THESIS

ACID MINE DRAINAGE IMPACTS IN THE UPPER ARKANSAS RIVER BASIN: A STUDY OF WATER QUALITY, TREATMENT EFFICIENCY, AND PREDICTED LONGEVITY

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ABSTRACT

ACID MINE DRAINAGE IMPACTS IN THE UPPER ARKANSAS RIVER BASIN: A STUDY OF WATER QUALITY, TREATMENT EFFICIENCY, AND PREDICTED LONGEVITY

Mining activity in the Sugarloaf and Leadville mining districts of Leadville, Colorado has impaired water quality in the Upper Arkansas River Basin. Tributary and main channel waters are often out of compliance with state water quality standards, and stream flora and fauna as well as human use of these waterways is threatened by acid mine drainage. This study aims to describe the impact historical mining activity has had on the waters of the Upper Arkansas River Basin by characterizing water quality, analyzing metal removal efficiency from both active and passive treatment sites in the area, and estimating the time it will take for drainage from mining tunnels to naturally comply with state water quality standards.

A comparison of instream dissolved concentrations of cadmium, copper, iron, lead, manganese, and zinc to state water quality standards shows waters of the Upper Arkansas River Basin are often out of compliance with chronic and/or acute standards. This is seen more frequently upstream from treatment sites and higher up in the tributary system than at tributary mouths or in the main channel of the Arkansas River. An examination of metal removal from the Leadville Mine Drainage Tunnel and Yak Tunnel water treatment plants along East Fork and California Gulch shows dissolved metal reduction between 33 and 100 percent compared with 0 to 84 percent at the passive Dinero Wetland Complex along Lake Fork. Finally, an analysis of projected longevity highlights the importance of clean-up plans for future mining projects with estimated impaired water quality continuing upwards of 2000 years at Yak Tunnel.

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1. INTRODUCTION

Contamination from mining waste is a part of hard rock mining's legacy and dates back to the Roman Empire (Robb and Robinson, 1995). Mine waste contamination is most commonly associated with water quality degradation as a result of acid rock drainage from flooded mine voids and from tailings and spoil heaps that are hydrologically connected to surface water. Contamination may persist for many decades or centuries and occurs at both active and abandoned mines (Younger, 1997; Wood, *et al.*, 1999; Younger, 2000; Demchak et al. 2004).

In the United States there are over 557,650 abandoned mines (Garavan et al., 2008 as cited by Cidu, 2011) and approximately 20,000 kilometers of streams and rivers are impacted by acid mine drainage—the majority of which receive effluent directly from abandoned mines (Skousen, 1995). In the Rocky Mountain region of Colorado, 18,382 abandoned mines and related features are identified on National Forest System lands (Sares *et al*., 2000). Total Colorado stream length impacted by abandoned mine lands in 2010 has been estimated at 908 kilometers (*Colorado Water Quality Assessment Report*) including at least 102 kilometers in the Upper Arkansas River Basin (*Watershed Quality Assessment Report*).

1.1. Acid Rock Drainage/Acid Mine Drainage Chemistry

Acid rock drainage results when sulfide rich minerals, most commonly pyrite, are exposed to oxidizing conditions and water. When these conditions are associated with metal or coal mining it is referred to as acid mine drainage. If water and/or air are removed from the acid producing drainage system, pyrite oxidation and subsequent acidification will cease (Skousen, 1995). Acid rock drainage tends to produce very small amounts of acidity in natural systems;

this is often neutralized in the environment (Skousen, 1995). In mining environments however, disturbance to the area resulting in increased surface area of an ore-containing body and the potential for increased hydrologic interaction with ore body creates more persistent acidity. Acid mine drainage continually threatens the surrounding environment, with drainage from surficial mines having a lesser impact than that from underground mines (Wood *et al*., 1999).

Documentation on mine discharge longevity is sparse and it is debated whether, depending on the mining environment, acid mine drainage could cease within the first 10 to 20 years after mine closure (Demchak *et al*., 2004) or persist for many decades or centuries (Younger, 1997; Cidu 2011). Acid generation occurs from water ingress into or through surficial workings, tailings, and spoil heaps, as water floods mine voids after pumping ceases, and in the zone of seasonal water table fluctuations.

The acidity in acid mine drainage is both hydrogen ion acidity, due the release of hydrogen ions into solution as pyrite or other metal-sulfides dissolve, and mineral acidity, or the acidity produced by mineral acids, which are lower in pH that what is obtained by aqueous carbon dioxide alone. The mineral acidity depends upon the metal sulfide in the rock but is commonly sulfuric acid from metal sulfides such as copper, iron, or zinc sulfides (Skousen, 1995; Bleam, 2012). Acid production is a self-perpetuating cycle as the acidic solution weathers the oxidized sulfide mineral surface, exposing a fresh face for new oxidation to occur. This oxidation releases mineral acids as well as hydrogen ions into solution, thus lowering pH or maintaining an acidic solution. Most acid mine drainage is characterized by a very low pH with high sulfate and iron concentrations (Skousen, 1995); there may also be high concentrations of other metals (Al, Mn, Pb, or Cd) depending on the specific ore.

Acid production in flooded voids is thought to have a finite life span because oxygen is depleted where void spaces become permanently flooded (Demchak *et al*., 2004). The decrease of acid mine drainage production from flooded mine voids is thought to be exponential where contaminant concentrations are assumed to halve during each time period of mine pool turnover (Glover, 1983 as cited by Demchak *et al*., 2004). The "first flush" stage of flooded mine voids for acid mine drainage represents vestigial acidity from the initial inundation of the abandoned workings (Younger and Banwart, 2002); the extreme longevity of acid mine drainage is then produced by the following "juvenile acidity" that results from ongoing pyrite oxidation in the zone of water table fluctuation (Younger, 1997).

