occurred downstream of the Balarat Creek confluence at 1.34 km and at 1.83 km. The Emmett adit and Balarat Creek exhibited the highest total and dissolved manganese concentrations sampled. Tributary total concentrations showed some variance between the two sampling events, with the Emmett adit increasing from 130,000 µg L<sup>1</sup> in April to 140,000 µg L<sup>1</sup> in June, and Balarat Creek increasing from 2,200  $\mu$ g L<sup>1</sup> to 3,400  $\mu$ g L<sup>1</sup>. Due to their low discharges relative to Little James Creek, the load contributions of the Emmett adit and Balarat Creek were low in April. The high load calculated for the Emmett adit in June was higher than adjacent instream load increases. Little James Creek instream loads increased at 1.34 km, and again at 1.55 km during both sampling events. No CDPHE

aquatic life criteria violations were observed in April; however, eight sites, located from 1.40 to 1.91 km, exceeded chronic aquatic life criteria in June.

## Little James Creek zinc

Like manganese, an average of 100% of total zinc was present as dissolved species during both April and June sampling events (Figures 40 and 41). April total zinc concentrations ranged from below the detection limit of 5  $\mu$ g L<sup>-1</sup> at 0 km and 0.33 km to 306  $\mu$ g L<sup>-1</sup> at 2.47 km, while June values ranged from a low of 91  $\mu$ g L<sup>1</sup> at 0 km to 650  $\mu$ g L<sup>1</sup> at 2.41 km. During both tests, zinc concentrations and loads increased at downstream of Balarat Creek at 1.34 km. Total and dissolved zinc loads increased again beginning at 1.55 km, near an unnamed mine waste pile. Again, the Emmett adit and Balarat Creek exhibited the highest total and dissolved concentrations in both the April and June sampling events. Total zinc concentrations measured in the Emmett adit flow increased from 17,000 µg L<sup>-</sup> <sup>1</sup> in April to 18,000 µg L<sup>-1</sup> in June, and Balarat Creek total zinc concentrations increased from 640  $\mu$ g L<sup>-1</sup> to 870  $\mu$ g L<sup>-1</sup>. Due to their lowdischarges relative to Little James Creek, the load contributions of the Emmett adit and Balarat Creek were low in April. The high load calculated for the Emmett adit in June exceeded adjacent instream load increases. At a hardness of 25 mg L<sup>-1</sup> CaCO<sub>3</sub>, chronic and aquatic life standards for zinc are equal. Twenty-three sites. located from 1.34 km to the



**Figure 38.** Little James Creek and tributary total and dissolved manganese concentrations and loads sampled on April 22, 2003.



**Figure 39.** Little James Creek and tributary total and dissolved manganese concentrations and loads sampled on June 17, 2003.

confluence with James Creek, exceeded aquatic life criteria during the April sampling event. All 33 sites sampled exceeded chronic and acute criteria in June.

#### Little James Creek copper

Dissolved and total copper concentrations measured during both the April and June sampling events followed a similar pattern of increases and spikes, with dissolved copper making up and average of 61% of total copper in April (Figure 42), and 81% in June (Figure 43). During April and June testing, copper concentrations and loads gradually increased from 0.43-1.83 km, with concentration spikes at 1.34 km and 1.83 km. Total copper concentrations measured in April ranged from 3.2 µg L<sup>-1</sup> at 0.33 km to 34 µg L<sup>-1</sup> at 1.83 km. Total copper concentrations measured in June ranged from 16  $\mu$ g L<sup>-1</sup> at 0.81 km to 41  $\mu$ g L<sup>-1</sup> at 1.47 km. In both sampling events, the Emmett adit showed the highest tributary total copper concentrations, at 3,000  $\mu$ g L<sup>-1</sup> in April and 130  $\mu$ g L<sup>-1</sup> in June. The unnamed tributaries at 1.96 km and 2.41 km were dry during the June sampling event, but showed high concentrations in April, with total copper measured at 106  $\mu$ g L<sup>-1</sup> and 62  $\mu$ g L<sup>-1</sup> <sup>1</sup>, respectively. Balarat Creek concentrations matched instream values during both sampling events. Dissolved copper made up 100% of total copper in the Emmett adit, Balarat Creek, and the 1.96 km tributary, but was 42% of the total in the 2.41 km tributary. During April and June sampling, 33 sites, located from 0.43 km to the downstream confluence with James Creek, exceeded chronic aquatic life criteria for copper. Thirty of these sites, beginning at 0.68 km, also exceeded acute standards in April and June.

## Little James Creek lead

Locations of total and dissolved lead concentration and load increases varied significantly between the April and June sampling events. In April (Figure 44), total lead concentrations averaged 16  $\mu$ g L<sup>-1</sup>, ranging from 0.8  $\mu$ g  $L^{-1}$  at 0.33 km to 29 µg  $L^{-1}$  at 1.34 km. April dissolved lead concentrations show little change along the stream reach and average only 18% of total instream lead, indicating that lead enters the stream primarily as colloidal species. Lead concentrations increase at 0.89 km near the Argo mine site, and again at 1.34 km, just downstream of the Balarat Creek inflow. Most of the increase is in total lead, suggesting colloidal sources; however, dissolved lead concentrations also increase slightly at the same distances. Lead concentrations remain generally steady for the remainder of the stream reach. Total and dissolved lead loads follow the pattern of concentration variations, with increases at 0.89 km and 1.34 km. Total lead loads gradually increase downstream of 1.34 km. Total and dissolved lead concentrations were highest in Balarat Creek, with total lead equal to 74  $\mu$ g L<sup>1</sup> (50% dissolved). The Emmett adit total lead concentration equaled 56 µg L<sup>-1</sup> (100% dissolved).



At the hardness values found in the stream, CDPHE acute and chronic standards for zinc are nearly the same.



**Figure 41.** Little James Creek and tributary total an dissolved zinc concentrations and loads sampled on June 17, 2003. At the hardness values found in the stream, CDPHE acute and chronic standards for zinc are nearly the same.



**Figure 42.** Little James Creek and tributary total and dissolved copper concentrations and loads sampled on April 22, 2003.



Figure 43. Little James Creek and tributary total and dissolved concentrations and loads sampled on June 17, 2003.

The unnamed tributary at 1.96 km was also higher than instream concentrations, at 25  $\mu$ g L<sup>-1</sup> (72% dissolved). Due to their low flows, these tributaries all carried small loads. Dissolved lead concentrations exceeded chronic aquatic life standards at 30 sites during the April sampling event. These sites were located at 0.43 km and from the Argo mine area at 0.89 km to the downstream confluence with James Creek.

Total lead concentrations measured in June ranged from 1.1  $\mu$ g L<sup>1</sup> at 0.77 km to 68  $\mu$ g L<sup>-1</sup> at 1.40 km, with 66% of lead present in the dissolved form (Figure 45). Increases in total and dissolved lead concentrations and loads begin near the Argo mine at 0.81 km, with a spike in total lead near the Burlington mine at 1.10 km. Total and dissolved concentrations increase again at 1.34 km, and remain high until 1.73 km. Dissolved concentrations equaled 100% of total lead in both the Balarat Creek and the Emmett adit flow, with total lead concentrations of 110  $\mu$ g L<sup>-1</sup> and 60  $\mu$ g L<sup>-1</sup>, respectively. Dissolved lead concentrations exceeded chronic aquatic life criteria at 30 sites during June sampling. All exceedances occurred from 0.81 km to confluence with James Creek.

## *Little James Creek stream bed sediments*

In the Little James Creek study reach, iron (Figure 46a) and aluminum (Figure 46b) concentrations followed similar spatial patterns. The largest spikes in concentrations of both iron and aluminum occurred at the end of the stream reach, near Bueno Mountain. Aluminum concentrations also showed lesser peaks near the mine waste rock piles at 0.68 km and at 2.42 km near the base of the streamside tailings and the inflow from the "Bueno Mountain gully".

Manganese (Figure 47a), zinc (Figure 47b), copper (Figure 48a), and lead (Figure 48b) sediment concentrations peaked at multiple, often corresponding, sites along the stream. Manganese, zinc, and copper concentrations show a similar pattern, with spikes near the Balarat Creek inflow, near the unidentified source at 1.83 km, and in the area of the streamside tailings and Bueno Mountain. Zinc and copper also show relatively high sediment concentrations in the upper portions of the study reach near the unnamed waste rock pile and the Argo mine workings. Sediment lead concentrations also increased downstream of the Argo mine, the Balarat Creek inflow, and the unidentified source at 1.83 km. The largest lead spike occurred just downstream of the streamside tailings and Bueno Mountain area.



Figure 44. Little James Creek and tributary total and dissolved lead concentrations and loads sampled on April 22, 2003.



Figure 45. Little James Creek and tributary total and dissolved lead concentrations and loads sampled on June 17, 2003.



Figure 46. Little James Creek total iron (a) and aluminum (b) sediment metal concentrations.



Figure 47. Little James Creek total manganese (a) and zinc (b) sediment metal concentrations.



Figure 48. Little James Creek total copper (a) and lead (b) sediment metal concentrations

#### Summary of Little James Creek stream metal and acidity sources

Table 7 shows the cumulative total metal load contributions for sites located along the Little James Creek. The stream water and stream bed sediment data identifies Balarat Creek as a primary dissolved and colloidal metal loading source to Little James Creek during both high and low flow conditions for iron, aluminum, manganese, zinc, copper, and lead. Although the Emmett adit drainage exhibited extremely high dissolved metal concentrations, the small flow of this stream prevented high loading contributions even during high flow sampling. Lead and copper loads increase downstream of the Argo mine site, and low flow data point toward a source of colloidal iron, copper, and lead at 1.10 km. Subsurface inputs of dissolved and total iron, aluminum, manganese, zinc, and copper loading were observed near the unnamed waste rock pile at 1.55 km during both high and low flow sampling events. Spikes in all metals near 1.83 km suggest an unidentified metal source in this area. Finally, the "Bueno Mountain gully", which flows near the downstream toe of the streamside tailings waste rock pile, added to total iron, aluminum, zinc, copper, and lead when flowing during the April 22 sampling. This tributary was dry on June 17, suggesting that it is an irregular contributor to the metal loading of Little James Creek.

**Table 7.** Cumulative metal loading contributions to Little James Creek under high and low stream flow conditions. Loads were determined with metal loading tracer dilution tests and synoptic sampling on April 22, 2003 and June 17, 2003.

