

A comparison of pre- and post-remediation water quality, Mineral Creek, Colorado[†]

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Abstract:

Pre- and post-remediation data sets are used herein to assess the effectiveness of remedial measures implemented in the headwaters of the Mineral Creek watershed, where contamination from hard rock mining has led to elevated metal concentrations and acidic pH. Collection of pre- and post-remediation data sets generally followed the synoptic mass balance approach, in which numerous stream and inflow locations are sampled for the constituents of interest and estimates of streamflow are determined by tracer dilution. The comparison of pre- and post-remediation data sets is confounded by hydrologic effects and the effects of temporal variation. Hydrologic effects arise due to the relatively wet conditions that preceded the collection of pre-remediation data, and the relatively dry conditions associated with the post-remediation data set. This difference leads to a dilution effect in the upper part of the study reach, where pre-remediation concentrations were diluted by rainfall, and a source area effect in the lower part of the study reach, where a smaller portion of the watershed may have been contributing constituent mass during the drier post-remediation period. A second confounding factor, temporal variability, violates the steady-state assumption that underlies the synoptic mass balance approach, leading to false identification of constituent sources and sinks. Despite these complications, remedial actions completed in the Mineral Creek headwaters appear to have led to improvements in stream water quality, as post-remediation profiles of instream load are consistently lower than the pre-remediation profiles over the entire study reach for six of the eight constituents considered (aluminium, arsenic, cadmium, copper, iron, and zinc). Concentrations of aluminium, cadmium, copper, lead, and zinc remain above chronic aquatic-life standards, however, and additional remedial actions may be needed. Future implementations of the synoptic mass balance approach should be preceded by an assessment of temporal variability, and modifications to the synoptic sampling protocol should be made if necessary. Published in 2009 by John Wiley & Sons, Ltd.

KEY WORDS acid mine drainage; synoptic sampling; temporal variation; mass balance; geochemistry; tracer injection

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INTRODUCTION

A variety of techniques have been used to quantify and characterize the effects of mining on instream water quality (Whyte and Kirchner, 2000; Brake *et al.*, 2001; Kimball *et al.*, 2001; McKnight *et al.*, 2001; Bird 2003; Schemel *et al.*, 2006). These techniques range from relatively simple mass balance approaches (Foos, 1997; Yu, 1998) to detailed models of reactive transport (Runkel *et al.*, 2007; Caruso *et al.*, 2008). Included within this range is the synoptic mass balance approach of Kimball *et al.* (2002, 2007), in which detailed spatial profiles of constituent load are developed. Under the synoptic approach, numerous stream and inflow locations are sampled for the constituents of interest, and estimates of streamflow are obtained by tracer dilution. Estimates of mass load at each stream location are then determined

as the product of concentration and streamflow. The resultant spatial profiles of mass load may be used to identify and rank sources of metal contamination (e.g. Kimball *et al.*, 2001; Runkel *et al.*, 2005).

The synoptic mass balance approach described above is used herein to evaluate the effectiveness of remedial measures undertaken for Mineral Creek, an acid mine drainage stream in southwestern Colorado. Pre- (1999) and post-remediation (2005) data sets provide a basis for this evaluation. Quantifying the effects of remediation is theoretically straightforward: spatial profiles of mass load from 1999 and 2005 may be directly compared for individual constituents; decreases in mass load over time, if present, suggest improved conditions that may be attributable to remediation. Despite this apparent simplicity, two confounding factors complicate the evaluation of remedial effectiveness. First, although both data sets were collected under nominally steady, low-flow conditions, both data sets appear to be affected by substantial temporal variation in constituent concentrations that occurred during synoptic sampling. The steady-state assumption that underlies the synoptic mass balance approach is

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therefore violated. Second, rainfall events prior to the 1999 synoptic sampling resulted in streamflow that was up to five times higher than that observed in 2005. This hydrologic variability may affect the comparison in that portions of the watershed contributing load in 1999 may not have been contributing in 2005 due to drier conditions and less water/rock interaction.

The primary goal of this paper is to quantify changes in water quality that may have occurred due to remedial activities conducted in the Mineral Creek headwaters. These remedial activities, conducted between September 1999 and August 2005, sought to improve water quality by controlling and/or removing important sources of metal contamination. Because of the high cost of mine-site remediation and the relative scarcity of cleanup funds, it is imperative that remedial actions result in quantifiable improvements to stream water quality. Improvements to water quality may be documented through post-remediation monitoring, such as the post-remediation synoptic sampling discussed herein. Although this evaluation of remedial effectiveness is a logical step in the cleanup process, it is the authors' experience that such post-remedial evaluations are rarely conducted (for exceptions, see Brake *et al.*, 2001, Owen *et al.*, 2007, Verplanck *et al.*, 2007). A secondary goal of the paper is to illustrate the use of synoptic data for comparative purposes, subject to the confounding issues described above. The techniques presented here may prove useful for evaluations at other mine sites undergoing remediation.

STUDY AREA AND REMEDIATION TO DATE

Mineral Creek originates at the top of Red Mountain Pass north of Silverton, Colorado (Figure 1), and flows ~15 km before entering the Animas River. The study reach begins in a small unnamed drainage that collects water from hillsides in the vicinity of the Longfellow mine and Koehler tunnel (Figure 1). This unnamed drainage merges with Mineral Creek, and the remainder of the study reach follows Mineral Creek (Figure 1). The 2-km study reach is constrained by a steep canyon (stream slope ~80 m/km), with stream depth during low-flow periods being <0.5 m, and stream width ranging from 1 to 3 m. The study reach follows the structural margin of the Silverton caldera, and numerous faults and fractures are exposed along the walls of the steep canyon. The caldera margin marks a substantial change in geology. Portions of the watershed east of the margin are within the Silverton caldera, and bedrock geology consists of hydrothermally altered Silverton Volcanics with dacitic intrusions associated with intense hydrothermal alteration and mineral deposits of the Red Mountain mining district. In contrast, portions of the watershed to the west of the caldera margin are underlain by bedrock of the San Juan Formation, with intermediate composition volcanic units that have been subject to weak to moderate hydrothermal alteration.

Numerous inflows along the study reach introduce metals and acidic waters. Most of the metal-rich, acidic

inflows drain alteration zones within the Silverton Volcanics, which are porphyritic andesitic flows, containing 15–25% phenocrysts of plagioclase and augite. In the study area, there is the local alteration to a quartz-sericite-pyrite assemblage, which contains complete replacement of plagioclase and potassium feldspar by fine-grained quartz, illite (sericite), and 10–20% finely disseminated and fracture-filling pyrite (Bove *et al.*, 2007a). Elevated metal concentrations are observed throughout the study reach, and pH ranges from 2.5 to 5.0. Under these conditions, precipitated hydrous iron oxides coat the streambed, and the stream is virtually devoid of typical montane aquatic life.

Sources of metal contamination within the study reach include numerous mines in the northeastern part of the watershed. This area constitutes the southern lobe of the Red Mountain mining district, where economically significant breccia-pipe chimney deposits were mined for silver, lead, and copper (Bove *et al.*, 2007b). The Longfellow mine, Junction mine, and Koehler tunnel are located up-gradient from the head of the study reach (Figure 1). Acidic drainage from the Junction mine and Koehler tunnel constitutes over one half of the flow entering the head of the study reach (Runkel *et al.*, 2009), resulting in stream pH < 3.0 and elevated concentrations of copper, lead, arsenic, and zinc (Runkel and Kimball, 2002; Kimball *et al.*, 2007). Immediately southeast of the Koehler tunnel lies the Carbon Lake mining area, where the Congress, Carbon Lake, and San Antonio mines are located. These mines are within a sub-watershed that drains to the southwest, with the unnamed drainage entering the study reach near the midpoint (1156 m, Figure 1). Additional mines and prospects in the western portion of the watershed are potential sources of metals to the study reach. Silver Ledge mine, for example, lies immediately adjacent to the study reach (Figure 1), and a large discharge from the mine dump is a known source of lead (Runkel and Kimball, 2002). Other potential sources include the Mineral Basin and Bullion King mines, located in the Mineral Creek and Porphyry Gulch headwaters, respectively (Figure 1).