1.2. Mining in Leadville and Water Quality Standards

Major metals produced in the Colorado mountain province are molybdenum, gold, silver, lead, and zinc; the chief mining products of Leadville are silver, zinc, lead, gold, and copper (Tweto, 1968) and silver, zinc, lead, and minor amounts of gold in the Sugarloaf District (Singewald, 1955). Leadville, Colorado is located within the upper Arkansas River watershed, and many of the headwater tributaries to the Arkansas River are located in and around Leadville. Mining in Leadville began in 1860 with the discovery of gold in California Gulch. As gold became depleted mining drastically diminished until the discovery of silver ore brought a second mining boom to the district in 1877 (Bureau of Reclamation, 2008). Mining has persisted on and off throughout history in Leadville. Sugarloaf District veins were discovered in the 1880s and had maximum output until 1893 when silver prices significantly decreased (Singewald, 1955). Unlike most mines in the area which had sporadic or semi-regular production until the first

World War, the Dinero Mine in the Sugarloaf District was in continuous operation until the 1920s (Singewald, 1955).

The Leadville Mining District has the Leadville Mine Drainage Tunnel that drains into the East Fork of the Arkansas River, and Yak Tunnel which drains into California Gulch—an intermittent tributary to the Arkansas River (Bureau of Reclamation, 2008). The Sugarloaf Mining District includes the Nelson Tunnel, Tiger Tunnel, and Dinero Tunnel. These tunnels drain abandoned mines in the area and eventually drain into Sugarloaf Gulch, a tributary to Lake Fork Creek, which then drains into the Arkansas River (Stratus Consulting Inc, 2009).

The table value standard equations provided by the Colorado Department of Public Health and Environment are designed to maintain the established beneficial use of a given stream segment. The Upper Arkansas River is classified for Agriculture, "these surface waters are suitable or intended to become suitable for irrigation of crops grown in Colorado and which are not hazardous as drinking water for livestock;" Aquatic Life Cold 1, "these are waters that (1) are currently capable of sustaining a wide variety of cold water biota…or (2) could sustain such biota but for correctable water quality conditions;" and Recreation class E, "these surface waters are used for primary contact recreation or have been used for such activities since November 28, 1975" (CDPHE, 2014a). Many stream segments of the Upper Arkansas River fall out of compliance with water quality standards and are on the 303(d) list for impaired water bodies. Section 303(d) of the Clean Water Act requires states to list their impaired water bodies that do not meet water quality standards for their given beneficial uses (CDPHE, 2011). In the case of some Upper Arkansas River tributaries like California Gulch, metal standards have been removed from the water quality standards because the bodies are so continually out of compliance (Johnson, per. comm., 2013, CDPHE, 2014b). However, the main body of the

Upper Arkansas River still must be in compliance with beneficial use water quality standards so treatment and dilution of these heavily contaminated sources is hoped to reduce contaminant concentrations.

1.3. Remediation Efforts

Active treatment through chemical dosing is usually needed to keep mine effluent within water quality standards during the first few years after mine closure and complete void flooding (Younger, 2000). However in Leadville, the mine drainage being treated is far past the initial closure stage; much of the mining there ceased before the 1900s with only a few mines remaining open after the 1920s and 1940s (Singewald, 1955). Considering the longevity of contaminated discharge from underground mines in Leadville, passive treatment options that utilize natural energy sources, like gravity, flow gradients, and microbial energy, may be more ecologically responsible than active treatment in the long run (Younger, 2000). In treating aboveground contamination, hydrologic intervention between water sources and ore containing rock may be a suitable option (Younger, 2000); though there may yet be need for active treatment if the passive treatment and hydrologic intervention put in place fail to bring water quality to state standards.

The most common mine flow treatment is direct or active treatment using traditional wastewater treatment plants and processes, like chemical dosing and accelerated settling of colloids. These treatment systems inject basic chemicals, most commonly calcium carbonate, calcium hydroxide, sodium carbonate, sodium hydroxide, and/or ammonia, into mine water effluent to raise pH and allow for metal precipitation (Skousen, 1995). The chemical used for dosing depends upon the pH required to precipitate the particular chemicals at any given mine;

for example, ferric iron converts to ferric hydroxide and precipitates at pH greater than 5.5 while ferrous iron converts to ferrous hydroxide and precipitates at pH greater than 9.0, and soluble manganese precipitates out as insoluble manganese at pH 10.0 (Skousen, 1995). For treatment, carbonate compounds only raise pH to 8.5 while hydroxide can raise pH to greater than 10.0 and ammonia addition can raise pH to 10.5 or 11 (Skousen, 1995). These treated waters are then directed to a settling basin to allow time for the metals to precipitate out before continuing through to the watershed. Sometimes active treatment requires an improvement to colloid settling efficiency if residence time in the settling basin does not allow for enough metal removal. In this case coagulation, flocculation, and oxidation stages are included in the active treatment system (Skousen *et al*., 1995). Alkaline reagents like aluminum sulfate are added to improve metal coagulation and activated silica is commonly added to improve flocculation; in both instances metals combine to form larger particles through attraction or adsorption thus allowing for increased settling rates (Skousen *et al*., 1995). Oxidation, or aeration of the treated water, is used to allow for metals to precipitate out of solution at a lower pH than would be required in a lower oxidative state (Skousen *et al*., 1995).

These types of active treatment for contaminated runoff provide rapid results and are effective in a large range of flow conditions. The addition of these chemicals requires proper storage and dispersal equipment, regular maintenance, and may require transport flumes or mixing cells for maximum efficiency (Means, 2006). Direct treatment is the most effective in ensuring there is minimal to no impairment of receiving water bodies; however it can be highly time and labor intensive and is not cost effective (Perry and Kleinmann, 1991; Demchak and McDonald, 2004; Wiseman *et al*., 2004; Whitehead and Prior, 2005; Cravotta, 2010, Gilbert *et al*., 2011). Common treatment steps for acidic, iron rich drainage characteristic of acid mine drainage include oxidation to convert highly soluble ferrous iron to the less soluble ferric form, alkali dosing to raise pH and lower metal solubility, and accelerated sedimentation of metals using flocculants or coagulants (Younger, 2000). Active treatment is not considered to be sustainable for long term treatment because of the high installation, labor, maintenance, and chemical costs (Skousen *et al*., 1995).