Source	Distance (km)	April Fe (%)	June Fe (%)	April Al (%)	June Al (%)	April Mn (%)	June Mn (%)	April Zn (%)	June Zn (%)	April Cu (%)	June Cu (%)	April Pb (%)	June Pb (%)
Undetermined source	0.37—0.64	6.8		3.1		< 1		2.3		5.4		1.0	
"Argo gully"	0.77—0.89	4.9	2.2	3.8	1.7	< 1	< 1	1.8	8.8	3.6	12.8	5.2	13.6
Emmett adit	1.18—1.23	< 1	11.7	1.1	27.4	1.0	13.4	1.1	18.7	< 1	17.1	< 1	4.8
Balarat Creek	1.23—1.34	30.4	58.3	20.1	64.1	23.9	86.3	17.6	61.0	16.0	37.2	20.5	62.7
Unnamed mine waste rock pile	1.55—1.83	11.2		31.8		42.8		31.1		32.8		12.5	
Unnamed tributary	1.85—1.91	< 1		9.3		2.4		9.4		3.7		2.2	
Streamside tailings and "Bueno Mountain gully"	2.36—2.41	6.4		9.4		6.1		5.5		6.1		9.8	
Subsurface inflow	2.59—2.68	2.2		4.6		8.1		8.4		8.1		8.5	
Subsurface inflow	2.76-2.87	20.7		9.4		8.7		10.2		9.8		34.8	

#### DISCUSSION

As shown by this study and others (e.g., Kimball *et al.*, 1995; 2001a), tracer dilution studies and synoptic sampling methods are reliable and efficient tools for characterization of watersheds with complex hydrology, mineralogy, and mining impacts. When possible, sampling at temporally, as well as spatially, frequent intervals provides a more complete picture of mining-related sources and their impacts. Tracer dilution studies and synoptic sampling are useful for both preliminary watershed characterization and ongoing monitoring of the effectiveness of reclamation projects.

The average cost of performing tracer dilution stream flow tests and synoptic sampling on Lefthand, James, and Little James Creek was approximately \$1000.00 per stream kilometer. This estimate is based on an average sample site spacing of 50 m, and includes the costs of chemicals, field equipment, and labor. This estimate also includes the costs of ICP-MS and ICP-AES analysis of monitoring and synoptic site samples for iron, aluminum, manganese, zinc, copper, lead, and lithium. This cost estimate does not include data analysis. The average cost per kilometer of stream will vary according to the frequency of synoptic sample sites, cost of labor, the number of analytes measured, and the technique used to measure these analytes.

Analysis of tracer dilution stream flow data provided information about the locations and magnitudes of surface and subsurface water inflows to Lefthand, James, and Little James Creeks. Instream changes in metal loads detected the locations and magnitudes of metal inputs to the streams. Finally, changes in stream chemistry— including metal concentrations, acidity, and hardness-- relate to the toxic effects of metals on stream biota and to the attenuation and transport of metals in the stream system.

## Stream flow

Stream flow rates measured by tracer dilution compared favorably with staff gage measurements of flow rate. Lefthand Creek average daily stream flow recorded on June 12, 2003, at a gage located at 40<sup>o</sup> 7' 32" 105<sup>o</sup> 18' 14" was 1,490 L s<sup>-1</sup> (*personal communication*, Hank Schmidt, Left Hand Water District, March 15, 2004), which was 19% lower than the stream flow of 1,830 L s<sup>-1</sup> measured with the lithium chloride tracer at the same site on the same date. Stream flow sampled at a staff gage on James Creek in Jamestown operated by the James Creek Watershed Initiative was measured at 990 L s<sup>-1</sup> on June 27, 2002 (Colorado River Watch, 2004). Stream flow at this site measured five days later with the sodium chloride tracer was 11% lower, at 880 L s<sup>-1</sup>. Discharge at the South St. Vrain Creek diversion to James Creek was 940 L s<sup>-1</sup> on June 27, 2002 (CDWR, 2002). Discharge from the diversion had decreased by 21% to 740 L s<sup>-1</sup> on July 2, 2002. The lower instream flow measured with tracer dilution on July 2 reflects the water diversion decrease.

Through comparison of current meter and tracer-dilution stream flow measurements, Zellweger *et al.* (1989) found that up to 25% of channel discharge in a small gravel-bed stream traveled as underflow through gravel in the hyporheic zone of the stream channel. The lithium chloride tracer data collected on June 12, 2003, indicates that approximately 19% of flow in this region of Lefthand Creek may be attributable to hyporheic flow. Variation in stream flow at that site may also be due to the comparison of an average of stream flow values collected over the period of one day with the stream flow at a single instant in time obtained with the tracer-dilution method. The lower flow in James Creek determined with the tracer dilution method on July 2, 2002, reflects the decrease in flow from the South St. Vrain diversion, as well as hyporheic zone flow that is not captured by the stream gage measurement.

Significant stream flow variations over short time periods are common in streams fed by high mountain snowmelt, particularly in the spring snowmelt period. Additionally, anthropogenic flow variations result from the management of stream water via reservoirs and diversion ditches. Anthropogenic stream flow manipulation plays an important role in the James and Lefthand Creek systems. On Lefthand Creek, controlled flow releases from the Left Hand Park Reservoir and Lake Isabelle, both located in the upper area of the watershed west of Highway 72, and the Gold Lake reservoir, which enters Lefthand Creek via Spring Gulch, affect downstream flow. Water releases from these reservoirs occurred in August, September, and October 2003 (Plummer, 2004), which did not correspond to the timing of tracer dilution and synoptic sample data presented here. Comparison of diversion stream flow data (CDWR, 2002) with staff gage data (Colorado River Watch, 2004) show that the diversion of water from the South St. Vrain Creek to James Creek added nearly the entire James Creek flow in June and July of 2002.

## Metal loadings and contaminant sources

The metal concentration and stream flow data collected from over 300 sample sites along nearly 45 km of stream provided information necessary to compare metal loading contributions for dozens of potentially contaminating mine sites. This spatially detailed data identifies stream reaches where metals enter the stream system, and allows for the comparison of the magnitude of metal contributions from mine sites (Kimball, 1997).

Along Lefthand Creek, inflow from the pyritic Dew Drop Mine and Big Five Mine Tunnel areas added the most upstream pH decreases and zinc and copper concentration increases, leading to the initial excedances of zinc and copper aquatic life water quality criteria. Total lead concentrations increased by nearly 400% in the 100 m downstream of the White Raven site, pointing toward the prevalence of lead sulfide minerals in the White Raven vein. Once the largest lead and silver ore producer in Boulder County, the silver-lead ore produced at this site ranged from 10 to 15% lead. Total zinc increases in this area reflect the presence of the zinc sulfide mineral sphalerite in the White Raven vein (Shea, 1988). Dispersed metal loading sources exist over the 18 km from the base of California Gulch to the inflow of James Creek, including the Tuscarora Gulch inflow and unidentified sources located from 4.35 to 8.96 km. At 19.48 km, at the inflow of an intermittent tributary draining Lee Hill, the highest relative total aluminum, manganese, zinc, and lead load increases were observed. Metal concentrations and loads in the tributary did not match instream increases, and the origin of metal increases in this area is uncertain. No significant metal loading sources were observed in the 10 km downstream of the James Creek confluence with Lefthand Creek.

In James Creek, surface flow from the Fairday Mine and subsurface inflows draining Bueno Mountain add the greatest metal loads to the stream. An unidentified source added the greatest cumulative percent of total zinc to James Creek between 2.62 and 2.80 km. Additional load contributions were added by Little James Creek and dispersed sources near the James Creek confluence with Lefthand Creek. Due to the low stream flow conditions at the time of sampling James Creek, loading results may underestimate the relative loads of sites located along James Creek.

Metal loading contributions and zinc and copper aquatic life criteria exceedences in Little James Creek begin at an unidentified source located between 0.37 and 0.64 km. Flow from the Argo Mine area added to metal loads. Inflows near the Emmett Adit mine water drainage and Balarat Creek were important metal loading contributors. The greatest increases occurred downstream of the Balarat Creek inflow; however, exact determination of the individual subsurface contributions of these sources is difficult due to their close proximity. Subsurface inflows from the unnamed mine waste pile near 1.55 km added the largest metal loads to Little James Creek during April sampling. This site also appeared to be a significant metal contributor in June; however, incomplete stream flow data prevented calculation of June load contributions at this site. Likewise, inflows from the Bueno Mountain area near the Streamside Tailings and from an unidentified source between 2.59 and 2.68 km added to instream metal loads during high flows, but were not measured during June sampling.

Tests of Little James Creek and the California Gulch segment of Lefthand Creek during high and low stream flow conditions demonstrated the lowest instream metal concentrations and greatest metal loads during spring high flow conditions. Conversely, the lowest metal loads, but highest concentrations and most frequent aquatic life criteria violations, occurred during low stream flow. These results suggest that inflows of snowmelt dilute instream metal concentrations, but add to the stream flow and thereby increase the total mass loading of metals to the stream (Caruso and Ward, 1998). Brooks *et al.* (2001) found a snowmelt-driven increase in zinc concentrations in mining-impacted stream reaches, resulting from flushing of zinc from mine workings. A brief, initial flush of metals may also occur in mined areas of the Lefthand Creek watershed; however, this effect was not observed at the times of sampling.

#### Metal speciation and partitioning

The interactions of colloids with metals in stream systems impacted by acid mine drainage influences the mobility, transport, and attenuation of metals in streams and stream bed sediments (Stumm and Morgan, 1981). Metal speciation and partitioning in waters influenced by acid mine drainage depend on intrinsic characteristics of the metals and external factors such as local mineralogy, pH, hardness, and stream flow. Stream pH drives chemical processes, influencing metal solubility and sorption onto mineral and organic surfaces. Hardness (calcium and magnesium) competes with metals for binding sites. Stream, tributary, and subsurface flow rates determine metal loads and dilution, and influence reaction kinetics and attenuation of metals in stream beds and the hyporheic zone.

Oxides and hydroxides of iron, aluminum, and manganese are the dominant metal sorbents in natural systems (Dzombak and Morel, 1990); iron and aluminum colloids have been identified as key transporters of zinc, copper, lead, and other tracer metals in Colorado stream systems impacted by acid mine drainage (Kimball *et al.*, 1995; Schemel *et al.*, 2000; Munk *et al.*, 2002). In particular, the high specific surface area of iron hydroxides, their strong interactions with metal ions, and their prevalence in acid mine drainage systems makes sorption to iron oxyhydroxides a key mechanism in attenuation of dissolved metals in streams (Younger *et al.*, 2002). Kimball *et al.* (1994; 1995) found that hydrous iron and aluminum oxides precipitate and aggregate to form colloids when acidic iron- and aluminum-rich mine waters flow into higher pH streams. These colloids settle to the stream bed and form the common orange and white stream bed coatings observed in streams impacted by acid mine drainage.