Several remedial actions that could improve water quality within the study reach have been undertaken by the Animas River Stakeholders Group, the San Juan Resource Conservation and Development Council, and the Sunnyside Gold Corporation (Finger *et al.*, 2007). These actions, undertaken from 1999 to 2004, have focused on the Longfellow-Koehler and Carbon Lake areas (Table I, Figure 1) as these areas contribute substantial loads to the upper Animas River (Kimball *et al.*, 2007). The primary action in the Longfellow-Koehler area is the placement of a bulkhead in the Koehler tunnel, in an effort to eliminate this source in its entirety. Prior to the placement of the bulkhead, the tunnel contributed up to 11.7 l/s of acidic, metal-rich flow to the headwaters of the study reach. This substantial source was initially blocked by the bulkhead, but a leak of 3.1 l/s was observed in May of 2005 (William Simon, Animas River Stakeholders Group, written communication,

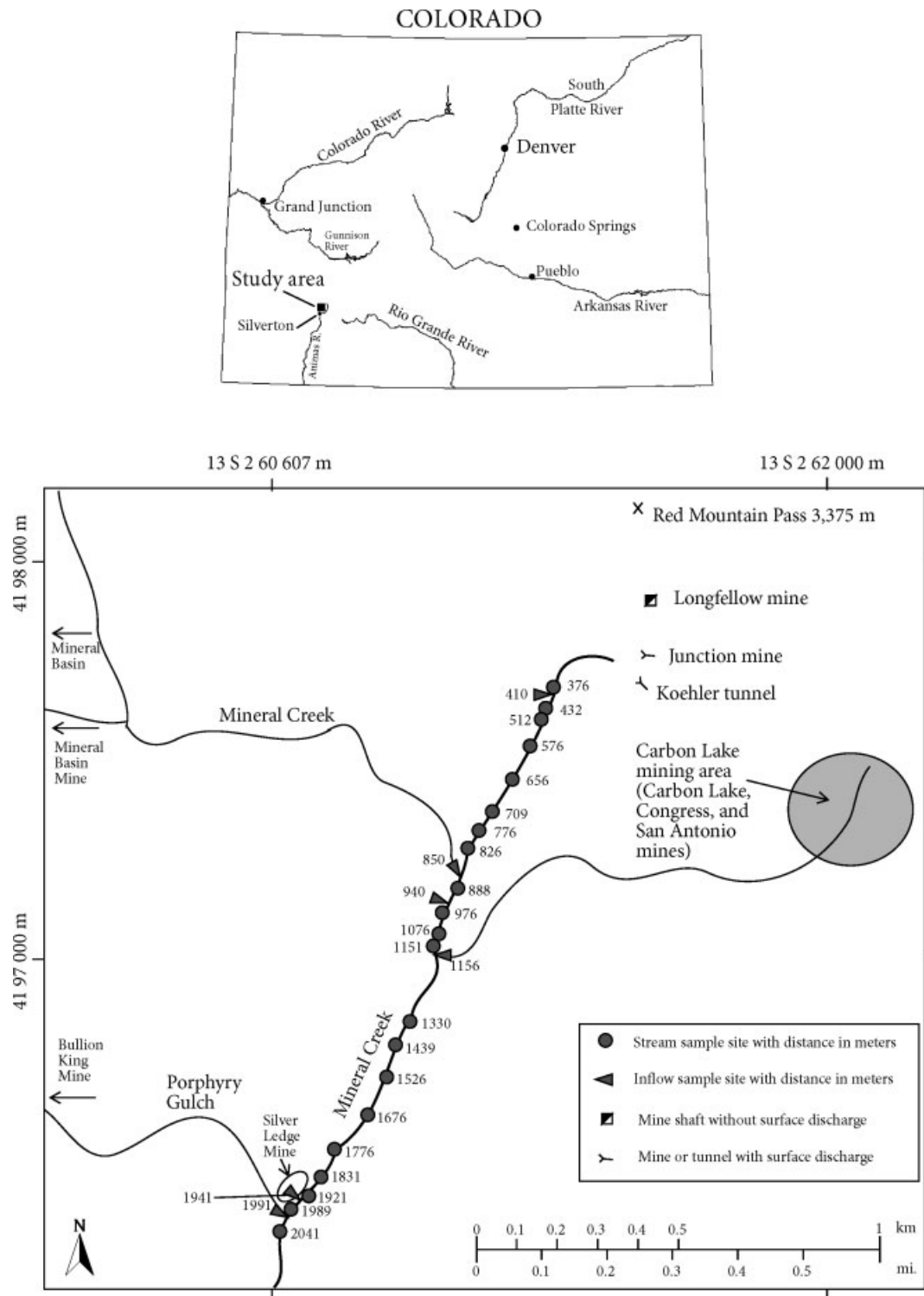


Figure 1. Mineral Creek study reach for September 1999 and August 2005 synoptic sampling

2008). Despite this leakage, placement of the bulkhead is expected to curtail mass loading at the head of the study reach, given the large decrease in acidic, metal-rich flow (leakage from the tunnel on August 12, 2005 was less than 0.3 l/s). Remedial activities in the Carbon Lake area include the removal of waste rock and mine dump material, and the reclamation of a diversion ditch (Table I). Reclamation of the diversion ditch is expected to have an effect on metal concentrations at low flow

as it restores flow to the Mineral Creek watershed that had been part of an inter-basin transfer. This restoration provides a source of clean water that should act to dilute metal concentrations. The removal of waste rock and mine dump material, in contrast, may not have an appreciable effect on water quality at low flow, as these materials are unlikely to be a major source during the dry conditions associated with low flow. Potential sources of contamination in the western portion of the watershed

Table I. Remediation projects, upper Mineral Creek, 1999–2005 (after Finger *et al.*, 2007)

Date	Location	Action	Purpose
1999	Carbon Lake mine	Removal of 1900 yd ³ of waste rock from stream channel	Reduce metal loading to Mineral Creek
2001	Koehler tunnel	Reduce infiltration into surface mine workings that drain into the Koehler tunnel	Reduce metal loading to Mineral Creek by reducing flow of Koehler tunnel
2003	Koehler tunnel	Install bulkhead in Koehler tunnel to stop acidic drainage	Reduce metal loading to Mineral Creek by preventing/reducing flow of Koehler tunnel
2003	Congress mine	Complete removal of Congress mine waste dump	Reduce metal loading to Mineral Creek by removing mine wastes and site beneficiation
2003	Vicinity of Carbon Lake mine	Reclamation of diversion ditch, wetlands, and stream; restore natural flow to Mineral Creek drainage that had been diverted to Uncompahgre watershed	Reduce metal loading to Mineral Creek by removing mine wastes and site beneficiation; increase dilution; decrease flow from Koehler tunnel by preventing infiltration
2004	San Antonio mine	Installed hydrologic controls, removal of waste from stream, consolidation and neutralization of waste, and revegetation	Reduce metal loading to Mineral Creek by stabilizing site and restoring streambed and riparian habitat

(Silver Ledge mine and mines in the Mineral Basin and Porphyry Gulch sub-watersheds, Figure 1) have not been remediated to date.

METHODS

Overview

The primary goal of this paper is to quantify changes in water quality that may have occurred due to the remedial activities described above. This goal will be accomplished by comparing constituent concentrations and mass loads from pre- (1999) and post-remediation (2005) data sets. These two data sets were collected using the synoptic mass balance approach of Kimball *et al.* (2002, 2007). This approach, used extensively in acid mine drainage streams, combines the tracer-dilution method with synoptic sampling (Bencala and McKnight, 1987; Bencala *et al.*, 1990; Kimball *et al.*, 2002). The tracer-dilution method provides estimates of streamflow, and synoptic sampling provides a description of instream and inflow chemistry.

Although both data sets cover the same geographical area, there are small differences between the 1999 and 2005 data sets in regard to the number of samples and sampling locations. In an effort to facilitate the comparison of pre- and post-remedial conditions, this paper will focus on sampling locations that are common to both data sets (21 stream and 6 inflow sample locations, Figure 1). In addition, the comparison will focus on the concentrations and loads of aluminium (Al), arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), and zinc (Zn). Data for additional sampling locations and constituents are presented by Runkel and Kimball (2002); Kimball *et al.* (2007); and Runkel *et al.* (2009).

Tracer injection and synoptic sampling

Continuous, constant rate injections of a concentrated lithium bromide tracer were initiated at the upstream end of the study reach on the day prior to synoptic sampling. Synoptic samples were collected on September 17, 1999 and August 22, 2005, after instream concentrations of the lithium bromide tracer had reached a steady-state plateau. Estimates of streamflow at each synoptic sampling location were determined by tracer dilution (Kilpatrick and Cobb, 1985). Tracer-dilution calculations and data tables documenting the attainment of a steady-state tracer plateau for the August 2005 data set are provided by Runkel *et al.* (2009). Collection of stream samples proceeded in the downstream-to-upstream direction to avoid contaminating samples with resuspended streambed materials. Stream samples were collected as rapidly as possible in an effort to minimize effects of diel metal fluctuations (Nimick *et al.*, 2005; Gammons *et al.*, 2007; elapsed time between adjacent stream samples was ~5 to 15 min). Sampled inflows ranged from small springs to well-defined tributaries such as Porphyry Gulch. Stream and inflow sampling sites are identified herein using a numeric value that indicates the distance (in meters) from the top of the study reach to a given sampling location. Samples were transported to a processing area where aliquots were prepared for cation and anion analyses. Processing included filtration using 0.45- μ m membranes, pH measurement, and preservation of samples for iron speciation. Aliquots for cation analysis were acidified to pH < 2.0. Total recoverable and dissolved cation concentrations were determined from unfiltered and filtered samples, respectively, using ICP-AES (1999 data) or ICP-MS (2005 data). Dissolved anion concentrations were determined from filtered, unacidified samples by ion chromatography.

In addition to the synoptic samples described above, temporal samples were collected at a subset of stream sites to document the attainment of a steady-state tracer plateau. These temporal samples were collected manually and/or by using automatic samplers. Temporal samples were filtered within 24 h and later analysed by ion chromatography to determine concentrations of the tracer (bromide) and ambient sulphate (Runkel *et al.*, 2009). Concentrations of sodium and zinc associated with the 2005 temporal samples were determined by atomic-absorption spectroscopy in the spring and summer of 2007 (Runkel *et al.*, 2009). The resulting time series of sodium, sulphate, and zinc concentrations are used herein to assess temporal variability. Additional details on sample collection and processing are provided by Runkel *et al.* (2009).