Passive treatment is an alternative to active treatment, and can be more cost effective than active treatment given the length of time that mine drainage persists. Passive treatment involves the use of natural energy sources like gravity induced flow along topographic gradients, photosynthesis, or microbial energy (Younger, 2000). Initial costs can be high for establishing passive treatment systems like constructed aerobic or anaerobic wetlands, limestone reactors, or limestone bedded transport channels; however long term maintenance costs are not as expensive as the chemicals, labor, and maintenance that would be required for active treatment at the same site (Perry and Kleinmann, 1991; Demchak and McDonald, 2004; Whitehead and Prior, 2005; Gilbert *et al*., 2011, Wei *et al*., 2011). Downsides to passive treatment are that each treatment system must be designed for the specific characteristics of a site, and they are only fully effective at the most common flow conditions (Robb and Robinson, 1995; Walton-Day *et al*., 2005; Nordstrom, 2011). Even with the disadvantage of high flows limiting hydraulic residence time in a passive system, the use of chemicals to directly treat only the occasional high flow event would still allow the passive system to be more cost effective for the entire lifespan of impaired water quality from mine effluent. Finally, passive systems are self-sustaining to some degree and can be integrated with the natural ecosystem unlike active treatment plants (Younger, 2000).

Hydrologic intervention involves minimizing hydrologic connectivity of storm flows and waterways with surface workings, tailings, and spoil piles. One such intervention is to cover exposures with a soil or geologic cap. A successful cap layer includes a coarse-grained, capillary break layer that prevents water in the ore containing piles from seeping out and an overlying low permeability layer that is often covered with vegetated topsoil to prevent additional infiltration (Younger, 2000). This does not always successfully disconnect waste materials from the surrounding hydrology and sometimes, given close proximity to water courses, more drastic intervention is necessary. Strategic diversion of flow paths through areas of known infiltration can help eliminate the acidic contribution of mine wastes to their surrounding environment. Also, full excavation of waste rock, either to a landfill or a location where capping would be successful, will eliminate the acid drainage from surface sources (Stratus Consulting Inc., 2009).

While active treatment systems tend to be most effective in treating long term acid mine drainage, they are not economically responsible systems for the entire life span of mine drainage due to high maintenance, operation, and chemical costs (Perry and Kleinmann, 1991; Robb and Robinson, 1995; Younger, 2000). Though there is sometimes a trade off in treatment efficacy with passive systems, the diminished long term costs of treatment is highly desirable. If passive treatment options can work for treating some of the acidic drainages in Leadville, Colorado, they may be more practical and beneficial options for treating other mine drainages in the area.

Both active and passive treatment systems are in place to treat acid mine drainage in the Upper Arkansas River Basin. This drainage is generated from several abandoned mine sites in Leadville, Colorado, including the Leadville and Sugarloaf mining districts. Treatment sites at different mine tunnel locations in Leadville include active systems at the Leadville Mine Drainage Tunnel (LMDT) Water Treatment Plant on the East Fork of the Arkansas River and Yak Tunnel Water Treatment Plant on California Gulch, and a passive treatment system at Dinero Tunnel upstream from Lake Fork.

1.4. Purpose Statement

The purpose of this research is to investigate the effect abandoned mine lands in and around Leadville, Colorado have on water quality in the Upper Arkansas River Basin. This is accomplished by characterizing water quality in the area, describing the efficiency of metal treatment for the remedial efforts in place, and estimating the duration in which contaminated mine drainage could impact the upper Arkansas River. The contaminants of concern in this study area include cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), and zinc (Zn) (Rowe, 1994; Neopane, 1997, Stratus Consulting Inc, 2010). Characterizing water quality in the Upper Arkansas River Basin provides a better understanding of basic water quality criteria like discharge, pH, electrical conductivity, and hardness as well as metal concentrations in the basin. Analyzing dissolved metal concentrations upstream and downstream from treatment in both active treatment systems and one passive treatment system displays the efficiency of the specific treatment and allows further understanding as to whether treatment satisfies state water quality standards. Finally, estimating the amount of time in which impaired drainage waters may enter the Arkansas River system creates a treatment framework by proposing an amount of time in which treatment must be provided.

1.5. Hypothesis/Objectives

Is water quality in the Upper Arkansas River Basin (UARB) impaired from acid mine drainage even with implementation of remediation efforts? To determine if active and passive treatment systems bring water quality in the UARB up to water quality standards the following objectives are investigated:

1. Characterize the water quality in the UARB.

1a. Spatially characterize general water quality and metal concentrations in the UARB and determine if they meet state water quality standards.

1b. Relate characterizations to remediation treatment sites.

2. Calculate removal efficiencies for pollutants of concern (Cd, Cu, Fe, Pb, Mn, and Zn) at each treatment site.
3. Calculate an estimated longevity of impaired acid mine discharge from upstream from treatment drainage sites.

2. METHODS

2.1. Site Description

Arkansas River headwaters originate in the Mosquito and Sawatch Mountain Ranges in Lake County, Colorado (Figure 1, Industrial Economics, Inc., 2006). In the valley between these mountain ranges, the Arkansas River receives waters from both perennial and intermittent drainages, including many tributaries draining the mining districts of Leadville, Colorado (Industrial Economics, Inc., 2006). Tributaries studied include the East Fork of the Arkansas River, California Gulch, and Lake Fork near Leadville, Colorado.

The Upper Arkansas River Basin in Leadville, Colorado has many abandoned mine sites and drainage tunnels that funnel mine drainage to surface waters (Industrial Economics, Inc., 2006). Tributaries to the Arkansas River that receive treated mine drainage water include the East Fork of the Arkansas River, California Gulch, and Lake Fork (Figure 1). There are portions of tributaries upstream of mine sites that have pristine water flowing in them, and other tributaries downstream of the treatment effluent that deliver pristine waters to the Arkansas River. For the purpose of this paper, pristine waters are defined as waters showing limited impairment to water quality from acid mine drainage in that water quality standards for dissolved metals are not exceeded.