The partitioning of metals between dissolved and colloidal phases can be examined in terms of distribution coefficients—conditional constants valid for a particular pH, temperature, and other external conditions which describe metal partitioning (Stumm, 1992). The observed distribution coefficient ( $K_D^{observed}$ ), as defined by Stumm (1992), requires measured colloidal masses, which were not obtained in this study. As a proxy for distribution coefficients, colloidal fractions ( $f_{coll}$ ) were defined as

$$f_{coll} = \frac{C_{colloid}}{C_{total}}$$

where *C* refers to concentration, and

$$C_{colloid} = C_{total} - C_{dissolved}$$

Comparison of the colloidal fraction of metals demonstrates spatial and seasonal variations in metal partitioning in Lefthand, James, and Little James Creek (Figure 49). Similar to the data presented here, Kimball *et al.* (1995) found clear partitioning trends among individual metals in the acid mine drainage-impacted upper Arkansas River in Colorado, such as the presence of iron primarily in the colloidal fraction. The consistently high colloidal concentrations of iron and aluminum in all of the stream reaches sampled suggest the occurrence of these metals as colloidal hydrous oxides under the spectrum of stream flow and chemical conditions present in the Lefthand Creek watershed.

The trends of zinc, copper, and lead colloidal partitioning observed in all of the stream reaches sampled reflect the surface complexation constants (K<sup>int</sup>) of these metals (Table 8). As suggested by its relatively low K<sup>int</sup> value and noted by many researchers (e.g. Dzombak and Morel, 1990; Fey *et al.*, 1999; Kimball *et al.* 1995; Schemel *et al.*, 2000; Munk *et al.*2002), partitioning of zinc to the colloidal phase occurs less readily than copper and lead colloidal partitioning (Figure 50).

Although manganese has the lowest K<sup>int</sup>, this metal exhibited varying tendencies to exist as dissolved or colloidal species, present in primarily the colloidal fraction in the high flow, low acidity reaches of Lefthand and James Creek, but as primarily dissolved species in the lower flow, acidic stream waters of Little James Creek and the California Gulch segment of Lefthand Creek. Kimball *et al.* (1995) also found increases in colloidal iron, aluminum, manganese, zinc, copper, and lead loads during high flow, likely resulting from re-suspension of iron colloids settled onto bed sediments. Eyrolle and Charmasson (2004) also found a stream flow rate dependency for iron and aluminum partitioning.

**Table 8.** Intrinsic acidity constants for manganese, zinc, copper, and lead as reported by Dzombak and Morel (1990).

	Mn <sup>2+</sup>	<b>Zn</b> <sup>2+</sup>	Cu <sup>2+</sup>	<b>Pb</b> <sup>2+</sup>
Log K <sup>int</sup>	-0.4	0.99	2.89	4.65



**Figure 49.** The average instream colloidal fraction of metals in Lefthand, James, and Little James Creek. Colloidal fractions measured in Little James Creek at high (April 2003) and low (June 2003) flows and California Gulch segment of Lefthand Creek at high (May 2003) and low (November 2003) are shown.



**Figure 50.** The average colloidal fractions of Mn, Zn, Cu, and Pb compared to the intrinsic surface complexation constant for each metal. Zn, Cu, and Pb show a consistent order with respect to each other. Mn showed no consistent behavior, which may be due to its occurrence as Mn oxide colloids in some stream segments.

## Stream pH and metal partitioning

The sorption of metals onto hydrous oxides depends upon stream water conditions, particularly the pH of the stream. The sorption process involves the bonding of metal cations to surface hydroxyl functional groups, which releases protons. This reaction of metal cations with surface hydroxyls explains the strong pH dependence of sorption reactions (Dzombak and Morel, 1990). As stream pH decreases, protons compete with metal cations for binding sites on surface hydroxyls. As stream acidity decreases, cation sorption onto hydrous oxides increases from 0 to 100% over a range of only a few pH units (Dzombak and Morel, 1990; Davis and Kent, 1990). The data collected in Lefthand, James, and Little James Creeks and their tributaries follow this trend. In the water discharging from the Big Five Tunnel (pH 3.93 on May 21, 2003), metals were present predominantly in the dissolved fraction. In Lefthand Creek below the Big Five Tunnel tributary confluence (pH 6.5), the colloidal fraction of metals increased. Similarly, Balarat Creek had a lower pH and greater abundance of dissolved metals than did Little James Creek.

Examining the colloidal fraction of metals as a function of the pH values found in the stream shows a general trend of Zn < Cu < Pb in the colloidal fraction, as expected according to the surface complexation constants (K<sup>int</sup>) discussed above (Figures 51 and 52). Again, manganese partitioning patterns varied between stream reaches. Lefthand and Little James Creeks showed generally consistent distributions of the colloidal fractions of manganese, zinc, copper, and lead. Relative colloidal partitioning of these metals as a function of pH in James Creek was more variable, which suggests colloidal metal partitioning in James Creek is influenced by direct colloidal inputs or stream chemical parameters other than pH, such as hardness.

Comparison of seasonal differences in colloidal fractions of metals in the California Gulch segment of Lefthand Creek (Figure 52) shows regular colloidal metal partitioning patterns for zinc, copper, and lead during high and low stream flow conditions. Manganese during both high and low stream flow sampling varied with pH, and showed no regular pattern. The colloidal fractions of manganese and zinc were lower during November sampling. During low flow conditions Lefthand Creek receives less infiltration of low-acidity snowmelt and rainfall, which leads to generally lower instream pH values. Higher instream acidity increases competition for binding sites, causing dissolved metals to stay in solution. Furthermore, a decrease in pH may re-dissolve soluble metals such as manganese and zinc that precipitated or sorbed to colloidal surfaces during periods of higher, less acidic flow conditions (Caruso and Ward, 1998).



**Figure 51.** The colloidal fractions of Mn, Zn, Cu, and Pb as related to stream acidity in Lefthand, James Creeks, and Little James Creeks.



**Figure 52.** The colloidal fraction of Mn, Zn, Cu, and Pb as related to stream acidity measured in the California Gulch segment of Lefthand Creek during high (May 2003) and low (November 2003) stream flow conditions. The circled area highlights lower acidity reference sites and a mixing zone downstream of a mine-impacted inflow.

During May sampling, the colloidal fractions of zinc, copper, and lead decrease sharply at a pH of 6, while colloidal fractions of manganese increase at this pH. These sites correspond to synoptic sample locations located in from 0 to 0.68 km, which includes reference sites and a mixing zone downstream of dissolved and colloidal inputs from the "Dew Drop Mine" tributary. These sites were not sampled in November.

# Stream hardness and metal partitioning

Stream water hardness indicates the complexing capacity of the water and, indirectly, the effective toxicity of metals in the system (CDPHE, 2001). Hardness serves as a general marker of stream toxicity potential; the actual effects of hardness on aquatic life may be related to the ions causing hardness or associated alkalinity (EPA, 2002). Hardness was measured as the sum of total calcium and magnesium concentrations, and was compared to colloidal partitioning of manganese, zinc, copper, and lead (Figure 53). Divalent cations, which are abundant in natural systems, compete with dissolved metals for surface binding sites on hydrous oxides and other solids, including biological tissues. This competition influences weaker-binding metals such as zinc more than stronger-binding metals, such as lead.

Figure 53 shows that a generally consistent ratio of zinc, copper, and lead colloidal fractions holds as a function of hardness. Again, manganese partitioning varies between the stream reaches. Comparison of seasonal variations in Little James Creek and the California Gulch segment of Lefthand Creek shows that hardness increased and the colloidal fractions of manganese, zinc, copper, and lead decreased during low flow in both stream reaches. Little James Creek showed the highest instream hardness values in the watershed, the result of calcium-rich rock formations in the area. Hardness in Little James Creek nearly doubled during low flow, corresponding to a nearly 50% decrease in the colloidal fraction of copper and lead. Manganese and zinc, which show a stronger pH dependency, were present nearly entirely as dissolved species in Little James Creek during both sampling events.

In the California Gulch segment of Lefthand Creek, synoptic sample sites located upstream of the Big Five Mine Tunnel inflow showed the lowest hardness (< 15 mg L<sup>-1</sup> CaCO<sub>3</sub> in May and < 20 mg L<sup>-1</sup> CaCO<sub>3</sub> in June). Manganese occurred in high colloidal fractions at these sites, while zinc, copper, and lead occurred primarily as dissolved species. Downstream of the Big Five Mine Tunnel inflow, the colloidal fraction of manganese decreases, while the colloidal fractions of zinc, copper, and lead increase. This colloidal fraction decrease for manganese reflects surface complexation site competition from both increased hardness and decreased pH. The increase in colloidal zinc, copper, and lead, which bind more strongly than manganese,



**Figure 53.** Colloidal fraction of Mn, Zn, Cu, and Pb in Lefthand Creek, Little James Creek, and the California Gulch segment of Lefthand Creek.

may indicate the increased availability of complexation sites on iron and aluminum oxyhydroxide surfaces input from the Big Five Mine Tunnel drainage. Examination of metal partitioning in Little James Creek and Lefthand Creek under varying flow conditions suggests that pH and hardness, as well as the availability of surface binding sites (Schemel *et al.*, 2000), influence metal partitioning. In Little James Creek, stream pH appears to have the greatest influence over manganese and zinc partitioning, while hardness showed a greater influence on copper and lead partitioning. In the California Gulch segment of Lefthand Creek, pH and availability of colloidal binding surfaces may have a greater influence than hardness on partitioning of all four metals studied.

## Stream bed sediment metals

Colloids in stream systems, which may be complexed with toxic metals, aggregate and settle onto stream bed sediments. Additionally, metal cations may sorb directly onto bed sediments. These two situations pose different scenarios of the kinetics of metal attenuation. The case of colloidal sorption or aggregation within the water column suggests a two-step process involving chemical kinetics related to sorption and physical kinetics involved with particle settling. In the second case, only chemical kinetics drive the attenuation of metals directly onto bed sediments. Church et al. (1997) found that the colloidal components of the bed sediments dominate stream bed sediment chemistry. In agreement with the patterns of metal colloidal partitioning discussed above, the ratios of stream bed sediment metal concentrations to water column colloidal and dissolved metal concentrations show general trends of colloidal metal partitioning, indicating that colloidalphase lead dominates, copper shows intermediate behavior, and dissolvedphase zinc and manganese dominate (Figures 54 and 55). Figures 18 to 20 and 45 to 47 from Results show that lead is removed from the water solution to solid surfaces within a short distance from the metal source. Copper, zinc, and manganese, which show more pH dependence and tend to remain in solution, travel farther from the metal source before incorporating into bed sediments. Similarly, stream bed sediment analyses by Church et al. (1997), Fey et al. (1999), and Hudson-Edwards et al. (2003) found that zinc shows the greatest mobility downstream of mining sources, copper travels an intermediate distance, and lead partitions to bed sediments within a short distance of the metal source.