Loading analysis

Under the synoptic mass balance approach (Kimball *et al.*, 2002, 2007), the study reach is divided into a number of stream segments that are demarcated by the synoptic stream sampling locations. Mass load at each stream location is generally defined as the product of streamflow and concentration:

$$M = CQ \quad (1)$$

where M is instream load (mass/time), C is instream concentration (mass/volume), Q is streamflow (volume/time), and C and Q are in consistent units (e.g. C in milligrams per liter and Q in liters per second). The change in instream load from one stream site to the next may be used to determine if a segment is a source or a sink for a given chemical constituent (Figure 2):

$$\Delta M_S = M_D - M_U \quad (2)$$

where ΔM_S is the within segment change in instream load, and the D and U subscripts denote values of instream load at the downstream and upstream sites, respectively. Given steady-state conditions, positive values of ΔM_S (increase in mass load with distance) indicate sources of constituent mass. Negative values of ΔM_S

(decrease with distance), in contrast, indicate sinks (attenuation of constituent mass due to chemical reactions). Loading analyses based on Equation (2) are subject to uncertainty due to analytical errors in the determination of chemical constituent and tracer concentrations. Although corrections for these errors have been proposed (Runkel *et al.*, 2005; Kimball *et al.*, 2007), such corrections will not be implemented herein due to the presence of temporal variability (i.e. errors in the mass balance approach attributable to temporal variability are much greater than analytical errors, such that the proposed corrections are unwarranted).

Sources of constituent mass may also be quantified using observed inflow data whenever a given stream segment brackets an observed inflow (Figure 2):

$$\Delta M_I = C_I (Q_D - Q_U) \quad (3)$$

where ΔM_I is the sampled inflow load, C_I is the inflow concentration, and $Q_D - Q_U$ is the within segment increase in streamflow (Figure 2). Under steady-state conditions, values of ΔM_S and ΔM_I should be of comparable magnitude whenever (1) the sampled inflow is representative of all the water entering the stream segment (Bencala and McKnight, 1987) and (2) the constituent of interest is not subject to instream reactions that remove constituent mass (e.g. precipitation, sorption). In the results that follow, calculations of mass load [Equations (1)–(3)] are based on total-recoverable constituent concentrations, unless noted otherwise.

RESULTS

Streamflow

Streamflow estimates for 1999 increase from 6.9 (376 m, Figure 1) to 172 l/s (2041 m); estimates in 2005 increase from 2.2 to 88 l/s. Differences in streamflow are attributable to rainfall events that preceded the 1999 synoptic sampling. Data from a SNOTEL station on Red Mountain Pass (NRCS, 2008) indicate that 3.6 cm of rainfall was recorded on the 3 days preceding the 1999 synoptic sampling, whereas 0.5 cm of rainfall was recorded for the 3-day period preceding the 2005 synoptic sampling. The effects of prior rainfall were directly observable in the field, as several inflows sampled in 1999 were not flowing in 2005. As a result, 1999 streamflow estimates are ~2 to 5.6 times higher than those observed in 2005 (Figure 3a).

For both years, large increases in streamflow are observed below the Mineral Creek (850 m) and Porphyry Gulch (1991 m) inflows that drain the west side of the watershed (Figure 1). These two inflows account for the bulk of the flow increase within the study reach (76 and 82% of the increase, 1999 and 2005, respectively). Another major inflow is the unnamed drainage from the Carbon Lake mining area (1156 m), accounting for 9.5 and 4.7% of the within study reach increase (1999 and 2005, respectively).

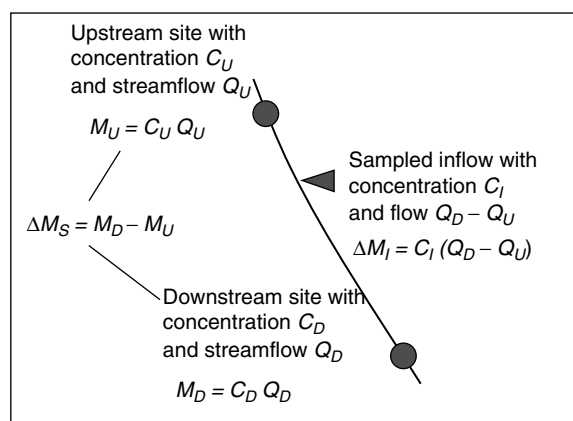


Figure 2. Generic stream segment used to illustrate calculations of mass load

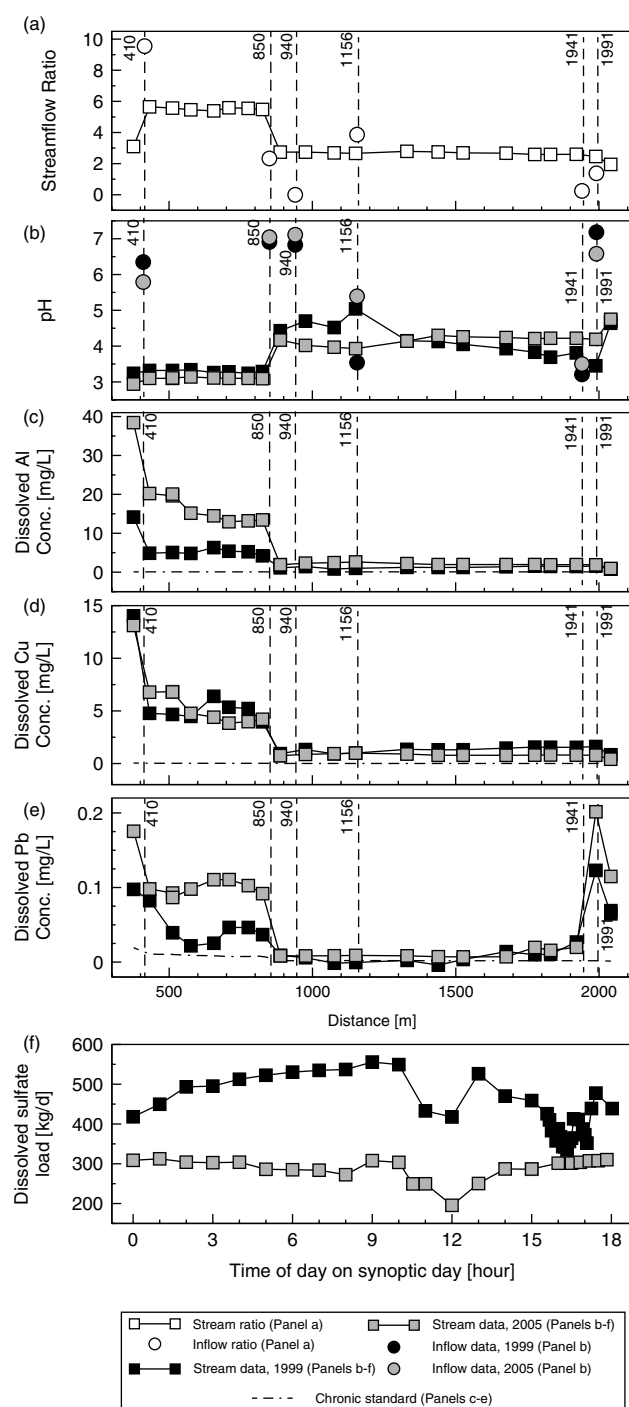


Figure 3. Comparison of 1999 and 2005 data for upper Mineral Creek: (a) ratio of 1999 streamflow to 2005 streamflow, (b) stream and inflow pH, (c–e) dissolved concentrations of Al, Cu, and Pb, (f) time series of sulphate load at 656 m (1999) and 576 m (2005). Vertical lines denote locations of inflow sites

Constituent concentrations and pH

Instream pH values for 1999 and 2005 show the same general pattern, with $\text{pH} < 3.4$ in the upper part of the study reach (< 850 m, Figure 3b). Farther downstream, pH increases in response to circumneutral inflow from Mineral Creek and Porphyry Gulch (850 and 1991 m, Figure 3b). Instream pH values in 2005 are lower than 1999 values for most of the study reach (< 1500 m, Figure 3b). In contrast, inflow pH values for 2005 are

higher than 1999 values for four of the six inflows considered (Figure 3b). The largest change in inflow pH from 1999 to 2005 is for the inflow draining the Carbon Lake mining area, where pH increased from ~ 3.5 to 5.4 (1156 m, Figure 3b).

The low-instream pH noted above produces an aqueous environment in which metals are highly soluble. As a result, five of the eight constituents considered behave conservatively, with total-recoverable concentrations approximately equal to dissolved concentrations. Three of the eight constituents (As, Fe, and Pb) are subject to reactive transport, with precipitation and sorption reactions resulting in the formation of solid phases in the water column (total recoverable $>$ dissolved; Runkel and Kimball, 2002).

Stream concentrations for six of the eight constituents (Al, Cd, Fe, Ni, Pb, and Zn) are generally higher in 2005 than in 1999. Al, Cd, and Zn concentrations show the same general pattern, with 2005 concentrations being much higher than 1999 concentrations in the upper part of the study reach (< 850 m), and 2005 concentrations exceeding 1999 concentrations by a smaller amount farther downstream (Figure 3c, Cd and Zn not shown). Concentrations of Fe, Ni, and Pb in 2005 also exceed 1999 concentrations. In contrast to the other constituents, As and Cu concentrations are approximately equal for the 2 years (Figure 3d, As not shown). Concentration profiles for Pb in both years differ from the other constituents, in that there is a large instream concentration increase due to the inflow from the Silver Ledge mine dump (1941 m, Figure 3e).