The East Fork of the Arkansas River drains directly into the Arkansas River with the Leadville Mine Drainage Tunnel (LMDT) located upstream from the Arkansas River confluence. The East Fork of the Arkansas River has pristine waters above the LMDT that, along with drainage from the LMDT, flow into the Leadville Mine Drainage Tunnel Water Treatment Plant located below the mine drainage tunnel; this is an active an active treatment plant that runs continuously (Bureau of Reclamation, 2008).

California Gulch is a historically ephemeral tributary south and downstream of the East Fork of the Arkansas that drains into the Arkansas River (Stratus Consulting Inc., 2009). The Yak Tunnel mine tunnel as well as the Yak Tunnel Water Treatment Plant are located along California Gulch. While the Leadville Mine Drainage Tunnel Water Treatment Plant on the East Fork of the Arkansas River is in continuous operation, the facility on California Gulch is not (Stednick, 2013). During Yak Tunnel Water Treatment Plant operation, flow in California tends towards perennial due to treatment plant discharge (Stratus Consulting Inc., 2009). This active treatment facility receives waters from the Yak Tunnel and discharges treated water to California Gulch. California Gulch has degraded water quality above the treatment plant but any flow that is not directly from Yak Tunnel bypasses Yak Tunnel Water Treatment Plant and flows on through California Gulch to the Arkansas River.

Downstream from the California Gulch confluence, Lake Fork discharges into the Arkansas River. Pristine waters from Turquoise Lake drain into Lake Fork which also receives effluent from natural and designed passive treatment sites. Sugarloaf Gulch, a tributary to Lake Fork, receives waters from Dinero Tunnel, an old mine tunnel which discharges contaminated waters to both a natural beaver pond wetland and constructed wetland/bioreactor, referred to as the Dinero Wetland Complex in this project. These wetlands then drain down Sugarloaf Gulch and meet with Lake Fork before flowing into the Arkansas River (Stratus Consulting Inc., 2009).

2.2. Data Source and Assumptions

Water quality data are provided by Tetra Tech (Tetra Tech, 2015) for each of the study sites in the UARB, these data include each study site used for this research project. The database is a collection of sampling data taken in the UARB from multiple different sources (e.g. Colorado State University, Bureau of Land Management, Environmental Protection Agency, and more) that has been compiled by Tetra Tech. Sites are chosen in association with each treatment location. Each treatment location has sites selected to represent waters characteristic of untreated and treated acid mine drainage waters, or waters upstream and downstream from treatment sites respectively, as well as waters characterizing tributary mouths where available and waters characterizing the main channel of the Arkansas River downstream from tributary confluence.

The Leadville Mine Drainage Tunnel outlet is located along the East Fork tributary of the Arkansas River. Waters upstream from the Leadville Mine Drainage Tunnel inlet are assumed to represent untreated mine drainage characteristic of mines being drained by the Leadville Mine Drainage Tunnel. These sites are collectively referred to as Stray Horse Gulch or SHG and include the sites SG-1, SHG07, SHG07A, SHG08, SHG09, SHG09A, SHG1, and SHG10. The locations for the above mentioned sites collectively representing SHG are described respectively as Stray Horse Gulch above Culvert Inlet, Upper Stray horse Gulch at Adelaide Park, Stray Horse Gulch, Stray Horse Gulch at diversion culvert at downstream edge of Mikados Retention Pond, Stray Horse Gulch 300 feet below Emmett retention pond, Parshall Flume in lower Stray Horse Gulch above 5th Street headwall, SHG1, and Stray Horse Gulch.

Waters downstream from the Leadville Mine Drainage Tunnel Water Treatment Plant are assumed to represent the characteristics of treated waters associated with mines drained by the Leadville Mine Drainage Tunnel. These sites are referred to as EF-2/3 and represent EF-2, East

Fork Arkansas River at Highway 24 Bridge and EF-3, East Fork Arkansas River at Highway 24 USGS gage. There are no sites available between EF-2/3 and the mouth of East Fork so there is no tributary mouth site associated with the Leadville Mine Drainage Tunnel Water Treatment Plant and East Fork. AR-1, the Arkansas River upstream of confluence with California Gulch, is the nearest site below the East Fork and Arkansas River confluence and is assumed to represent waters characteristic of main channel Arkansas River downstream from the East Fork and Leadville Mine Drainage Tunnel Water Treatment Plant.

The Yak Tunnel mine drainage tunnel outlet is located along the California Gulch tributary to the Arkansas River. Unlike the SHG sites, there are no sites provided above the Yak Tunnel inlet in the provided database. Therefore site CG-1, California Gulch immediately upstream of the Yak Tunnel Portal, is assumed to represent water characterizations associated with the mine waters drained by the Yak Tunnel. CG-2, California Gulch just downstream from Yak Tunnel Water Treatment Plant discharge is assumed to represent waters in California Gulch after treatment at the Yak Tunnel Water Treatment Plant. Waters at the mouth of California Gulch are assumed to be represented by site CG-6, California Gulch immediately upstream of confluence with Arkansas River. Finally waters characteristic of the main channel of the Arkansas River downstream from California Gulch and the Yak Tunnel Water Treatment Plant are assumed to be represented by site AR-3A, Arkansas River approximately 0.5 miles downstream of confluence with California Gulch.

The Dinero Wetland Complex is located along Sugarloaf Gulch, a tributary to Lake Fork. This complex receives waters from Dinero Tunnel then discharges into Lake Fork, a tributary to the Arkansas River. A collection of sites, collectively referred to as SL Up, are assumed to represent waters characteristic of those associated with Dinero Tunnel mine drainage waters.

These sites include SL5A, SL6, SL7, SL7A, and SL9, described respectively as: Sugarloaf below tailings (1), Sugarloaf below tailings (2), Sugarloaf above tailings, Sugarloaf below tailings (3), and Sugarloaf HW Tailings. SL11, Sugarloaf Gulch at Lake Fork, referred to as SL Down in this report, is assumed to represent waters characteristic of those that have passed through the Dinero Wetland Complex. Waters at the mouth of Lake Fork are assumed to be represented by the site LF-1, Lake Fork immediately upstream of the confluence with the Arkansas River. Waters in the main channel of the Arkansas River downstream from the Lake Fork confluence and Dinero Wetland Complex are assumed to be represented by site AR-4, Arkansas River approximately 0.5 miles downstream of confluence with Lake Fork.