**Figure 54.** The relationship of stream bed sediment metal concentrations to dissolved and colloidal water concentrations in Little James Creek. Solid squares represent colloidal metal concentrations, while open squares represent dissolved metal concentrations.



**Figure 55.** The relationship of stream bed sediment metal concentrations to dissolved and colloidal water concentrations in the California Gulch segment of Lefthand Creek. Solid squares represent colloidal metal concentrations, while open squares represent dissolved metal concentrations.

## SITE RANKING AND REMEDIATION PRIORITIZATION

A diverse collection of stakeholders in watershed decisions bring an equally diverse set of experiences, background knowledge, and desired outcomes to the table when discussing watershed issues. Complex ownership and land use histories, distrust of government agencies, differences in understanding of technical issues, and social or historical ties with the benefits of the legacy of mining are examples of just a few other issues that further complicate unified decision-making. Similar to other areas, the Lefthand Creek watershed also hosts a dissimilar set of residents, landowners, and other stakeholders varying from weekend hikers and offhighway vehicle recreationalists to long-term residents and former mine operators. Mine remediation-related issues in the Lefthand Creek watershed may also be confounded by the fact that the vast majority of potable water consumers who are most at risk from toxic metal pollution-the 14,000 customers of the Left Hand Water District—live east of the contamination sources and frequently have little to no knowledge of or direct experience Although reaching agreement among diverse with the mine sites. stakeholders poses many challenges, a vast array of sources maintain that watershed remediation plans which are implemented through broad community consensus have the greatest potential for attaining long-lasting remediation successes (for example, Center for Watershed Protection, 1998; Kenney et al., 2000; EPA, 1995b; 1997b; 2001). Because of the scientific nature of metals pollution, and in an effort to avoid potential conflicts of interest, prioritization of mine sites in the Lefthand Creek watershed for remedial actions requires a strong scientific basis that takes into account CDPHE standard violations and metal loading inputs. Once sites are prioritized, development and implementation of reclamation plans necessitates a careful balance of both scientific information and community interests.

The EPA and multiple other regulatory agencies, governments, and watershed organizations recognize the challenges inherent in site prioritization. Appendix F of the EPA's National Hardrock Mining Framework (1997) states,

"Establishing priorities that will guide remediation efforts leading to environmental improvement is one of the most important challenges facing regulatory authorities as well as interested stakeholders...we must develop a process that ensures that our efforts go to areas and sites that will yield the greatest benefits in the most cost-effective manner."

The Framework lists the following criteria to consider and evaluate when setting priorities:

- Extent and type of environmental and human health risk.
- Total administrative and mitigation costs.
- Technical feasibility.
- Cost-effectiveness of activity.
- Partnership potential.
- Source of funds.
- Ownership.
- Institutional capabilities.

The Framework identifies and describes multiple examples of ranking methods pertinent to abandoned mine land remediation, including the Montana Abandoned and Inactive Mines Scoring System (AIMSS), the Bureau of Mines Abandoned Mine Lands Inventory and Hazard Evaluation Handbook, the Colorado Demonstration Project Program, the Rocky Mountain Headwaters Initiative, the South Dakota Abandoned Mined Lands Inventory Act, the CERCLA Hazard Ranking System, and priority ranking under Clean Water Act §303(d). In the decade since the Framework was written, numerous other public- and private-sector ranking systems have been developed. For the purposes of this report, only two of the myriad ranking systems will be examined here: the EPA's CERCLA Hazard Ranking System (HRS), upon which many other systems are based, and priority ranking under Clean Water Act §303(d), which contrasts with the HRS system.

# The Hazard Ranking System

The EPA developed the Hazard Ranking System (HRS) as a tool to evaluate threats associated with the release or potential release of hazardous substances from a waste site, and to determine site inclusion on the CERCLA NPL (EPA, 1990). The HRS assesses existing and potential threats to human and environmental health based on four contaminant migration pathways: ground water, surface water, soil, and air. With respect to each pathway, sites are scored on three factor categories: the likelihood of release or exposure, characteristics of the contaminating waste, and targets (i.e., potential receptors of risk). Normalized site scores range from 0 to 100, and any site that scores at least 28.50 qualifies for inclusion on the NPL (EPA, 1990). Data samples and site investigations form the basis of HRS scoring; value-based scoring criteria are not included in this site prioritization method.

# Priority ranking under Clean Water Act §303(d)

Section 303(d) of the Clean Water Act, which established the state TMDL programs, requires that states take into account the severity of pollution affecting streams, as well as the relative value and benefit of the stream reach to the state (EPA, 1991). The EPA's TMDL guidance (1991) emphasizes the following key factors for states to consider when prioritizing waters with TMDLs:

- Risk to human health and aquatic life
- Degree of public interest and support
- Recreational, economic, and aesthetic importance
- Vulnerability or fragility of a particular water body as an aquatic habitat

In contrast to the HRS, priority ranking under §303(d) includes value-based factors such as the degree of public interest and support. In the case of multistakeholder decision processes, such as that employed by the LWOG, both ranking systems suggest potential, but contrasting, advantages. The databased, quantitative approach of the HRS may reduce potential conflicts among individuals who place different worth on particular sites as a result of their different uses or experiences with those sites. However, the factors of public interest, aesthetic value, and vulnerability of a site, which are included in the §303(d) system, empower stakeholders to weigh their experience, values, and ideals against hard data. The costs and benefits of employing data- or value-based approaches should be considered when developing a watershed-level priority ranking system for the Lefthand Creek watershed.

# Metal standards - and loadings-based ranking system

The stream pH, metal concentration, and metal loading data presented in this report provide a set of spatially detailed parameters that served as the foundation for a scientific, standards- and loadings- based site prioritization system. Similar to the HRS, empirical, science-based data provide the foundations for the metal standards- and loadings-based ranking system developed and applied here. This system provides a preliminary method of site comparison. Factors such as aesthetics, degree of public interest, and habitat vulnerability, which are used in the priority ranking system under §303(d) of the Clean Water Act, could be applied by interested stakeholders to further distinguish between sites receiving similar scores using the preliminary standards- and loadings-based ranking system.

Potentially contaminating sites, identified with metal loading tracer tests and synoptic sampling, located along Lefthand, James, and Little James Creeks were scored according to observed instream chronic and acute aquatic life criteria violations and according to relative cumulative dissolved metal loading contributions to the stream. Applying a simple binary scoring system (Table 9, also Appendix A), sites received a single point for each violation of chronic iron, aluminum, manganese, zinc, copper, lead, or pH aquatic life chronic exposure criteria. Sites also received a single point for each violation of aluminum, manganese, zinc, copper, and lead aquatic life acute exposure criteria. To compare dissolved metal loading contributions from each site, a point was given to each site for contribution of more than 5%, 10%, 15%, and 25% of the cumulative instream dissolved loads for iron, aluminum, manganese, zinc, copper, and lead. To correct for weighting of the scoring system towards downstream sites with higher instream stream flow and thereby higher metal loads, a single point was subtracted from sites contributing more than 5% of the cumulative instream flow. The maximum possible score was 37 points. Sites were categorized into three priority categories: low priority (0—4 points), medium priority (5—9 points), and high priority (10—37 points).

Analysis of metal loading tracer dilution tests and synoptic sampling conducted along Lefthand Creek indicated sixteen sites with potential toxic metal impacts to the stream. Only the Big Five Mine Tunnel received a high priority ranking, with a score of 16 points. Nine sites received medium priority ranking, and six sites received low priority ranking (Table 10). Of the six potentially contaminating sites identified along James Creek, three sites received high priority ranking, two sites received medium priority ranking, and one site received low priority ranking (Table 11). Of the ten potentially contaminating sites identified along Little James Creek, seven sites received high priority ranking, one site received medium priority ranking, and two sites received low priority ranking (Table 12).

	Possible Score
Exceeds chronic standards	
Fe	1
Al	1
Mn	1
Zn	1
Cu	1
Pb	1
pH	1
Exceeds acute standards	
Fe	1
Al	1
Mn	1
Zn	1
Cu	1
Pb	1
Adds over 5% of dissolved load	
Fe	1
Al	1
Mn	1
Zn	1
Cu	1
Pb	1
Adds over 10% of dissolved load	
Fe	1
Al	1
Mn	1
Zn	1
Cu	1
Pb	1
Adds over 15% of dissolved load	-
Fe	1
Al	1
Mn	1
Zn	1
	1
PD	1
Auds over 25% of dissolved load	1
<u>Fe</u>	1
Al	1
	1
	1
	1
rD Adds over 5% of stream flow	1
Auus over 570 of sueam now	1
	-1
TOTAL POSSIBLE SCODE	27
I O I AL I OBDIDLE BOOKE	51

**Table 9.** Metal standards- and loadings-based priority ranking scoring system.

**Table 10.** Potentially contaminating sites impacting Lefthand Creek, identified and ranked according to empirical metal concentration and loading data collected May--June, 2003.

\_

Source	Distance (km)	Primary contaminants of concern	Score	Priority
Hillside seep	0.46—0.61	pH, Pb	2	low
"Dew Drop mine" tributary	0.61—0.68	pH, Zn, Cu	5	medium
Big Five Mine Tunnel	1.18—1.29	pH, Zn, Cu, Pb	16	high
White Raven mine	1.55—1.71	pH, Zn, Cu	5	medium
Unnamed mine opening	1.99—2.19	pH, Zn, Cu	5	medium
Indiana Gulch	2.42—2.54	pH, Mn, Zn, Cu	2	low
Loder Smelter	2.66—3.21	pH, Zn, Cu	5	medium
Unnamed triubtary	6.98—7.19	pH, Zn, Cu, Pb	9	medium
Unidentified source	8.48-8.96	pH, Zn, Cu, Pb	7	medium
Spring Gulch	10.64— 11.43	pH., Zn, Cu, Pb	5	medium
Prussian mine waste pile	12.60— 13.01	pH, Zn, Cu, Pb	6	medium
Slide mine	13.16— 13.50	pH, Zn, Cu	6	medium
Nugget Gulch	17.9818.35	Cu, Pb	3	low
"Lee Hill" gulch	19.25— 19.48	Cu	2	low
Carnage Canyon gulch	24.14— 24.31	Al, Cu	3	low
Sixmile Creek	26.09— 26.39	Mn, Cu	3	low

**Table 11.** Potentially contaminating sites impacting James Creek, identified and ranked according to empirical metal concentration and loading data collected in July 2002.