Dissolved concentrations of Al, Cd, Cu, and Zn exceed the chronic aquatic-life standards established by the State of Colorado (CDPHE, 2000) along the entire study reach in both 1999 and 2005 (Figure 3c–d, Cd and Zn not shown). Similarly, Pb concentrations exceed the chronic standard over the entire length of the study reach in 2005 and most of the study reach in 1999 (Figure 3e); As concentrations in 1999 and 2005 exceed the chronic standard in the upper part of the study reach (< 850 m). Ni concentrations, in contrast, are below the chronic standard in both years.

Temporal variability

During the 2005 synoptic sampling, a sonde employed at 826 m recorded a $\sim 400 \mu\text{S}/\text{cm}$ decrease in specific conductance over a 2.5 h period (decreasing $\sim 25\%$ from 1030 to 1300 h). This decrease in specific conductance suggests substantial temporal variation in constituent concentrations that is verified by the sodium, sulphate, and zinc concentrations from the temporal samples collected to document tracer plateau (Figure 4). The observed variations in sodium, sulphate, and zinc suggest that the additional constituents considered here were also subject to temporal variation during the 2005 synoptic sampling. For the case of 1999, sulphate data from temporal samples suggest that constituent concentrations varied by a smaller, but nonetheless substantial, amount during the 1999 synoptic sampling.

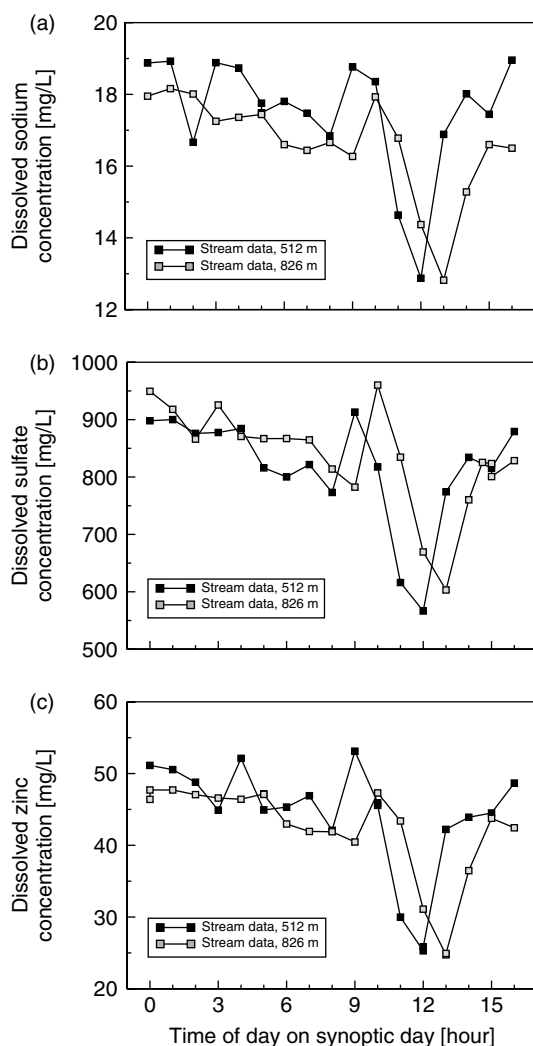


Figure 4. Temporal data at 512 and 826 m on August 22, 2005 for upper Mineral Creek: (a–c) dissolved concentrations of sodium, sulphate, and zinc

To illustrate the effects of temporal variation on constituent loads, time series of instream sulphate load from stream sites at 576 m (2005) and 656 m (1999) are calculated using Equation (1) and synoptic streamflow estimates (this analysis assumes steady streamflow during the time period of interest; this assumption is based on the observed tracer data that exhibits a nominally steady plateau). Although the data used to calculate sulphate loads for 1999 and 2005 are not from the same location, the sites are in close proximity to each other (80 m) and no observable inflows enter between the two locations. This observation is confirmed by the near equality of streamflow estimates for the two sites (0.03 and 0.06 l/s differences were documented in 1999 and 2005, respectively). As such, temporal data from the two sites are directly comparable, and the temporal variation in 1999 and 2005 loads can be assessed. Substantial variation in sulphate load occurred between the hours of 0900 and 1500 on synoptic days in both 1999 and 2005, with minimum loads occurring at ~1200 h (Figure 3f).

Spatial loading profiles

Spatial profiles of instream load [Equation (1)] for the eight constituents are shown in Figure 5 (panels a, b, g, h, m, n, s, t). Instream loads were higher in 1999 than 2005 for six of the eight constituents considered (Figure 5a, b, g, h, m, t). Instream loads of Ni and Pb were comparable in 1999 and 2005 (Figure 5n, s).

DISCUSSION

Streamflow, constituent concentrations, and pH

Synoptic data sets from 1999 and 2005 are used herein to quantify changes in water quality that may be attributable to remedial activities in the Mineral Creek headwaters. Comparison of pre- (1999) and post-remediation (2005) data sets is confounded by hydrologic differences between the 2 years. As shown in Figure 3a, 1999 streamflows are over five times higher than 2005 flows in the upper part of the study reach (410–850 m), and approximately two times higher farther downstream (>850 m). This hydrologic difference has two potential effects. First, the rainfall events that preceded the 1999 sampling may have had a dilution effect, as dilute runoff led to additional streamflow. As a result of this dilution effect, 1999 constituent concentrations should be lower than those observed in 2005, and pH should be higher. This effect may confound the evaluation of remedial effectiveness by leading to increases in pH under the wetter 1999 conditions. Increases in pH may promote pH-dependent reactions (precipitation and sorption) that act to remove constituent mass. Pre-remediation concentrations and mass loads may have therefore been higher if less rainfall had preceded the 1999 synoptic sampling.

A second hydrologic effect is due to potential differences in the source areas within the watershed that contribute flow under various flow regimes. The wetter conditions observed in 1999, for example, may have produced a source area effect, in which more areas of the watershed were contributing constituent mass relative to the drier conditions in 2005. This source area effect may have important implications for evaluating remedial effectiveness as it complicates the comparison of the pre- and post-remediation data sets. For example, unremediated source areas may be contributing constituent mass under the wetter 1999 flow regime, and not contributing in 2005 due to drier conditions and less water/rock interaction. This hydrologic effect could lead to incorrect conclusions, as the lack of contribution from an unremediated source area in 2005 due to drier conditions could be erroneously attributed to remedial activities.

Although the dilution and source area effects appear to have the opposite effects on water quality, they are not mutually exclusive. The dilution effect is clearly seen in the upper part of the study reach (<850 m), where the 1999 stream concentrations are dilute relative to 2005 concentrations (Figure 3c, e). The primary sources in the upper part of the study reach, the Koehler tunnel and Junction mine, discharge at a relatively constant rate over

the hydrologic year, and the lower stream concentrations observed in 1999 are attributable to dilution of these sources (although flow from the Junction mine and Koehler tunnel may increase in response to rainfall, this increase is small relative to the increase in flow associated with dilute surface runoff). This hydrologic effect may be quite large, as it appears to swamp the effects of remediation (i.e. the Koehler tunnel bulkhead should result in lower 2005 stream concentrations relative to 1999; 2005 stream concentrations are higher, however, due to the dilution in 1999). The source area effect, the idea that more source areas contribute at higher flow, can

be seen in the inflow data. Inflow concentrations from 1999 exceed 2005 concentrations at most inflow locations for six of the eight constituents considered (Al, As, Cd, Cu, Fe, and Zn; Figure 5c, d, i, j, o, v). Similarly, inflow pH is generally lower in 1999 than 2005 (Figure 3b), indicating additional contributions of acidic source water.

The contrast between stream (1999 < 2005) and inflow (1999 > 2005) concentrations may be explained by the dilution and source area effects described above. Stream concentrations are largely controlled by sources in the upper part of the study reach (Koehler tunnel and Junction mine, Figure 1), and the dilution effect leads to lower