In addition to assumptions about site representativeness, not all of the data entries are measured values; there are a series of qualifiers used by the reporting laboratories to identify interpreted lab data (Table 1). Values that are reported but below the method detection limit or between the method detection limit and practical quantitation limit may be treated in several different ways. It is common for these values to be treated as a zero, to be treated as the actual detection limit value, or to be treated as a value between zero and the detection limit--frequently as half of the reported value; this provides usable data with values or concentrations lower than what is initially reported (Gilbert, 1987). For the purposes of this study, data with lab qualifiers are treated as the reported value. Doing this gives higher metal concentrations than would be used if the reported value were halved or treated as zero thus providing an additional margin of safety. Analyzing for higher concentrations in the UARB gives a greater margin of safety in analyzing whether metal concentrations are in compliance with state water quality standards up- and downstream from mine drainage treatment, though it has the potential to overemphasize water quality impairment.

2.3. Water Quality Characterization

Water quality is characterized by stream discharge, pH, hardness, and electrical conductivity and by determination of metal concentrations and water quality standards for each study site. Metal concentration calculations are taken from dissolved metal concentrations for this study as the Colorado Department of Public Health and Environment's Water Quality Control Commission has determined that "standards for most metals should be expressed as dissolved" form instead of total recoverable form (CDPHE 2014b). Many water quality parameters and metal concentrations reported throughout this paper are in the form of mean annual value. This was determined by compiling provided data for each studied parameter by month for each study site, taking the mean value of each month's data, then taking the mean of all monthly means for each site.

Water quality standards for metals are from the table value standard equations provided by the Colorado Department of Public Health and Environment (CDPHE 2014b, Table 2). Acute metal standards represent the constituent concentration that is lethal to 50 percent of the population during the time period in which a single sample is collected or the average of samples collected in a one day period; chronic metal standards represents the concentration that should not be exceeded for a representative sample or average of samples in a 30-day period while protecting 95 percent of the population from toxic effects (CDPHE 2014b). Water quality standards are calculated using hardness for each metal except iron. According to the Colorado Department of Public Health and Environment, the hardness used to determine table value standard metal concentrations "should be based on the lower 95 percent confidence limit of the mean hardness value at periodic low flow criteria as determined from a regression analysis of site-specific data… Where a regression analysis is not appropriate, a site-specific method should be used" (CDPHE 2014b). In lieu of conclusive results from a regression analysis at selected sites, median hardness values are used for a site-specific method of table value standard determination (Stednick 2013).

The hardness value used is not to exceed 400 mg/L $CaCO_3$, (CDPHE 2014b) this exceedance occurs at two study sites, CG-2 and CG-6 (Table 4). Due to this exceedance, water quality standards at these two sites are therefore determined using the maximum allowable hardness of 400 mg/L $CaCO_3$. No hardness data are available at SL Up or SL Down so water quality standards are not calculated at these sites. An approximation of SL Up and SL Down compliance is gleaned by comparing metal concentrations at these sites to the standards from the CG-1 site. Electrical conductivity seen at both SL Up and SL Down is most closely equal to CG-1 electrical conductivity values (Figure 7), and the relationship between electrical conductivity and hardness shows a positive linear correlation (Figure 6).

The Upper Arkansas River has designated beneficial use classes of Agriculture, Aquatic Life Cold 1, and Recreation E. Waters with this beneficial use class must have a pH between 6.5 and 9.0, and metal concentrations in each river segment must not exceed allowable concentrations for arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc (Table 2). There are two sets of table value standards for the UARB; one for all tributaries to the Arkansas River and the main channel of the Arkansas River above California Gulch and one for the main channel of the Arkansas River below the confluence with California Gulch (CDPHE 2014b). However, the standard equations only differ for chronic cadmium concentrations (Table 2). It is important to note that California Gulch, a tributary to the Arkansas River, has been so consistently out of compliance with water quality standards that it no longer has water quality control on metal concentrations (Johnson, per. comm., 2013); for the purposes of this report, water quality in California Gulch is held to the same water quality standards as other tributaries in the UARB.

2.4. Treatment Removal Efficiency

Removal efficiency compares the metal concentration upstream from treatment (C_{in}) with the metal concentration downstream treatment (C_{out}) (Broadwell 2001):

$$\% \text{ Removal} = [(C_{in} - C_{out})/ C_{in})] * 100 \qquad \text{(Equation 1)}$$

where

C_{in} is the concentration in the influent

C_{out} is the concentration in the effluent

To determine removal efficiency metal concentrations from upstream and downstream sampling sites at the Leadville Mine Drainage Water Treatment Plant, the Yak Tunnel Water Treatment Plant, and the Dinero Wetland Complex are used. Data for this analysis have been partitioned where constituent measurements are only used from days where there are recorded measurements from both the up- and downstream of treatment sites, this is done to capture the closest representation of actual removal efficiency among study sites. The LMDT Water Treatment Plant went online in March 1992, and the Yak Tunnel Water Treatment Plan also went online in 1992 (Bureau of Reclamation, 2008). Below the Dinero Tunnel is an existing wetland/beaver pond complex that has been impacted by the drainage from the tunnel. Additional work at Dinero Wetland Complex was completed in 2004 when two large waste piles were relocated and capped with limestone-lined settling ponds placed in the areas where the waste piles once were. Installation of a bulkhead was also completed in September 2009 to reduce the flow of acidic mind drainage to the wetland (Stratus Consulting Inc. 2009). Data for the up- and downstream LMDT and Yak Tunnel sites are divided where only data post-treatment initiation are used in the analyses of metal treatment. The Dinero Wetland Complex does not have a distinction of treatment initiation due to the nature of the area prior to additional waste removal and reduction.