Source	Distance (km)	Primary contaminants of concern	Score	Priority
John Jay mine	0.40— 0.73	Zn	2	low
Fairday mine	1.34— 1.71	Mn, Zn, Cu, Pb	13	high
Unidentified source	2.62— 2.80	Zn, Pb	7	medium
Unidentified source	3.7—4.1	Al, Mn, Zn, Cu	11	high
Bueno Mountain	4.27— 4.82	Al, Mn, Zn, Cu, Pb	15	high
Castle Gulch	8.74— 8.92	Al, Mn, Cu	7	medium

**Table 12.** Potentially contaminating sites impacting Little James Creek, identified and ranked according to empirical metal concentration and loading data collected in April 2003.

Source	Distance (km)	Primary contaminants of concern	Score	Priority
Unnamed mine	0.37— 0.64	Al, Cu, Pb	4	medium
"Argo gully"	0.77— 0.89	Al, Cu	5	medium
Emmett adit	1.18— 1.23	pH, Al, Zn, Cu	4	low
Balarat Creek	1.23— 1.34	pH, Al, Mn, Zn, Cu, Pb	20	high
Unnamed mine waste rock pile	1.55— 1.62	pH, Al, Mn, Zn, Cu, Pb	16	high
Unidentified source	1.73— 1.83	pH, Al, Mn, Zn, Cu, Pb	27	high
Unnamed tributary	1.85— 1.91	pH, Al, Mn, Zn, Cu, Pb	12	high
Streamside tailings and "Bueno Mountain gully"	2.36— 2.41	pH, Al, Mn, Zn, Cu, Pb	11	high
Unidentified source	2.59— 2.68	pH, Al, Mn, Zn, Cu, Pb	13	high
Unidentified source	2.76— 2.87	pH, Al, Mn, Zn, Cu, Pb	13	high

### SUMMARY AND CONCLUSIONS

In this study, applying the techniques of tracer dilution tests and synoptic sampling for characterization of the Lefthand Creek watershed provided a spatially detailed set of water quality data for over 40 km of streams. Analysis of changes in metal loadings identified potential sources of contamination. Comparison of metal concentrations to CDPHE aquatic life water quality criteria helped to correlate the metal loading data with impacts on stream biota. Relative instream metal loadings and water quality criteria violations provided an empirical basis for comparison of the relative impacts of potential contamination sources and prioritization of these sites for future reclamation.

In addition to serving as characterization and prioritization tools for the Lefthand Creek watershed, stream pH, metal loadings, and metal concentrations, as well as stream bed sediment metal concentrations, provided useful information about metal speciation behavior and partitioning in a stream system impacted by acid mine drainage. An understanding of the relationships of the dissolved and colloidal phases of metals is crucial in order to develop effective remediation plans for the Lefthand Creek watershed and other mountainous watersheds suffering from water quality degradation related to acid mine drainage.

By considering the collective impacts of all contaminating mine sites in the watershed as well as identifying the individual contaminant contribution of each site, the Lefthand Watershed Oversight Group can approach reclamation planning on a watershed level. This allows the group and involved landowners and agencies to target the sites that will provide the greatest improvement to overall water quality. Prioritization and targeting of key sites allows the stakeholders to, in turn, identify and pursue applicable legal opportunities and funding avenues for future reclamation activity. Furthermore, the empirical data collected for this study provides an important set of baseline water quality data which stakeholders can apply to evaluate the effectiveness of future reclamation strategies.

#### REFERENCES

33 U.S.C. 1254(b)(3), §104(a)(1), 1972. Public Law 92-500, as amended.

- 33 U.S.C. §1329, 1994. Title 33, Chapter 26, Subchapter III. January 24, 1994.
- H.R. 2869, 2002. Small Business Liability Relief and Brownfields Revitalization Act. Public Law 107-118.
- Apodaca, L. E., Driver, N. E., and Bails, J. B., 2000. Occurrence, transport, and fate of trace elements, Blue River Basin, Summit County, Colorado: An integrated approach. Environmental Geology 39[8].
- Archuleta, A., 2004. USFS Abandoned Mines Lands Coordinator, *personal communication*. May 14, 2004.
- ARSG, 2002. Animas River Stakeholders Group. Draft legislation: Pilot Project, Good Samaritan Provision for Abandoned and Inactive Mined Land Remediation Act. June 15, 2002.
- Bencala, K.E., McKnight, D.M., Zellweger, G.W., 1990. Characterization of transport in an acidic and metal-rich mountain stream based on lithium tracer injection and simulations of transient storage. Water Resources Research 26[5], 989-1000.
- Brooks, P. D., McKnight, D. M, and Bencala, K. E., 2001. Annual maxima in Zn concentrations during spring snowmelt in streams impacted by mine drainage. Environmental Geology 40, 1447-1454. July 11, 2001.
- Buxton, Herbert T., Nimik, David A., von Guerard, Paul, Church, S. E., Frazier, Ann G., Gray, John R., Lipin, Bruce R., Marsh, Sherman P., Woodward, Daniel F., Kimball, B. A., Finger, Susan E., Ischinger, Lee S., Fordham, John C., Power, Marth S., Bunck, Christine M., and Jones, John W., 1997. A Science-Based, Watershed Strategy to Support Effective Remediation of Abandoned Mine Lands. Presented at the Fourth International Conference on Acid Rock Drainage (ICARD) May 30-June 6, 1997.
- Caruso, B. S. and Ward, R. C., 1998. Assessment of nonpoint source pollutoin from inactive mines using a watershed-based approach. Environmental Management 22[2], 225-243.
- CDPHE, 2003. Colorado Department of Public Health and Environment. Colorado's Section 303(d) Listing Methodology. September 9, 2003.

- CDPHE, 2001. Colorado Department of Public Health and Environment. Regulation No. 31: Basic Standards and Methodologies for Surface Water.
- CDWR, 2002. Colorado Division of Water Resources. Lefthand Diversion at So. St. Vrain Creek near Ward, Colorado.
- Center for Watershed Protection (1998). *Rapid Watershed Planning Handbook: A Comprehensive Guide for Managing Urbanizing Watersheds.* Ellicot City, Maryland.
- Church, S. E., 1993. Geochemical and lead-isotope data from stream and lake sediments, and cores from the upper Arkansas River drainage: Effects of mining at Leadville, Colorado on heavy-metal concentrations in the Arkansas River. United States Geological Survey. Open File Report 93-534.
- Church, S. E., Kimball, B.A., Fey, D.L., Ferderer, D.A., Yager, T.J., and Vaughn, R.B., 1993. Source, transport, and partitioning of metals between water, colloids, and bed sediments of the Animas River, Colorado. United States Geological Survey. Open File Report 97-0151.
- Cobb, H. S., 1988. Prospecting our Past: Gold, Silver, and Tungsten Mills of Boulder County. The Book Lode, Longmont, Colorado.
- Colorado River Watch, 2004. Unpublished data. Stream flow and water quality parameters for James Creek from January 21, 1993 to July 31, 2003.
- Colorado Nonpoint Source Program, 2004. FY 2004 Grant Opportunity: Guidance for Prospective Project Sponsors.
- C.R.S. 02-087 §1, 2002. Article 22, Title 39, as amended. June 3, 2002.
- CWPF, 2003. Colorado Watershed Protection Fund: Grant Program Guidance. Colorado Watershed Protection Fund.
- CWPF, 2004. Colorado Watershed Protection Fund 2003 Projects. Colorado Watershed Protection Fund website. http://www.cowaterfund.org/ Accessed March 10, 2004.
- Dzombak, D. A. and Morel, F. M. M., 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons, Inc.

- EPA, 1990. United States Environmental Protection Agency. The Revised Hazard Ranking System: Background Information. Office of Solid Waste and Emergency Response. Quick Reference Fact Sheet. Publication 9320.7-03FS.
- EPA, 1991. United States Environmental Protection Agency. Guidance for Water Quality-Based Decisions: The TMDL Process. Chapter 2. Office of Water. EPA 440/4-91-001.
- EPA, 1993. United States Environmental Protection Agency. The Hazard Ranking System Guidance Manual - Fact Sheet. Office of Solid Waste and Emergency Response. PB93-963356.
- EPA, 1994. United States Environmental Protection Agency. Memorandum of agreement between the Colorado Department of Public Health and Environment and the United States Environmental Protection Agency, Region VIII.
- EPA, 1995a. United States Environmental Protection Agency. Analytical Results Report for Expanded Site Inspection: Captain Jack Mill, Ward, Colorado.
- EPA, 1995b. United States Environmental Protection Agency Office of Water. The Watershed Approach and Reinvention - How Different Agencies are Charting their Course. EPA 840-N-95-001.
- EPA, 1996. United States Environmental Protection Agency. Watershed Approach Framework . EPA 840-S-96-001.
- EPA, 1997a. United States Environmental Protection Agency and Office of Water. EPA's National Hardrock Mining Framework. Report 833-B-97-003.
- EPA, 1997b. United States Environmental Protection Agency. Community-Based Environmental Protection: A Resource Book for Protecting Ecosystems and Communities. United States Environmental Protection Agency and Office of Policy, Planning and Evaluation. EPA 230-B-96-003.
- EPA, 2001. United States Environmental Protection Agency. Protecting and Restoring America's Watersheds: Status, Trends, and Initiatives in Watershed Management. EPA-840-R-00-001. 2001.
- EPA, 2002. United States Environmental Protection Agency. HRS Documentation Record for the Captain Jack Mill. August 1, 2002.