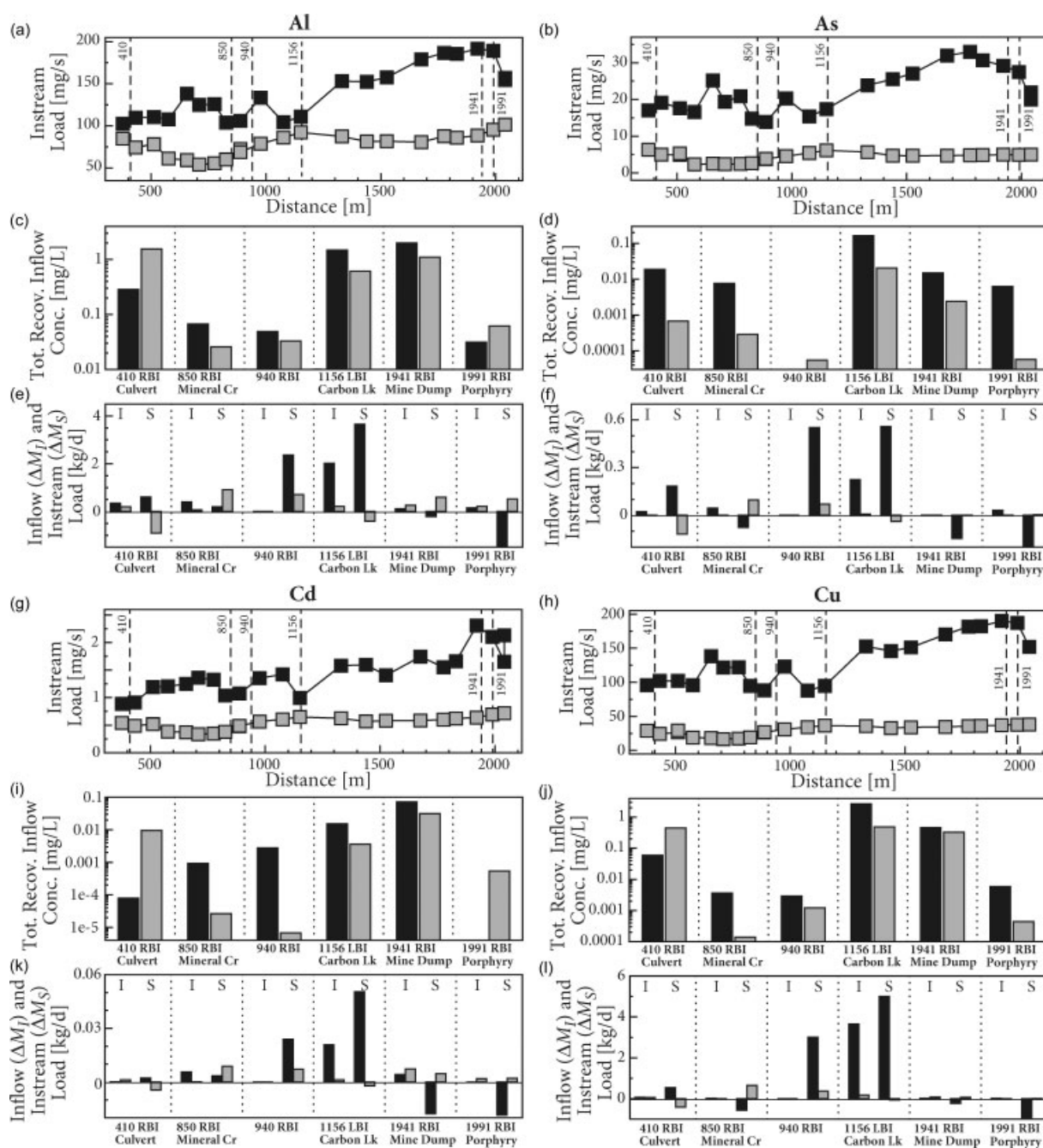


Figure 5. Comparison of 1999 (black symbols) and 2005 (grey symbols) constituent data for upper Mineral Creek: (a, b, g, h, m, n, s, t) spatial profiles of instream load (vertical lines denote locations of inflow sites), (c, d, i, j, o, p, u, v) total-recoverable concentrations at six inflow sites, (e, f, k, l, q, r, w, x) sampled inflow load (ΔM_I) and change in instream load (ΔM_S) for six stream segments with sampled inflows (values of ΔM_I and ΔM_S are denoted by I and S, respectively)

concentrations under the wetter, more dilute conditions observed in 1999. Lower in the watershed (i.e. inflows at 850, 940, 1156, and 1941 m), the source area effect is predominant, leading to lower inflow pH and higher inflow concentrations in 1999.

Effects of temporal variability

The primary quantities for the determination of mass loads and comparative analyses under the synoptic mass balance approach are the spatial profiles of instream load (Kimball *et al.*, 2002, 2007). This standard approach of quantifying mass loading by synoptic sampling is compromised in the present case due to temporal variability in constituent concentrations (Figure 3f, Figure 4). The

effects of temporal variation on the synoptic mass balance approach are illustrated using sulphate data from the 2005 synoptic sampling. In Figure 6a, the observed temporal sulphate profile from 1989 m has been shifted backward to reflect the sulphate profile that passed several upstream sampling locations (888, 976, 1076, 1151, 1330, and 1431 m), where the time shift for each sampling location is based on tracer travel time. Comparison of the shifted profile with the synoptic sampling time (vertical line, Figure 6a) indicates that different parts of the temporal profile were sampled at each location. The sample at 888 m, for example, was sampled at a time when the sulphate pulse was at its minimum, and samples at 976, 1076, and 1151 m were collected at progressively

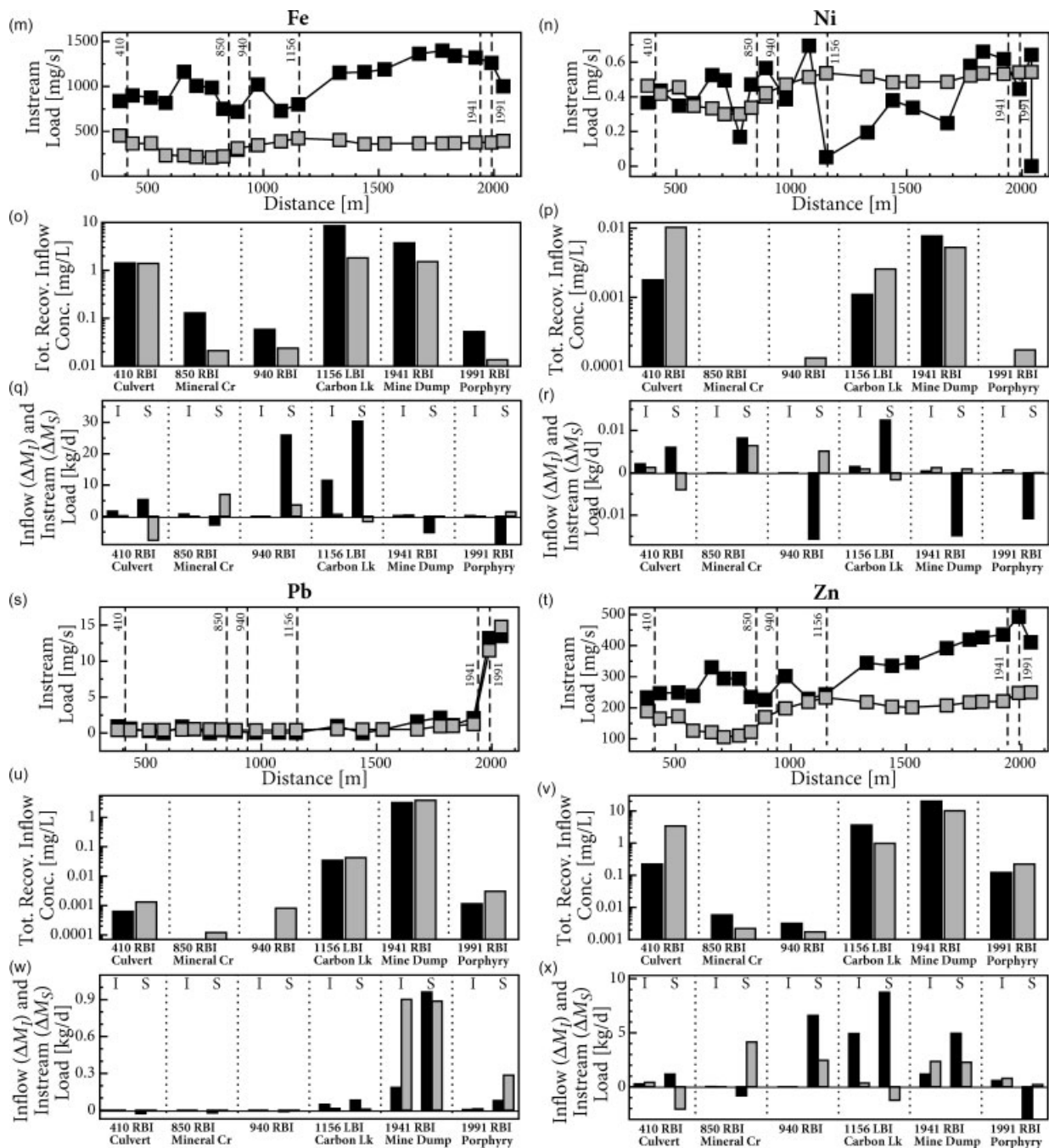


Figure 5. (Continued)