2.5. Mine Drainage Longevity

A two-step analysis will be utilized to estimate the longevity of acid mine drainage. Metal concentrations in underground mining follow an exponential decay with a half-life equal to the time required to fill all mine void space and turnover (Glover, 1983 as cited by Demchak *et al*., 2004). This period, often referred to as the first flush (or vestigial acidity), may not be captured or adequately represented by the data period of record as the study sites closed well before data collection began (Younger, 1997). However, as the rate of exponential decay remains constant throughout time, the average concentration of each constituent from the beginning and end of the period of record can be used to estimate decay constants (Equation 3). The decay constant can then predict the amount of time required for metal concentrations to meet water quality standards at a site (Equation 4).

Following this stage of acidic drainage would be juvenile acidity (Younger, 1997), the persistence of which tends be near asymptotic levels and depends upon mine void system hydrology and sulfide content of the remaining ore body. As exponential decay continues, constituent concentrations eventually become asymptotic and water table fluctuations in the mine pool may lead to an indefinite persistence of metals in mine drainage waters (Younger, 1997).

To determine the amount of time needed for constituents to reach asymptotic concentrations data from upstream of the wastewater treatment plant along California Gulch

(CG-1) will be used; it is important to use metal concentrations in untreated waters so the results are tailored to metal concentrations in drainage waters instead of treated waters. As this analysis aims only to show a prediction of contaminated drainage persistence representative of the study area, analysis is only performed at California Gulch; this site has the most robust data for analysis as it has the longest period of record of all study sites upstream from treatment and is comprised of only one sample site rather than a merger of sites. Heavy metal concentrations reported at this site are most representative of acid mine drainage metal concentrations in the area as no treatment has yet occurred. With metal concentrations from the start and end of the period of record, the decay constant for each constituent can be determined using the following equation:

$$C(t) = C_0 e^{-kt} \qquad \text{(Equation 2)}$$

rearranged to

$$k = -\left(\ln\left(\frac{C(t)}{C_0} \right) \Big/ t \right) \qquad \text{(Equation 3)}$$

where

C(t) is the concentration at time t

C_0 is the initial/first recorded concentration

t is the time of flushing in days

The time required for metal concentrations to reach water quality standards can then be determined using the following equation:

$$t = -\left(\ln\left(\frac{C(t)}{C_0} \right) \Big/ k \right) \qquad \text{(Equation 4)}$$

where

$C(t)$ is the water quality standard concentration

C_0 is the initial/first recorded concentration

k is the decay constant determined using Equation 3

For this analysis, C_0 and $C(t)$ are calculated using the average values for each constituent during the first three years of record between 1994 and 1996, and the final three years of record between 2009 and 2011 in order to better eliminate outliers and properly represent the data trends. The period of record for establishing the decay constant in this analysis is 15 years, from 1995 to 2010. Ten percent minimum and maximum error bounds are added for each metal to provide for a margin of error in the analysis. To calculate minimum and maximum boundaries, the decay constant calculated for each constituent remained the same but the initial and final concentrations are altered by positive or negative 10 percent. The time required for contaminant concentrations to meet water quality standards can vary for each constituent at a treatment site (data analysis from Cidu, 2011), therefore the maximum time required to treat mine effluent will correlate to the constituent with the lowest decay constant. If a contaminant's asymptotic concentration does not meet water quality standards, some form of treatment would be required for the waters to be in compliance.

3. RESULTS

3.1. Water Quality Characterization

Water quantity, or the discharge measured at a sample site, generally increases as distance from the source increases, as watershed drainage area increases. This is seen at each study tributary as flow increases moving down each tributary (Table 4, Figure 2). Upstream from the Leadville Mine Drainage Tunnel Water Treatment Plant at SHG mean annual discharge is 0.79 cfs. After these waters flow through the Leadville Mine Drainage Tunnel with other waters drained by the tunnel and go through the treatment process they join in with the East Fork and total flow volume increases to 41 cfs at EF-2/3. This increase also occurs along California Gulch with a mean annual increase in discharge from 0.6 to 1.7 cfs up and downstream of the Yak Tunnel Water Treatment Plant. Discharge continues to increase down California Gulch with a mean annual discharge of 2.4 cfs at CG-6 at the mouth of California Gulch. Sugarloaf Gulch and Lake Fork exhibit this increase in flow through the tributary system as well where mean annual discharge increases from 0.91 to 1.1 cfs up- and downstream from treatment in the Dinero Wetland Complex, and continues to increase as Sugarloaf Gulch flows into Lake Fork where mean annual discharge is 47 cfs at LF-1. Water quantity increase with distance from source is also seen in the main channel of the Arkansas River as mean annual flow increases from 72 cfs at the first sampling site in the Arkansas River (AR-1) to 121 cfs at the final sampling site (AR-4) (Table 4).

pH is a representation of proton activity in a solution, a higher pH represents less proton activity while a lower pH indicates higher proton activity (Brezonik and Arnold, 2011). Mean annual pH is within the acceptable range of 6.5 to 9.0 at each tributary mouth and main channel sampling site but falls below this range for some of the sites associated with treatment complexes (Table 4). Mean annual pH above the Leadville Mine Drainage Water Treatment Plant at SHG is 4.78; mean annual pH does increase downstream from treatment to 7.75 at EF-2/3. Treatment in California Gulch is not enough to bring mean annual pH within the acceptable range with an upstream from treatment pH of 4.97 at CG-1 increasing only to 6.15 at CG-2 downstream from the treatment plant. pH is not raised to within water quality standards from treatment at the Dinero Wetland Complex either where mean annual pH increases from 3.76 above the wetland complex to 4.36 below the complex. While pH does not meet water quality standards downstream from treatment by Yak Tunnel Water Treatment Plant and the Dinero Wetland Complex, pH continues to increase downstream from these sites and is in compliance by the time flow exits each tributary. Mean annual pH does not exceed the allowable range during the entire period of record, though there are instances where reported pH values exceed 9.0 at 3 of the 11 sites: AR-1, CG-6, and AR-4. There are also instances were pH measurements drop below the lower standard limit of 6.5 at all 11 sites (Table 4, Figure 3).