- EPA, 2003a. United States Environmental Protection Agency. Lefthand Creek Watershed Case Study: Use of NPL as Catalyst for Abandoned Mine Cleanup. November 11, 2003.
- EPA, 2003b. United States Environmental Protection Agency. Region 8 -Superfund: Captain Jack Mill. U.S. Environmental Protection Agency website, accessed March 10, 2004. December 12, 2003.
- EPA, 2003c. United States Environmental Protection Agency Solid Waste and Emergency Response. Brownfields 2003 Grant Fact Sheet: Peanut Mine, Inc., Crested Butte, Colorado. EPA 500-F-03-159.
- EPA, 2003d. United States Environmental Protection Agency. 2003 Watershed Summaries: Targeted Watersheds Under the 2003 Watershed Initiative. U.S.Environmental Protection Agency website, accessed March 10, 2004. October 9, 2003
- EPA, 2003e. United States Environmental Protection Agency. Region 9 -Regional Geographic Initiatives: EPA Region 8 Project Proposal Guidance. U.S.Environmental Protection Agency website, accessed March 10, 2004. October 27, 2003.
- Eyrolle, F., and Charmasson, S., 2004. Importance of colloids in the transport within the dissolved phase (<450 nm) of artificial radionuclides from the Rhone river towards the Gulf of Lions (Mediterranean Sea). Journal of Environmental Radioactivity 72, 273-286.
- Federal Register, 2003. 68[196]. pp. 58333-58341. October 9, 2003.
- Ferrey, S., 2001. *Environmental Law: Examples and Explanations*. Gaithersburg, New York: Aspen Law & Business.
- Fey, D. L., Church, S. E., and Finney, C. J., 1999. Analytical results for 35 mine-waste tailings cores and six bed-sediment samples, and an estimate of the volume of contaminated material at Buckeye Meadow on Upper Basin Creek, northern Jefferson County, Montana. United States Geological Survey. Open File Report 99-537.
- Hudson-Edwards, K.A., Macklin, M.G., Jamieson, H.E., Brewer, P.A., Coulthard, T.J., Howard, A.J., Turner, J.N., 2003. The impact of tailings dam spills and clean-up operations on sediment and water quality in river systems: the Rios Agrio-Guadiamar, Aznalcollar, Spain. Applied Geochemistry 18, 221-239.

- JCWI, 2000. James Creek Watershed Initiative. 2000 State of the Watershed Report: James Creek, Colorado.
- Kenney, D. S., McAllister, S. T., Caile, W. H., and Peckham, J. S., 2000. *The New Watershed Source Book: A Directory and Review of Watershed Initiatives in the Western United States.*
- Kimball, B. A., Broshears, R. E, Bencala, K. E., and McKnight, D. M., 1994. Coupling of Hyrdologic Transport and Chemical Reactions in a Stream Affected by Acid Mine Drainage. Environmental Science and Technology 28[12], 2065-2073.
- Kimball, B. A., Callender, E., and Axtmann, E. V., 1995. Effects of colloids on metal transport in a river receiving acid mine drainage, upper Arkansas River, Colorado, USA. Applied Geochemistry 10, 285-306.
- Kimball, 1997. Use of tracer injections and synoptic sampling to measure metal loading from acid mine drainage. United States Geological Survey. Report FS-245-96.
- Kimball, B. A., Runkel, R. L., Walton-Day, K., and Bencala, K. E., 2001a. Assessment of Metal Loads in watershed affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA. Applied Geochemistry 16.
- Kimball, B. A., Runkel, R. L., and Gerner, L. J., 2001b. Quantification of minedrainage inflows to Little Cottonwood Creek, Utah, using a tracerinjection and synoptic sampling study. Environmental Geology 10, 1390-1404.
- LWTF, 2002. Lefthand Watershed Task Force. Final Report to the Boulder County Board of Health. March 11, 2002.
- Plummer, T.L., 2004. Superintendant, Left Hand Ditch Company. Written correspondence to Kathry Hernandez, EPA Project Manager for the Lefthand Creek Watershed. March 8, 2004.
- Runkel, R. L. and Kimball, B. A., 2002. Evaluating remedial alternatives for an acid mine drainage stream: application of a reactive transport model. Environmental Science and Technology 36, 1093-1101.
- Schemel, L. E., Kimball, B. A., and Bencala, K. E., 2000. Colloid formation and metal transport through two mixing zones affected by acid mine drainage near Silverton, Colorado. Applied Geochemistry 15, 1003-1018.

- Schmidt, Hank, 2004. *Personal communication*. Hank Schmidt, Water Treatment Manager, Left Hand Water District. March 15, 2004
- Shea, V.R., 1988. Geology of the White Raven Mine, Ward Mining District, Boulder County, Colorado. November 28, 1988.
- Stumm, W. and Morgan, J. J., 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, Inc.
- Stumm, W., 1992. Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems. John Wiley & Sons, Inc.
- USGS, 2004. United States Geological Survey National Water Informatoin System. NWISWeb Data for Colorado for USGS gage 06724500, Left Hand Creek near Boulder, Colorado. Available online at http://waterdata.usgs.gov/co/nwis, accessed January 5, 2004.
- Walsh, 2003. Walsh Environmental Scientists and Engineers, LLC. Limited Impact Special Review Application: Burlington Mine Reclamation Project, Boulder County, Colorado.
- WQCD, 2002. Total Maximum Daily Load Assessment: Little James Creek, Boulder County, Colorado. Water Quality Control Division and Colorado Department of Public Health and Environment. June 20, 2002.
- Younger, P. L., Banwart, S. A., and Hedin, R. S., 2002. *Mine Water: Hydrology, Pollution, Remediation.* Kluwer Academic Publishers.
- Zellweger, G. W., Avanzino, R.J., and Bencala, K.E., 1989. Comparison of tracer dilution and current-meter discharge measurements in a small gravel-bed stream, Little Lost Man Creek, California. United States Geological Survey Water-Resources Investigations Report 89-4150.

# **APPENDIX A**

The following tables show the results of priority ranking based on pH and metal aquatic life criteria violations and relative contributions of dissolved metal loads for Lefthand, James, and Little James Creeks.

Lefthand Creek		
Site	Hillside seep	"Dew Drop mine" tributary
Stream distance (km)	0.460.61	0.610.79
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn		1
Cu		1
Pb	1	
pH	1	1
Exceeds acute standards		
Fe		
Al		
Mn		
Zn		1
Cu		1
Pb		
Adds over 5% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu ph		
PD		
Adds over 10% of dissolved load		
Al Mp		
Zn		
Ph		
Adds over 15% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn	1	
Cu		
Pb		
Adds over 5% of stream flow		
TOTAL SCORE	2	5
(of 37)	LOW	MEDIUM

Lefthand Creek		
Site	Big Five mine tunnel	White Raven mine
Stream distance (km)	1.181.29	1.651.79
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	1
Cu	1	1
Pb	1	
рН	1	1
Exceeds acute standards		
Fe		
Al		
Mn		
Zn	1	1
Cu	1	1
Pb		
Adds over 5% of dissolved load		
Fe		
Al		
Mn	1	
Zn	1	
Cu	1	
Pb		
Adds over 10% of dissolved load		
Fe		
Al		
Mn	1	
Zn	1	
Cu	1	
Pb		
Adds over 15% of dissolved load		
Fe		
Al		
Mn	1	
Zn		
Cu	1	
Adds over 25% of dissolved load		
AI	1	
Mn	1	
Zn Cr	1	
	1	
Adds over 5% of stream flow		
	10	-
IUTAL SCORE	10	5 MEDUD <i>I</i>
(01 37)	HIGH	MEDIUM

Lefthand Creek		
Site	Unnamed mine opening	Indiana Gulch
Stream distance (km)	1.992.19	2.422.54
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	
Cu	1	
Pb		
pH	1	
Exceeds acute standards		
Fe		
Al		
Mn		
Zn	1	
Cu	1	
Pb		
Adds over 5% of dissolved load		
Fe		
Al		
Mn		1
Zn		1
Cu		1
Pb		
Adds over 10% of dissolved load		
Fe Al		
Al		
Dh		
Adds over 15% of diss load		
Fo		
Mn		
Zn		
Cu		
Ph		
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 5% of stream flow		
		-1
TOTAL SCORE	5	2
(of 37)	MEDIUM	LOW

Lefthand Creek		
Site	Loder Smelter	Unnamed tributary
Stream distance (km)	2.973.21	7.3
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	1
Cu	1	1
Pb		
рН	1	1
Exceeds acute standards		
Fe		
Al		
Mn		
Zn	1	1
Cu	1	1
Pb		
Adds over 5% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		1
Adds over 10% of dissolved load		
Fe		
Al		
		1
PD		1
Adds over 15% of dissolved load		
Ai Mn		
7n		
Ph		1
Adds over 25% of dissolved load		
Fe		
Mn		
Zn		
Cu		
Ph		1
Adds over 5% of stream flow		
ridus over 070 of stitum flow		
TOTAL SCORE	5	9
(of 37)	MEDIUM	MEDIUM

Lefthand Creek		
Site	Unidentified source	Spring Gulch
Stream distance (km)	9.11	11.43
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	1
Cu	1	1
Pb		
рн	1	1
Exceeds acute standards		
Fe		
Al		
	1	1
		1
Dh		1
Adds over 5% of dissolved load		
Fe		
Mn		
Zn		
Cu		1
Pb	1	
Adds over 10% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb	1	
Adds over 15% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu pl		
Adds over 25% of dissolved load		
Mn		
7n		
Cu		
Ph		
Adds over 5% of stream flow		
		-1
TOTAL SCORE	7	5
(of 37)	MEDIUM	MEDIUM

Lefthand Creek		
Site	Prussian Mine	Slide Mine
Stream distance (km)	12.7613.01	13.1613.50
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	1
Cu	1	1
Pb	1	
pH	1	1
Exceeds acute standards		
Fe		
Al		
Mn	1	1
Zn		
Cu		1
Adds over 5% of dissolved load		
Fe Al		
Al		1
		1
Ph		
Adds over 10% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 15% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 5% of stream flow		
IUIAL SUUKE		
(01 37)		

Lefthand Creek		
Site	"Lee Hill" gulch	Carnage Canyon
Stream distance (km)	19.2519.48	24.3124.47
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn		
Cu	1	1
Pb		
pH		
Exceeds acute standards		
Fe		
Al		
	1	1
Dh	1	
Adds over 5% of dissolved load		
Fo		
		1
Mn		1
Zn		
Cu		
Pb		
Adds over 10% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 15% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 25% of dissolved load		
Fe		
AI		
Mn		
Zn Cu		
Auds over 5% of stream flow		
TOTAL SCOPE	9	2
(of 37)	LOW	LOW

Lefthand Creek	
Site	Sixmile Creek
Stream distance (km)	26.0926.39
Exceeds chronic standards	
Fe	
Al	
Mn	
Zn	
Cu	1
Pb	
рн	
Exceeds acute standards	
Al	
	1
Ph	1
Adds over 5% of dissolved load	
Fe	
Al	
Mn	1
Zn	-
Cu	
Pb	
Adds over 10% of dissolved load	
Fe	
Al	
Mn	
Zn	
Cu	
Pb	
Adds over 15% of dissolved load	
Fe	
Al	
Mn Z	
Zn	
Dh	
PD Adds over 95% of dissolved load	
Fo	
Mn	
Zn	
Cu	
Pb	
Adds over 5% of stream flow	
TOTAL SCORE	3
(of 37)	LOW