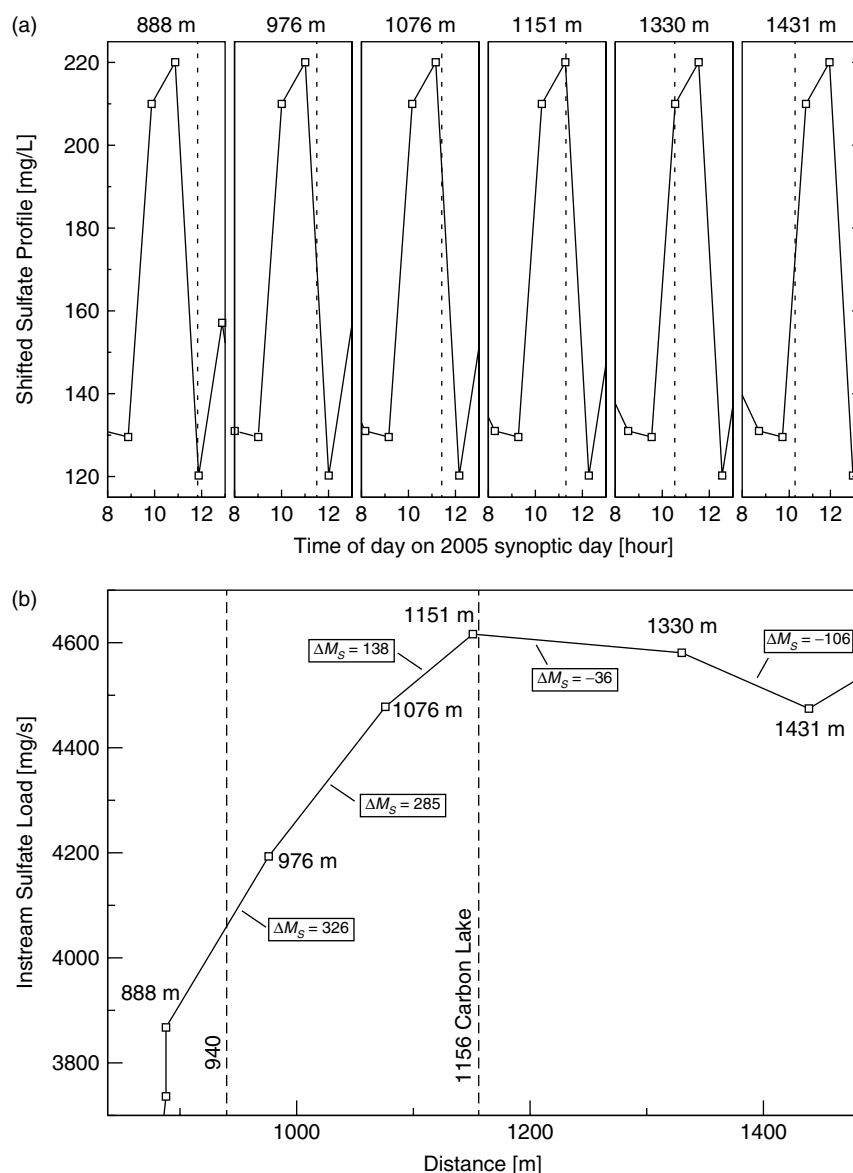


Figure 6. Effect of temporal variation on synoptic sampling: (a) temporal profile of sulphate concentration from 1989 m that has been shifted in time to reflect the sulphate profile that passed the upstream locations. Vertical line represents synoptic sampling time at upstream locations, (b) spatial profile of sulphate load that results from synoptic sampling during period of temporal variability. Increases ($+\Delta M_S$) and decreases ($-\Delta M_S$) in load are an artifact of the temporal variation, rather than actual sources and sinks

higher locations on the sulphate curve (Figure 6a). After peaking at 1151 m, lower concentrations were sampled at 1330 and 1431 m. The effect of sample collection time on sample concentration (Figure 6a) has a direct effect on calculated loads as the observed increases in sulphate concentration from 888 to 1151 m lead to increases in load (positive values of ΔM_S , Figure 6b), while the lower concentrations at 1330 and 1431 m lead to decreases (negative values of ΔM_S , Figure 6b).

Under the steady-state conditions associated with most synoptic studies, increases and decreases in load are attributed to sources and sinks (Kimball *et al.*, 2002, 2007). This interpretation is not plausible for the present case, however, as the positive and negative values of ΔM_S are clearly artefacts of the mass balance error associated with temporal variability. Failure to consider the effects of temporal variability would lead to the

identification of false sources (stream segments with positive ΔM_S) and false attenuation (negative ΔM_S), as noted by Gammons *et al.* (2007). Examples of false sources and false attenuation include the inflow at 940 m, where ΔM_S is erroneously high, and the inflow draining the Carbon Lake mining area (1156 m), where attenuation is falsely indicated (Figure 6b). As shown in Figure 6, the presence of false sources can lead to false attenuation (i.e. the positive values of ΔM_S in the stream segments preceding the Carbon Lake inflow are erroneously high; this leads to negative values of ΔM_S that are also in error).

The mass balance error due to temporal variability leads to large discrepancies between ΔM_S and the sampled inflow load [ΔM_I , Figure 2, Equation (3)]. For well-defined segments, where the sampled inflow comprises the bulk of inflowing water, values of ΔM_S and ΔM_I

should be comparable (e.g. Runkel *et al.*, 2005). Differences in ΔM_S and ΔM_I for the 2005 data set are most notable at the 410 m and Carbon Lake (1156 m) inflows, where ΔM_I values identify a source, and negative ΔM_S indicate attenuation (Figure 5e, f, k, l, q, r, x). Although such attenuation is possible for reactive constituents, the attenuation shown for seven of the eight constituents is unlikely given the conservative transport noted earlier. Another indication of temporal variation in the 2005 data set is at the Mineral Creek inflow (850 m), where ΔM_S values are several times larger than ΔM_I (Figure 5e, f, k, l, q, r, x). Given the magnitude and well-defined nature of the Mineral Creek inflow, such large discrepancies between ΔM_S and ΔM_I are attributable to temporal variability.

In contrast to the present case, the effects of temporal variation may be more subtle in other studies. As shown above, the effects of temporal variation may be diagnosed for stream segments with sampled inflows by comparing values of ΔM_S and ΔM_I . Unfortunately, this diagnostic tool is unavailable when the stream segment of interest does not include a sampled inflow. Positive values of ΔM_S in these segments are normally attributed to 'unsampled inflow' (sources of constituent mass that enter via unsampled waters, such as diffuse groundwater inflow; Kimball *et al.*, 2002, 2007; Mayes *et al.*, 2007), but such sources may be falsely identified in the presence of temporal variability. As such, great care must be taken when interpreting values of ΔM_S when temporal variation is suspected.

Cause of temporal variability

Most studies documenting temporal variation in metal concentration include data that exhibit relatively smooth, cyclic behaviour that may be attributed to environmental forcing functions such as temperature, pH, and sunlight (e.g. McKnight *et al.*, 2001; Nimick *et al.*, 2005; Chapin *et al.*, 2007; Gammons *et al.*, 2007). The observed data from Mineral Creek, in contrast, exhibit an abrupt change in concentration that does not appear to be related to environmental factors that would affect instream processes (Figure 4). The decrease in sodium, sulphate, and zinc concentrations observed at 512 and 826 m exhibits a distinct time lag (Figure 4) that is indicative of a change in source loading, rather than instream processing (i.e. the concentration change is driven by changes at the source; these changes are transported downstream). The exact location of the source can not be determined using the 2005 data set, as temporal data upstream of 512 m were not collected. A likely location is the Koehler tunnel, as the tunnel drains various underground mine workings and multiple flow paths. Data supporting this hypothesis were collected in September 2008, when a sonde recorded specific conductance at the mouth of the tunnel. Temporal variation in conductivity observed at the mouth of the tunnel in 2008 was similar in magnitude and timing to the variation in conductance documented at 826 m in 2005 (conductance at the mouth of the tunnel dropped by $\sim 300 \mu\text{S}/\text{cm}$ over a ~ 5 h period, while

discharge from the tunnel remained steady). The physical and/or biogeochemical processes responsible for this variation in source loading are unknown at this time and are a potential area of future research.

Spatial loading profiles and the Koehler tunnel bulkhead

As discussed in the previous subsections, hydrologic differences and temporal variability may confound the interpretation of synoptic data collected to assess remedial effectiveness. Fortunately, the primary hydrologic effect in the upper portion of the study reach is dilution, and the low pH in the upper portion leads to conservative transport for most constituents. As a result, hydrologic differences between pre- and post-remediation data sets do not affect values of mass load in the upper part of the study reach, as mass load is not affected by pure dilution (the lower part of the study reach is considered in the subsection that follows). In regard to temporal variability, the substantial variation documented herein produces erroneous values of ΔM_S . Fortunately, the goal of the present study is not source identification but rather evaluating the effectiveness of remediation. As discussed below, this evaluation may be made by examining the overall loading profiles, rather than the results of individual stream segments using ΔM_S .

Post-remediation (2005) profiles of instream load are consistently lower than the pre-remediation (1999) profiles over the entire study reach for six of the eight constituents considered (Al, As, Cd, Cu, Fe, and Zn; Figure 5a, b, g, h, m, t). This reduction occurs despite the fact that post-remediation concentrations are generally higher than pre-remediation concentrations (Figure 3c, e). The consistent difference between 1999 and 2005 loads strongly suggests an improvement in water quality due to remediation. Further, the reduction in load occurs at the very first sampling site (376 m), suggesting that the improvement stems from remediation in the Longfellow-Koehler area of the Mineral Creek headwaters (Figure 1). This finding is not surprising given the large reduction in flow from the Koehler tunnel (Table I), the largest source within the study reach for most of the constituents considered (Kimball *et al.*, 2007). The decrease in flow from the Koehler tunnel leads to 70, 63, 46, 39, 19, and 17% reductions in load at 376 m for Cu, As, Fe, Cd, Zn, and Al, respectively. Although these percentages may be influenced by temporal variability, the overall conclusion of improved post-remediation conditions is not, as the load reduction is maintained along the entire study reach (Figure 5a, b, g, h, m, t). In addition, the temporal sulphate loads show reduced post-remediation loads over the course of the entire synoptic day (Figure 3f), with an average reduction of 34%.

In contrast to most of the other constituents, the primary source of Pb within the study reach is the inflow at 1941 m, an inflow that drains the unremediated area around the Silver Ledge mine dump. Owing to the unremediated nature of the Silver Ledge area, instream loads of Pb for the 2 years are nearly identical (Figure 5s).