Water hardness is a measure of the divalent cations in the water including forms of iron, manganese, zinc, and copper (Brezonik and Arnold, 2011)—each a metal of concern from mining activity in the basin. Hardness at study sites can increase or decrease downstream from treatment (Table 4). Mean annual hardness decreases downstream from treatment at the Leadville Mine Drainage Tunnel Water Treatment Plant from 192 mg/L $CaCO_3$ at SHG above the treatment facility to 125 mg/L $CaCO_3$ at EF-2/3 downstream. Hardness continues to decrease downstream from where the East Fork flows into the Arkansas River with a mean annual hardness of 95 mg/L $CaCO_3$ at AR-1. Hardness increases downstream from treatment at the Yak Tunnel Water Treatment Plant along California Gulch. Mean annual hardness at CG-1 prior to treatment at Yak Tunnel is 236 mg/L $CaCO_3$ and increases to 826 mg/L $CaCO_3$ below treatment at CG-2. Mean annual hardness decreases to 456 mg/L $CaCO_3$ at CG-6 at the mouth of California Gulch and again to 121 mg/L $CaCO_3$ at AR-3A downstream from the confluence of California Gulch and the Arkansas River. Hardness data are not available for SL Up and SL Down sites up and downstream from the Dinero Wetland Complex on Lake Fork. However mean annual hardness increases from 38 mg/L $CaCO_3$ at the mouth of Lake Fork to 73 mg/L $CaCO_3$ in the Arkansas River at AR-4 downstream from the Lake Fork confluence.

Electrical conductivity, or specific conductance, is a measure of the electric carrying capacity of a solution (Brezonik and Arnold, 2011). Electrical conductivity has a positive correlation with hardness in the Upper Arkansas River Basin (Figure 6) and shows similar trends with hardness because of this correlation. Just as is seen with hardness, electrical conductivity and discharge have an inverse relationship where high conductivity measurements correlate to lower discharge measurements and low conductivity measurements correlate to higher discharge measurements.

3.2. Metal Concentrations and Water Quality Standards

The overall trend seen amongst reported dissolved metal concentrations is a decrease with increased distance downstream from mine tunnel source along each tributary. The highest concentrations are reported upstream from treatment sites, these then decrease downstream from treatment and again at the tributary mouth. In some instances metal concentrations are again lower below confluence with the main channel, but in other cases concentrations increase in the Arkansas River. An exception to this pattern occurs along California Gulch where waters at the tributary mouth, site CG-6, have higher reported concentrations for iron and manganese than what are reported downstream from treatment at CG-2 (Figures 8-13).

When comparing water quality degradation between the three mine tunnels, or upstream from treatment sites, Yak Tunnel at CG-1 has the highest reported dissolved concentrations for most of the studied metals, followed by the LMDT at SHG, and then the Dinero Tunnel at SL Up (Figure 8-13). This pattern breaks for zinc where concentrations reported at each drainage tunnel are equivalent (Figure 13), and manganese where concentrations reported from the Dinero Tunnel exceed those reported at the other two tunnels, and Yak Tunnel has the lowest reported dissolved manganese concentration (Figure 12).

The occurrence of water quality standard exceedances follows a similar trend as what is seen with dissolved metal concentrations in that exceedance of the standard decreases with distance from tributary mine tunnel source. There are two causes for this decrease in standard exceedance: decreases in dissolved metal concentration moving through each tributary system and in some cases increases in the water quality standard as hardness increases throughout the tributary system (Figures 8 to 13 and Table 2).

3.3. <u>Treatment Removal Efficiency</u>

Positive removal efficiencies indicate a reduction in metal concentration during the treatment process. Dissolved metal concentrations for each studied metal are lower at each of the three downstream from treatment sites than the associated upstream from treatment site with the exception of lead at the Dinero Wetland Complex, for which all values reported for the analysis are listed as below the method detection limit (Table 6). However once removal efficiencies are adjusted to account for the change in discharge downstream from each treatment site, many metals display a negative removal efficiency at each of the two active treatment sites. Negative removal efficiencies indicate an increase in the constituent value during the treatment process. pH increases downstream from treatment at each studied active treatment site indicating reduced acidity, and hardness is higher downstream from treatment at the Yak Tunnel Water Treatment Plant.

Dilution adjusted removal efficiency at the Leadville Mine Drainage Tunnel Water Treatment Plant remains positive for cadmium, iron, manganese, and zinc, but becomes negative for both copper and lead (Table 6). Without accounting for dilution, each metal has a removal efficiency greater than 99 percent at the LMDT Treatment Plant. There is however an increase in mean annual discharge from 0.36 cfs at SHG to 113 cfs at EF-2/3 that contributes to this apparent removal success and results in apparent discharge of dissolved metals from the system rather than retention (Table 4 and Table 6). Downstream from treatment at the LMDT plant, each paired study mean metal concentration is in compliance with water quality standards for AR-1, immediately downstream from the East Fork confluence; upstream from treatment at the LMDT plant mean metal concentrations are higher than water quality standards for each studied metal (Table 7, Figure 14). Mean pH increases from 4.85 at SHG upstream from treatment at the LMDT Treatment Plant to 7.13 at EF-2/3 downstream from treatment, bringing pH into compliance with water quality standards downstream from water treatment. Mean hardness decreases downstream from treatment from 233 mg/L $CaCO_3$ at SHG to 79 mg/L $CaCO_3$ at EF-2/3; there is no water quality standard for hardness.