James Creek		
Site	John Jay mine	Fairday mine
Stream distance (km)	0.400.73	1.341.71
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	1
Cu		
Pb		1
pH		
Exceeds acute standards		
Fe		
Al		
Mn		
Zn	1	1
Cu		
Pb		
Adds over 5% of dissolved load		-
Fe		1
Al		
Mn	1	1
Zn	1	1
Cu Dh		
		1
Adds over 10% of dissolved load		1
Al		1
		1
		1
Ph		1
Adds over 15% of dissolved load		1
Fe		
Al		
Mn		
Zn		
Cu		1
Pb		1
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		1
Adds over 5% of stream flow		
	-1	-1
TOTAL SCORE	2	13
(of 37)	LOW	HIGH

James Creek		
Site	Unidentified source	Unidentified source
Stream distance (km)	2.622.80	3.543.72
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	1
Cu		
Pb		
pH		
Exceeds acute standards		
Fe		
Al		
Mn		
Zn	1	1
Cu		
Pb		
Adds over 5% of dissolved load		
Fe		1
Al		1
Mn		1
Zn	1	1
Cu		1
Pb	1	
Adds over 10% of dissolved load		1
Fe Al		1
Al		
	1	1
	1	
Dh		
Adds over 15% of dissolved load		
Fo		1
		1
Mn		1
Zn	1	
Cu	1	
Ph		
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn	1	
Cu	1	
Pb		
Adds over 5% of stream flow		
		-1
TOTAL SCORE	7	11
(of 37)	MEDIUM	HIGH

James Creek		
Site	<b>Bueno Mountain</b>	Castle Gulch
Stream distance (km)	4.274.82	8.748.92
Exceeds chronic standards		
Fe		
Al		
Mn		
Zn	1	
Cu		
Pb		
pH		
Exceeds acute standards		
Fe		
Al		
Mn		
Zn	1	
Cu		
Pb		
Adds over 5% of dissolved load		
Fe	1	1
Al	1	1
Mn	1	1
Zn	1	
Cu	1	1
Pb	1	
Adds over 10% of dissolved load		
Fe		
Al	1	1
Mn	1	1
Zn	1	
Cu	1	1
Pb	1	
Adds over 15% of dissolved load		
Fe		
Al		
Mn	1	1
Zn	1	
Cu		
Pb	1	
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 5% of stream flow		
	-1	-1
		~
TOTAL SCORE	15	7
(ot 37)	HIGH	MEDIUM

Little James Creek		
Site	Unnamed mine	Argo gully
Stream distance (km)	0.370.43	0.770.89
Exceeds chronic standards		
Fe		
Al	1	1
Mn		
Zn		
Cu	1	1
Pb	1	
pН		
Exceeds acute standards		
Al		
Mn		
Zn		
Cu		1
Pb		
Adds over 5% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu	1	1
Pb	1	1
Adds over 10% of dissolved load		_
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 15% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 5% of stream flow		
	-1	
TOTAL SCORE	4	5
(of 37)	LOW	MEDIUM

Little James Creek		
Site	Emmett adit	Balarat Creek
Stream distance (km)	1.181.23	1.231.34
Exceeds chronic standards		
Fe		
Al	1	1
Mn		
Zn		1
Cu	1	1
Pb		
pH	1	1
Exceeds acute standards		
Al		1
Mn		
Zn		1
Cu	1	1
Pb		
Adds over 5% of dissolved load		
Fe		1
Al		1
Mn		1
Zn		1
Cu		1
Pb		1
Adds over 10% of dissolved load		
Fe		1
Al		1
Mn		1
Zn		1
Cu		
Pb		1
Adds over 15% of dissolved load		
Fe		
Al		1
Mn		1
Zn		1
Cu		
Pb		
Adds over 25% of dissolved load		
Fe		
Al		1
Mn		
Zn		1
Cu		1
Pb		
Adds over 5% of stream flow		
		-1
TOTAL SCORE	4	20
(of 37)	LOW	HIGH

Little James Creek		
Site	Unnamed waste rock pile	Unidentified source
Stream distance (km)	1.551.62	1.731.83
Exceeds chronic standards		
Fe	1	1
Al	1	1
Mn		
Zn	1	1
Cu	1	1
Pb	1	1
pH	1	1
Exceeds acute standards		
Al	1	1
Mn		
Zn	1	1
Cu	1	1
Pb		
Adds over 5% of dissolved load		
Fe		1
Al	1	1
Mn	1	1
Zn	1	1
Cu	1	1
Pb	1	1
Adds over 10% of dissolved load		
Fe		1
Al		1
Mn	1	1
Zn	1	1
Cu	1	1
Pb		
Adds over 15% of dissolved load		
Fe		1
Al		1
Mn		1
Zn		
Cu		1
Pb		
Adds over 25% of dissolved load		
Fe		1
Al		1
Mn		1
Zn G		
Cu N		1
Adds over 5% of stream flow	1	
	-1	-1
TOTAL SCODE	10	97
IUTAL SCORE	16	
(ot 37)	HIGH	HIGH

Little James Creek		
		Streamside tails &
Site	Unnamed tributary	Bueno tributary
Stream distance (km)	1.851.91	2.362.47
Exceeds chronic standards		
Fe		
Al	1	1
Mn		
Zn	1	1
Cu	1	1
Pb	1	1
pH	1	1
Exceeds acute standards		1
Al	1	1
Mn	1	1
Zn		
Cu ph		
ru Adda over 50/ of descelared log d		
Auus over 5% of dissolved 10ad		
	1	1
Mn	1	1
	1	1
	1	
Ph	1	1
Adds over 10% of dissolved load	1	1
Fe		
Al	1	
Mn	-	
Zn		
Cu		
Pb		
Adds over 15% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 25% of dissolved load		
Fe		
Al		
Mn		
Zn		
Cu		
Pb		
Adds over 5% of stream flow		
	-1	-1
TOTAL SCORE	12	11
(of 37)	HIGH	HIGH