Carbon Lake mining area

The primary remedial activities in the lower portion of the study reach were conducted in the Carbon Lake mining area (Table I), an area that supplies water to an unnamed drainage that enters the study reach near the midpoint (1156 m, Figure 1). Assessing the effectiveness of remedial activities conducted in the Carbon Lake area is more complicated than that for the Koehler tunnel, for three reasons. First, the comparison of pre- and post-remediation data sets may be subject to a hydrologic source area effect, in which 2005 concentrations and loads are lower than those in 1999 simply because portions of the Carbon Lake sub-watershed were not contributing at the lower flows observed in 2005. Second, the high degree of temporal variability within the 2005 data set precludes the use of ΔM_S for source identification; as noted earlier, 2005 ΔM_S values for the stream segment bracketing the Carbon Lake inflow (1156 m) falsely indicate attenuation, rather than a source (Figure 5e, f, k, l, q, r, x). Third, the remedial activities conducted in the Carbon Lake area (Table I) are more subtle than the large reduction in flow from the Koehler tunnel. For example, the primary effect of reclaiming the diversion ditch is dilution, an effect that can only be seen in the mass loads if it results in a pH change. Further, the remaining activities in the Carbon Lake area have focused on the revegetation and/or the removal of tailings piles and mine dumps. Although these actions can dramatically improve water-quality conditions associated with rainfall-runoff events, they may do little to affect loading under the low-flow conditions of the 1999 and 2005 synoptic studies.

In light of the temporal variability discussed above, the effectiveness of remedial activities in the Carbon Lake area is evaluated using inflow data, rather than stream data. Of the six inflows considered here, the Carbon Lake inflow (1156 m) is the only inflow draining a remediated portion of the watershed. As such, changes in inflow chemistry from 1999 to 2005 should be greater for the Carbon Lake inflow than for the unremediated inflows. Analysis of the pre- (1999) and post-remediation (2005) inflow data suggests that remedial activities in the Carbon Lake area had a positive effect on stream water quality. This conclusion is based on several lines of evidence. First, pH of the Carbon Lake inflow increased from 3.5 to 5.4 from 1999 to 2005 (Figure 3b). The remaining inflows either exhibited a smaller increase or a decrease over the same time period. Second, six of the eight constituents (Al, As, Cd, Cu, Fe, and Zn) show a decrease in concentration from 1999 to 2005 for the Carbon Lake inflow (Figure 5c, d, g, h, o, v). Of the six inflows considered, the Carbon Lake inflow exhibits the largest reduction in concentration for Zn (73%), the second largest reduction for Al (59%) and Fe (79%), and the third largest reduction for Cd (77%) and Cu (82%). Third, of the six inflows considered, the Carbon Lake inflow is the only inflow to show a decrease in sampled inflow load (ΔM_I) from 1999 to 2005 for all eight constituents (Figure 5e, f, k, l, q, r, w, x). Of the six inflows, the Carbon Lake inflow had the largest reduction

in ΔM_I for Al (89%), Fe (94%), and Zn (93%), the second largest reduction in Cd (94%), Cu (95%), and Pb (68%), and the fourth largest for As (97%) and Ni (40%).

The lines of evidence presented above suggest that remedial actions in the Carbon Lake area (Table I) had a positive effect on pH, constituent concentration, and constituent load. This finding should be considered in light of two important caveats. First, the chemistry of the unnamed drainage from the Carbon Lake area may be subject to temporal variations like those documented herein for the main study reach. This concern is alleviated somewhat by noting that the Carbon Lake inflow was sampled at similar times of day in 1999 and 2005 (12:30 and 11:15, respectively) and under similar weather conditions. Further, the changes in water quality (increase in pH and decrease in constituent concentrations) documented by the 2005 data set are consistent with other post-remediation data (William Simon, Animas River Stakeholders Group, written communication, 2008). Second, 1999 concentrations and loads may be higher than those from 2005 due to the source area effect discussed previously. The drier conditions observed in 2005 may have led to less loading from the Carbon Lake area simply because some areas of the sub-watershed were dry relative to 1999 conditions. Although the source area effect cannot be ruled out, this concern is alleviated somewhat by the fact that the changes in pre- and post-remediation chemistry for the Carbon Lake inflow are more substantial than those observed for the remaining inflows, as indicated by the lines of evidence presented above. Given these caveats, additional research may be needed to draw firm conclusions in regard to the effectiveness of remedial activities conducted in the Carbon Lake mining area.

Field implications

Successful implementation of the synoptic mass balance approach relies on the attainment of nominally steady-state conditions with respect to both streamflow and water chemistry. Deviations from steady-state conditions lead to inaccuracies in the mass balance approach, as shown by the analysis presented herein (Figure 6) and the work of Gammons *et al.* (2007). For the case of the 2005 Mineral Creek synoptic sampling, steady-state conditions were assumed at the time of sampling; the effects of temporal variation were only noticed upon review of the specific conductance data collected by the instream sonde. Information on the temporal variation obtained prior to the synoptic sampling may have led to changes in sampling strategy that would reduce error in the mass balance approach. Sample collection could have proceeded in an upstream-to-downstream direction, for example, rather than the downstream-to-upstream protocol that is typically employed. Such a change may have led to a decrease in the mass balance error due to temporal variability, as the sampling team would have been moving in the same direction as the constituent pulse. Mass balance error could have been further reduced by employing Lagrangian sampling, in which estimates of

travel time are used to sample a parcel of water as it moves downstream (Blevins and Fairchild, 2001).

These observations lead to two recommendations. First, reconnaissance should be conducted prior to synoptic sampling to determine the extent of temporal variability in a given system. For the case considered here, this reconnaissance could be based on specific conductivity measurements made prior to synoptic sampling. Other cases may arise, however, in which temporal changes in constituent concentration may not lead to a noticeable change in specific conductance. These cases may require the collection and analysis of constituent samples in order to document the presence/absence of temporal variability. The lead time required for this case could be greatly reduced though the use of *in situ* analysis (Chapin *et al.*, 2007). Second, Lagrangian sampling should be considered whenever substantial temporal variability is suspected. To date, most synoptic studies have implemented a downstream-to-upstream sampling protocol, in an effort to avoid contaminating samples with resuspended streambed materials. Given the upstream-to-downstream sampling sequence underlying the Lagrangian approach, sample contamination due to resuspension is more likely. This contamination can be minimized in some cases by minimizing the instream presence of project personnel. This precaution may be impractical at some mountainous locations, however, as site-to-site travel along the streambank may be difficult at best. The sampling protocol selected will ultimately depend on the extent of temporal variability, study goals, and site-specific factors such as site accessibility.

Implications for remediation and remediation monitoring

Despite the extensive remedial activities in the Mineral Creek headwaters to date (Table I), post-remediation concentrations of Al, Cd, Cu, Pb, and Zn remain above chronic aquatic-life standards along the entire study reach (Figure 3c–e, Cd and Zn not shown). The further reductions necessary to meet aquatic-life standards may require additional remedial measures, such as the installation of an active treatment system. An active treatment system for the Mineral Creek headwaters appears to be feasible, given that the dominant sources (the Junction mine and Koehler tunnel) are point sources with relatively small amounts of flow. Continuous, year-round operation of an active treatment system at the high elevation of the Mineral Creek headwaters may prove to be cost prohibitive, however, and alternative treatment systems should be investigated.

The foregoing analysis utilizes pre- and post-remediation data sets and the synoptic mass balance approach to assess the effectiveness of remedial measures. This approach is advantageous in that it provides both a spatial and temporal component (the pre- and post-remediation data sets provide the spatial detail needed to assess the effects of different remedial actions; e.g. actions affecting the Koehler tunnel and the Carbon Lake mining area). A disadvantage of the approach, as demonstrated herein, is the potential for hydrologic variability

to confound data interpretation. Because of this disadvantage, additional approaches may be needed to fully evaluate the effects of remedial actions. One such approach is the collection of streamflow and concentration data at one or more flow locations over the course of the hydrologic year. The resultant data set of streamflow and concentration data may be used to develop regression equations for the estimation of annual loads (Runkel *et al.*, 2004; Leib *et al.*, 2007). Pre- and post-remediation estimates of annual load may then be used to assess the effects of remedial actions.

CONCLUSIONS

The foregoing analysis has direct implications for similar studies of contaminated streams and specific implications for Mineral Creek. The primary conclusions are as follows:

- Hydrologic effects may confound the use of synoptic stream data for comparative purposes such as the evaluation of remedial effectiveness. Differing hydrologic conditions may lead to two different, but not mutually exclusive, effects. The dilution effect may lead to lower concentrations and mass loads under higher flow regimes, due to simple dilution and increases in pH. The source area effect, in contrast, may lead to higher concentrations and mass loads under higher flow regimes as more areas of the watershed contribute at high flow.
- Temporal variation in constituent concentrations may confound the interpretation of synoptic stream data by violating the steady-state assumption that underlies the synoptic mass balance approach. Although small temporal variations in constituent concentration may be acceptable, more substantial variations may lead to the appearance of 'false sources' and 'false attenuation' in which changes in instream load are an artifact of mass balance errors rather than physical/chemical processes. Of particular concern is the case of 'unsampled inflow', where small increases in instream load are attributed to diffuse groundwater sources (Kimball *et al.*, 2002, 2007; Mayes *et al.*, 2007). These sources may be hard to distinguish from false sources that arise due to temporal variability.
- Despite the confounding factors noted above, there is a clear decrease in load at the head of the Mineral Creek study reach that is attributable to the placement of a bulkhead on the Koehler tunnel. Instream loads at the head of the study reach decreased by 70, 63, 46, 39, 19, and 17% for Cu, As, Fe, Cd, Zn, and Al, respectively. The long-term effectiveness of the bulkhead should be further evaluated at a later date, however, due to the potential for leakage (i.e. water behind the bulkhead could reemerge elsewhere; Alpers *et al.*, 2003; Kimball *et al.*, 2007).
- Analysis of the pre- and post-remediation inflow data suggests that remedial activities in the Carbon Lake mining area had a positive effect on stream water

- quality. This conclusion should be viewed as tentative, however, due to the potential effects of temporal variability and differences in hydrologic source areas.
- The presence/absence of temporal variability should be documented prior to synoptic sampling campaigns. If present, the effects of temporal variability can be reduced by employing upstream-to-downstream sampling protocols (e.g. Lagrangian sampling), rather than the commonly used downstream-to-upstream approach. The advantage of upstream-to-downstream sampling should be weighed against the increased potential of sample contamination due to the resuspension of streambed materials.
 - Post-remediation concentrations of Al, Cd, Cu, Pb, and Zn exceed State of Colorado aquatic-life standards over the entire study reach. Further reductions in instream concentrations needed to meet aquatic-life standards may require additional remedial measures, such as the installation of an active treatment system.

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REFERENCES

- Alpers CN, Nordstrom DK, Spitzley J. 2003. Extreme acid mine drainage from a pyritic massive sulfide deposit: the Iron Mountain end-member. In *Environmental Aspect of Mine Wastes, Short Course Series*, vol. 31, Jambor JL, Blowes DW, Ritchie AIM (eds). Mineralogical Association of Canada: Vancouver British Columbia, Canada; 407–430.
- Bencala KE, McKnight DM. 1987. Identifying in-stream variability—Sampling iron in an acidic stream. In *Chemical Quality of Water and the Hydrologic Cycle*, Averett RC, McKnight DM (eds). Lewis Publishers, Inc: Chelsea Michigan, USA; 255–269.
- Bencala KE, McKnight DM, Zellweger GW. 1990. Characterization of transport in an acidic and metal-rich mountain stream based on a lithium tracer injection and simulations of transient storage. *Water Resources Research* **26**: 989–1000.
- Bird DA. 2003. Characterization of anthropogenic and natural sources of acid rock drainage at the Cinnamon Gulch abandoned mine land inventory site, Summit County, Colorado. *Environmental Geology* **44**: 919–932.
- Blevins D, Fairchild J. 2001. Applicability of NASQAN data for ecosystem assessments on the Missouri River. *Hydrological Processes* **15**(7): 1347–1362.
- Bove DJ, Yager DB, Mast MA, Dalton JB. 2007a. Alteration map showing major faults and veins and associated water-quality signatures of the Animas River watershed headwaters near Silverton, southwest Colorado. U.S. Geological Survey, Scientific Investigations Map 2976.
- Bove DJ, Mast MA, Dalton JB, Wright WG, Yager DB. 2007b. Major styles of mineralization and hydrothermal alteration and related solid- and aqueous-phase geochemical signatures. In *Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed*, Professional Paper 1651, Church SE, von Guerard P, Finger SE (eds). U.S. Geological Survey: San Juan County, Colorado; 160–230.
- Brake S, Connors K, Romberger S. 2001. A river runs through it: impact of acid mine drainage on the geochemistry of West Little Sugar Creek pre- and post-reclamation at the Green Valley coal mine, Indiana, USA. *Environmental Geology* **40**: 1471–1481.
- Caruso BS, Cox TJ, Runkel RL, Velleux ML, Bencala KE, Nordstrom DK, Julien PY, Butler BA, Alpers CN, Marion A, Smith KS. 2008. Metals fate and transport modelling in streams and watersheds: state of the science and USEPA workshop review. *Hydrological Processes* **22**(19): 4011–4021.
- CDPHE (Colorado Department of Public Health and Environment). 2000. Regulation no. 31—The basic standards and methodologies for surface water (5 CCR 1002-31), as amended on October 30, 2001. State of Colorado, Denver, Colorado, 58.
- Chapin TP, Nimick DA, Gammons CH, Wanty RB. 2007. Diel cycling of zinc in a stream impacted by acid rock drainage: Initial results from a new in situ Zn analyzer. *Environmental Monitoring and Assessment* **133**: 161–167.
- Finger SE, Church SE, von Guerard P. 2007. Potential for successful ecological remediation, restoration, and monitoring. In *Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed*, Professional Paper 1651, Church SE, von Guerard P, Finger SE (eds). U.S. Geological Survey: San Juan County, Colorado; 1067–1078.
- Foos A. 1997. Geochemical modeling of coal mine drainage, Summit County, Ohio. *Environmental Geology* **31**: 205–210.
- Gammons CH, Milodragovich L, Belanger-Woods J. 2007. Influence of diurnal cycles on metal concentrations and loads in streams draining abandoned mine lands: an example from High Ore Creek, Montana. *Environmental Geology* **53**: 611–622.
- Kilpatrick FA, Cobb ED. 1985. *Measurement of Discharge using Tracers*. Book 3, Chapter A16, U.S. Geological Survey Techniques of Water-Resource Investigations, U.S. Geological Survey; 52.
- Kimball BA, Runkel RL, Gerner LJ. 2001. Quantification of mine-drainage inflows to Little Cottonwood Creek, Utah, using a tracer-injection and synoptic-sampling study. *Environmental Geology* **40**: 190–1404.
- Kimball BA, Runkel RL, Walton-Day K, Bencala KE. 2002. Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA. *Applied Geochemistry* **17**: 1183–1207.
- Kimball BA, Walton-Day K, Runkel RL. 2007. Quantification of metal loading by tracer injection and synoptic sampling, 1996–2000. In *Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed*, Professional Paper 1651, Church SE, von Guerard P, Finger SE (eds). U.S. Geological Survey: San Juan County, Colorado; 417–495.
- Leib KJ, Mast MA, Wright WG. 2007. Characterization of mainstem streams using water-quality profiles. In *Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed*, Professional Paper 1651, Church SE, von Guerard P, Finger SE (eds). U.S. Geological Survey: San Juan County, Colorado; 543–570.
- Mayes WM, Gozzard E, Potter HAB, Jarvis AP. 2007. Quantifying the importance of diffuse minewater pollution in a historically heavily coal mined catchment. *Environmental Pollution* **151**: 165–175.
- McKnight DM, Kimball BA, Runkel RL. 2001. pH dependence of iron photoreduction in a rocky mountain stream affected by acid mine drainage. *Hydrological Processes* **15**: 1979–1992.
- Natural Resources Conservation Service (NRCS), US Department of Agriculture. 2008. *Site Information and Reports for Red Mountain Pass (site no. 713, station ID 07m33s)*. <http://www.wcc.nrcs.usda.gov/snotel/snotel.pl?sitenum=713&state=co>. Cited 29 Sept 2008.
- Nimick DA, Cleasby TE, McCleskey RB. 2005. Seasonality of diel cycles of dissolved trace metal concentrations in a Rocky Mountain stream. *Environmental Geology* **47**: 603–614.
- Owen JR, Anderson C, Simon W. 2007. Effects of mine remediation on water quality and benthic macroinvertebrates in the upper Animas River watershed, southwest Colorado. *Water Resources Impact* **9**(5): 9–13.

- Runkel RL, Crawford CG, Cohn TA. 2004. *Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers*. Book 4, Chapter A5, U.S. Geological Survey Techniques and Methods, U.S. Geological Survey: Reston Virginia, USA; 69.
- Runkel RL, Kimball BA. 2002. Evaluating remedial alternatives for an acid mine drainage stream: Application of a reactive transport model. *Environmental Science & Technology* **36**: 1093–1101.
- Runkel RL, Kimball BA, Walton-Day K, Verplanck PL. 2005. Geochemistry of Red Mountain Creek, Colorado, under low-flow conditions, August 2002. U.S. Geological Survey, Scientific Investigations Report 2005–5101, 78.
- Runkel RL, Kimball BA, Walton-Day K, Verplanck PL. 2007. A simulation-based approach for estimating premining water quality: Red Mountain Creek, Colorado. *Applied Geochemistry* **22**: 1899–1918.
- Runkel RL, Kimball BA, Steiger JI, Walton-Day K. 2009. *Geochemical Data for Upper Mineral Creek, Colorado, Under Existing Ambient Conditions and During an Experimental pH Modification*, August 2005, Data Series 442. U.S. Geological Survey: Reston Virginia, USA; 41 (<http://pubs.usgs.gov/ds/442/>).
- Schemel LE, Cox MH, Runkel RL, Kimball BA. 2006. Multiple injected and natural conservative tracers quantify mixing in a stream confluence affected by acid mine drainage near Silverton, Colorado. *Hydrological Processes* **20**(13): 2727–2743.
- Verplanck PL, Church SE, Smith KE. 2007. *Understanding Contaminants Associated with Mineral Deposits*, Fact Sheet 2007–3079. U.S. Geological Survey: Reston Virginia, USA; 4.
- Whyte DC, Kirchner JW. 2000. Assessing water quality impacts and cleanup effectiveness in streams dominated by episodic mercury discharges. *The Science of the Total Environment* **260**: 1–9.
- Yu JY. 1998. A mass balance approach to estimate the dilution and removal of the pollutants in stream water polluted by acid mine drainage. *Environmental Geology* **36**: 271–276.