Site         Unidentified source         Unidentified source           Stream distance (km)         2.59-2.68         2.76-2.87           Exceeds chronic standards	Little James Creek		
Stream distance (km)         2.59-2.68         2.76-2.87           Exceeds chronic standards	Site	Unidentified source	Unidentified source
Exceeds chronic standards         I           Fe         I         I           Re         I         1           Mn         I         1           Zn         1         1           Cu         1         1           Pb         1         1           PH         1         1           PH         1         1           Exceeds acute standards         I         I           Zn         1         1         I           Mn         I         1         I           Zn         1         1         I           Cu         1         1         I           Pb         I         1         I           Adds over 5% of dissolved load         I         I           Fe         I         I         I           Mn         1         I         I           Cu         1         I         I           Cu         1         I         I           Mn         1         I         I           Adds over 10% of dissolved load         I         I           Fe         I         I <td< th=""><th>Stream distance (km)</th><th>2.592.68</th><th>2.762.87</th></td<>	Stream distance (km)	2.592.68	2.762.87
Fe       -       -         Al       1       1         Al       1       1         Mn       -       -         Zn       1       1         Cu       1       1         pH       1       1         pH       1       1         Exceeds acute standards       -         Al       1       1         Mn       -       -         Zn       1       1         Mn       -       -         Zn       1       1         Cu       1       1         Pb       -       -         Adds over 5% of dissolved load       -       -         Fe       -       -       -         Al       1       1       1         Zn       1       1       -         Cu       1       1       -         Adds over 10% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Mn       -       -       -         Cu       -       -       -	Exceeds chronic standards		
Al       1       1         Mn       -       -         Zn       1       1         Cu       1       1         Pb       1       1         pH       1       1         pH       1       1         Mn       -       -         Zn       1       1         Mn       -       -         Zn       1       1         Cu       1       1         Zn       1       1         Cu       1       1         Zn       1       1         Zn       1       1         Zn       1       1         Zn       1       1         Cu       1       1         Ads over 10% of dissolved load       -         Fe       -       -         Al       -       -         Mn <t< td=""><td>Fe</td><td></td><td></td></t<>	Fe		
Mn       1       1         Zn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         pH       1       1         Exceeds acute standards       -         Al       1       1         Mn       -       -         Zn       1       1         Mn       -       -         Cu       1       1         Pb       -       -         Adds over 5% of dissolved load       -       -         Fe       -       -       -         Al       1       1       1         Mn       1       1       -         Cu       1       1       1         Zn       1       1       -         Cu       1       1       -         Mn       1       1       -         Zn       1       1       -         Cu       1       -       -         Pb       1       -       -         Adds over 15% of dissolved load       -       -         Fe	Al	1	1
Zn       1       1         Cu       1       1         Cu       1       1         Pb       1       1         PH       1       1         Exceeds acute standards	Mn		
Cu       1       1         Pb       1       1         pH       1       1         Exceeds acute standards       1       1         Al       1       1         Mn       1       1         Cu       1       1         Mn       1       1         Cu       1       1         Pb       1       1         Adds over 5% of dissolved load       -         Fe       -       -         All       1       1         Mn       1       1         Cu       1       1         Cu       1       1         Cu       1       1         Adds over 10% of dissolved load       -         Fe       -       -         All       -       -         Mn       -       -         Zn       -       -         Cu       -       -         Pb       1       -         Adds over 15% of dissolved load       -         Fe       -       -         All       -       -         Mn       -       - <td>Zn</td> <td>1</td> <td>1</td>	Zn	1	1
Pb       1       1         pH       1       1         Exceeds acute standards       1       1         Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Ads over 5% of dissolved load       -         Fe       -       -         Al       1       1         Mn       1       1         Zn       1       1         Mads over 5% of dissolved load       -         Fe       -       -         Al       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Pb       1       -         Cu       -       -         Pb       1       -         Adds over 15% of dissolved load       -         Fe       -       -         Adds over 25% of dissolved load<	Cu	1	1
pH       1       1         Exceds acute standards       -         Al       1       1         Mn       -       -         Zn       1       1         Cu       1       1         Qu       1       1         Adds over 5% of dissolved load       -       -         Fe       -       -         Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       -       -         Cu       -       -         Pb       1       -         Adds over 15% of dissolved load       -       -         Fe       -       -       -         Adds over 25% of dissolved load       -       -         Fe       -       - <td< td=""><td>Pb</td><td>1</td><td>1</td></td<>	Pb	1	1
Exceeds acute standards         I         I           Al         1         1           Mn         1         1           Zn         1         1           Cu         1         1           Pb         1         1           Adds over 5% of dissolved load         -         -           Fe         -         -           Al         1         1         1           Mn         1         1         1           Mn         1         1         1           Cu         1         1         1           Cu         1         1         1           Cu         1         1         1           Ads over 10% of dissolved load         -         -           Fe         -         -         -           Al         -         -         -           Mn         -         -         -           Zn         -         -         -           Ads over 15% of dissolved load         -         -         -           Fe         -         -         -         -           Al         -         -	pH	1	1
Al       1       1         Mn       -       -         Zn       1       1         Cu       1       1         Pb       -       -         Adds over 5% of dissolved load       -       -         Fe       -       -         Al       1       1       1         Mn       1       1       1         Zn       1       1       1         Cu       1       1       1         Pb       1       1       1         Cu       1       1       1         Pb       1       1       1         Adds over 10% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Cu       1       -       -         Pb       1       -       -         Adds over 15% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Cu       -       -       -         Pb       -       -       -	Exceeds acute standards		
Mn       1       1         Zn       1       1         Cu       1       1         Pb       -       -         Adds over 5% of dissolved load       -       -         Fe       -       -         Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Adds over 10% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Mn       -       -       -         Zn       1       -       -         Cu       -       -       -         Pb       1       -       -         Adds over 15% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Mn       -       -       -	Al	1	1
Zn       1       1         Cu       1       1         Pb       -       -         Adds over 5% of dissolved load       -       -         Fe       -       -         Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       1       -         Cu       -       -         Pb       1       -         Adds over 15% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Mn       -       -       -         Zn       -       -       -         Adds over 25% of dissolved load       -       -         Fe       -       -       -      <	Mn		
Cu       1       1         Pb       -       -         Adds over 5% of dissolved load       -       -         Fe       -       -         Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -       -         Fe       -       -         Al       -       -         Adds over 10% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Cu       -       -       -         Zn       1       -       -         Cu       -       -       -         Pb       1       -       -         Adds over 15% of dissolved load       -       -       -         Fe       -       -       -       -         Al       -       -       -       -         Adds over 25% of dissolved load       -       -       -         Fe       - <td< td=""><td>Zn</td><td>1</td><td>1</td></td<>	Zn	1	1
Pb         Image: Market in the second s	Cu	1	1
Adds over 5% of dissolved load       I         Fe       I       1         Al       1       1         Mn       1       1         Cu       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       I       I         Fe       I       I         Al       I       I         Mn       I       I         Zn       I       I         Adds over 10% of dissolved load       I       I         Fe       I       I       I         Al       I       I       I         Mn       I       I       I         Cu       I       I       I         Adds over 15% of dissolved load       I       I         Fe       I       I       I         Adds over 25% of dissolved load       I       I       I         Fe       I       I       I       I         Adds over 25% of dissolved load       I       I       I         Fe       I       I       I       I         Al       I       I <td>Pb</td> <td></td> <td></td>	Pb		
Fe       I       I         Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Ads over 10% of dissolved load       I       I         Fe       I       I         Al       I       I         Mn       I       I         Zn       I       I         Mn       I       I         Cu       I       I         Pb       1       I         Cu       I       I         Pb       1       I         Adds over 15% of dissolved load       I       I         Fe       I       I       I         Al       I       I       III         Que       I       IIII       IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	Adds over 5% of dissolved load		
Al       1       1         Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Fe       Image: Comparison of the solved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Al       Image: Comparison of the solved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Fe       1       Image: Comparison of the solved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Fe       Image: Comparison of the solved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Adds over 25% of dissolved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Fe       Image: Comparison of the solved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Adds over 25% of dissolved load       Image: Comparison of the solved load       Image: Comparison of the solved load       Image: Comparison of the solved load         Fe       Image: Comparison of the solved load       Image: Comparison of the solved load	Fe		
Mn       1       1         Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       I       I         Fe       I       I         Adds over 10% of dissolved load       I       I         Fe       I       I       I         Al       I       I       I         Mn       I       I       I       I         Zn       I       I       I       I         Cu       I       I       I       I         Adds over 15% of dissolved load       I       I       I         Fe       I       I       I       III         Adds over 15% of dissolved load       I       IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	Al	1	1
Zn       1       1         Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       -       -         Cu       -       -         Pb       1       -         Adds over 15% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Adds over 15% of dissolved load       -       -       -         Fe       -       -       -       -         Al       -       -       -       -         Mn       -       -       -       -         Cu       -       -       -       -         Pb       -       -       -       -         Ads over 25% of dissolved load       -       -       -         Fe       -       -       -       -         Al       -       -       -       -         Mn       -       -       <	Mn	1	1
Cu       1       1         Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       1       -         Cu       -       1         Pb       1       -         Adds over 15% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Mn       -       -       -         Al       -       -       -         Mn       -       -       -         Zn       -       -       -         Cu       -       -       -         Pb       -       -       -         Ads over 25% of dissolved load       -       -       -         Fe       -       -       -       -         Al       -       -       -       -         Mn       -       -       -       -       -         Zn       -       -       -       -       -       -	Zn	1	1
Pb       1       1         Adds over 10% of dissolved load       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       1       -         Cu       -       -         Pb       1       -         Adds over 15% of dissolved load       -       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       -       -         Al       -       -         Mn       -       -         Zn       -       -         Cu       -       -         Pb       -       -         Adds over 25% of dissolved load       -       -         Fe       -       -       -         Al       -       -       -         Mn       -       -       -         Zn       -       -       -         Cu       -       -       -         Pb       -       -       -         Adds over 25% of stream flow       -       -	Cu	1	1
Adds over 10% of dissolved load       Image: constraint of the second seco	Pb	1	1
Fe       Image: Constraint of the second secon	Adds over 10% of dissolved load		
AlImage: state of the state of t	Fe		
Mn       I         Zn       1         Cu       I         Pb       1         Adds over 15% of dissolved load       I         Fe       I         Al       I         Mn       I         Zn       I         Zu       I         Mn       I         Zn       I         Cu       I         Pb       I         Adds over 25% of dissolved load       I         Fe       I         Al       I         Mn       I         Zn       I         Cu       I         Pb       I         Adds over 25% of dissolved load       I         Fe       I       I         Al       I       I         Mn       I       I         Zn       I       I         Cu       I       IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	Al		
Zn       1         Cu       -         Pb       1         Adds over 15% of dissolved load       -         Fe       -         Al       -         Mn       -         Zn       -         Cu       -         Pb       -         Adds over 25% of dissolved load       -         Fe       -         Adds over 25% of dissolved load       -         Fe       -         Al       -         Mn       -         Zn       -         Cu       -         Pb       -         Adds over 25% of dissolved load       -         Fe       -       -         Al       -       -         Mn       -       -         Zn       -       -         Cu       -       -         Pb       -       -         Adds over 5% of stream flow       -         TOTAL SCORE       13       13	Mn		
Cu       I       Image: constraint of the system of	Zn		1
Pb       1         Adds over 15% of dissolved load       -         Fe       -         Al       -         Mn       -         Zn       -         Cu       -         Pb       -         Adds over 25% of dissolved load       -         Fe       -         Al       -         Mn       -         Pb       -         Adds over 25% of dissolved load       -         Fe       -         Al       -         Mn       -         Zn       -         Cu       -         Pb       -         Adds over 5% of stream flow       -         TOTAL SCORE       13       13	Cu		
Adds over 15% of dissolved loadImage: constraint of the second secon	Pb	1	
Fe       I       I         Al       I       I         Mn       I       I         Zn       I       I         Cu       I       I         Pb       I       I         Adds over 25% of dissolved load       I       I         Fe       I       I         Al       I       I         Mn       I       I         Zn       I       I         Cu       I       I         Mn       I       I         Zn       I       I         Cu       I       I         Pb       I       I         Adds over 5% of stream flow       I       I         TOTAL SCORE       13       13	Adds over 15% of dissolved load		
AlImage: constraint of the systemMnImage: constraint of the systemZnImage: constraint of the systemPbImage: constraint of the systemAdds over 25% of dissolved loadImage: constraint of the systemFeImage: constraint of the systemAdds over 25% of dissolved loadImage: constraint of the systemFeImage: constraint of the systemAlImage: constraint of the systemAlImage: constraint of the systemMnImage: constraint of the systemZnImage: constraint of the systemCuImage: constraint of the systemPbImage: constraint of the systemAdds over 5% of stream flowImage: constraint of the systemImage: constraint of the systemImage: constraint of the systemTOTAL SCORE1313Image: constraint of the systemImage: constraint of the systemImage: constraint of the systemImage: constraint of the system	Fe		
MnImage: constraint of the systemZnImage: constraint of the systemCuImage: constraint of the systemPbImage: constraint of the systemAlImage: constraint of the systemMnImage: constraint of the systemZnImage: constraint of the systemCuImage: constraint of the systemPbImage: constraint of the systemAdds over 5% of stream flowImage: constraint of the systemTOTAL SCORE1313(of 37)HICHHICH	Al		
ZnImage: constraint of the second systemCuImage: constraint of the second systemPbImage: constraint of the second systemAdds over 25% of dissolved loadImage: constraint of the second systemFeImage: constraint of the second systemAlImage: constraint of the second systemAlImage: constraint of the second systemAlImage: constraint of the second systemMnImage: constraint of the second systemZnImage: constraint of the second systemCuImage: constraint of the second systemPbImage: constraint of the second systemAdds over 5% of stream flowImage: constraint of the second systemImage: constraint of the second systemImage: constraint of the second systemTOTAL SCORE1313Image: constraint of the second systemImage: constraint of the	Mn		
CuCuPbImage: Constraint of the systemAdds over 25% of dissolved loadImage: Constraint of the systemFeImage: Constraint of the systemAlImage: Constraint of the systemMnImage: Constraint of the systemZnImage: Constraint of the systemCuImage: Constraint of the systemPbImage: Constraint of the systemAdds over 5% of stream flowImage: Constraint of the systemImage: Constraint of the systemImage: Constraint of the systemTOTAL SCORE1313Image: Constraint of the systemImage: Constraint o	Zn		
Pb       Image: constraint of the second secon	Cu		
Adds over 25% of dissolved load     Image: Constraint of the second	Pb		
Fe     Image: Constraint of the second	Adds over 25% of dissolved load		
Ai     Image: Mail of the second			
Min     Image: Constraint of the second	AI		
Zn     Cu       Cu     -1       Pb     -1       Adds over 5% of stream flow     -1       TOTAL SCORE     13       I3     13       (of 37)     HICH	Nin 7		
Cu     Cu       Pb	Zn Cu		
PD     PD       Adds over 5% of stream flow     -1       -1     -1       TOTAL SCORE     13       (of 37)     HICH			
Auds over 5% of stream flow     -1     -1       TOTAL SCORE     13     13       (of 37)     HICH     HICH			
TOTAL SCORE 13 13	Adds over 5% of stream flow	1	1
TOTAL SCORE     13       (of 37)     HICH		-1	-1
IUTAL SUUKE         IS         IS           (of 37)         HICU         UICU	TOTAL SCORE	19	19
	(of 37)	НСН	НСН