Removal efficiency at Yak Tunnel Water Treatment Plant is not as high as at LMDT Water Treatment Plant, but is between 33 and 65 percent for each studied metal (Table 6). However, dilution adjusted removal efficiency at the Yak Tunnel Water Treatment Plant decreases removal success for each metal and becomes negative for all metals except copper and lead (Table 6). Upstream from treatment, each of these metals is above the acute water quality standard for AR-3A, the site in the Arkansas River immediately downstream from California Gulch (Table 7). Downstream from treatment, all metal concentrations remain above water quality standards with the exception of manganese, not the metal with the highest removal efficiency for this site, which is in compliance with AR-3A standards (Table 6 and 7, Figure 14). Mean pH is closer to compliance downstream from treatment at the Yak Tunnel Water Treatment Plant with an increase from 3.77 at CG-1 upstream from treatment to 4.98 at CG-2 downstream from treatment, but falls below the state standard range of 6.5 to 9.0 (Table 4). Mean hardness increases downstream from treatment at the Yak Tunnel Water Treatment Plant from 139 mg/L $CaCO_3$ at CG-1 upstream from treatment to 765 mg/L $CaCO_3$ downstream at CG-2.

Not including lead, the Dinero Wetland Complex has metal removal efficiency between 26 and 84 percent for each studied metal (Table 6). Unlike the active treatment facilities studied, dilution adjusted removal efficiency remains positive and improves for all metals downstream from treatment at the Dinero Wetland Complex (Table 6). Mean discharge decreases from 1.6 cfs at SL Up to 0.78 cfs at SL Down, resulting in an apparent increase in removal efficiency. Upstream from treatment treatment in the Dinero Wetland Complex, mean metal concentrations are out of compliance with Arkansas River water quality standards; downstream from treatment mean annual concentrations decrease for each studied metal but are still greater than in-stream standards for AR-4 (Table 7, Figure 14). Mean annual pH is out of compliance with water quality standards both up- and downstream from treatment at the Dinero Wetland Complex, and even decreases downstream from treatment from 3.65 upstream from the wetland complex to 3.59 downstream. Hardness data are not available for SL Up and SL Down sites.

3.4. Mine Drainage Longevity

Drainage longevity differs for each metal (Figure 15), because of this the acute standards are shown for both CG-1 and AR-3A as AR-3A is the nearest site with set water quality standards. The initial time for this analysis is 1995; time to compliance is adjusted to the time needed to reach compliance from today, in 2018. The minimum time to compliance with applied CG-1 standards for all metals based on average predicted concentrations is less than one year for manganese; maximum time to compliance is 293 years for zinc. Minimum time to AR-3A standard compliance based on average predicted concentrations is one year for manganese and a maximum time of 353 years for zinc (Table 8). As the minimum time to compliance for the entire system is dictated by the metal that takes the longest time to reach water quality standards, the shortest time to CG-1 compliance using the average predicted concentrations would be 293 years, and 353 years to AR-3A standards (Table 8).

With 10 percent error bounds, the absolute minimum time to CG-1 standard compliance would be 115 years and to AR-3A standard compliance would be 140 years (Table 8). Data are not available for maximum predicted times to compliance for zinc, the metal that has the longest minimum and average predicted time to compliance; but maximum compliance for CG-1 and AR-3A standards could respectively exceed 1500 and 2000 years (Table 8).

4. DISCUSSION

4.1. Water Quality Characterization

Hard-rock mining activity threatens both surface- and groundwater throughout the western United States with metals and acidity (Runkel *et al.*, 2007). Acidic drainage is a common concern in mine land drainage. Mean annual pH above each studied treatment site is acidic with values ranging between 3.76 and 4.97 depending upon the system. These pH values increase with distance from source. Lowest pH along each tributary tends to be found upstream of the treatment site, pH then increases downstream from treatment and continues to increase or remain circumneutral at the tributary mouths and in the main channel of the Arkansas River.

An initial increase in pH downstream from treatment sites can be attributed to the treatment process in place. The active treatment sites along East Fork and California Gulch use chemical dosing to raise pH and allow metals to fall out of solution, the elevated pH remains downstream from the treatment process. While the removal analysis from paired-date data sets shows a decrease in pH downstream from the Dinero Wetland Complex, mean annual pH from all-site data does increase downstream from the wetland. The removal of dissolved metals from effluent waters can reduce hydrogen activity and increase pH; but high flow or the need for wetland maintenance, like removal of accumulated sediment waste, may reduce metal removal and result in no pH change or a lower pH downstream from the wetland. Active treatment allows for the precise pH adjustment needed to treat a system by bringing pH to the ranges required for specific metals to precipitate out; chemical dosing can be adjusted based on initial pH of untreated waters and there can be a multi-stage setup allowing for different pH stages to effectively treat different metals. pH control is not attainable with passive treatment as the alterations to pH occurs due to metals falling out of solution, binding with clay or other particles, being taken up by plants, or dissolving and re-entering the system. The change in pH in passive systems results from metals leaving or entering the waters versus basic chemical dosing in active treatment raising pH to allow metals to precipitate out.

pH increases further downstream from treatment sites and into the main channel of the Arkansas River are likely due to the dilution from increased discharge further downstream as well as natural attenuation that occurs as waters move through the system (Schemel et al., 2000; Stednick, 2012). Contributing area for the watershed increases with distance downstream from source and unaffected waters, or waters with minimal degradation from acidic sources, flow into the system and further raise pH in each tributary. This same effect is seen downstream from tributary confluence with the Arkansas River where large volumes of higher pH water in the main channel meets with smaller volumes of lower pH waters from the tributaries, resulting in a higher pH than what is seen in the tributary system.

While the near neutral pH at tributary mouths (Table 4) seems to contradict the concern for acidic damages to waterways downstream of mined lands (Perry, 1991; Robb, 1995), near neutral pH is not an abnormal occurrence is these areas (Smith *et al*., 2000; Apodaca *et al*., 2000; Butler *et al*., 2008). Acidic waters draining from fluvial tailings deposits had minimal effect on pH in the Arkansas River, where pH was between 7.2 and 8.2 in the studied reach (Smith *et al*., 2000). Waters of the Blue River Basin in the Breckenridge Mining District are threatened by acidity during low flow periods when dilution from snowmelt contribution ceases, and in high flow periods where increases in acidic groundwater contribution occur. However, surface water pH remains between 7.5 and 8.1 (Apodaca *et al*., 2000). Metal laden, acidic waters from the

Clear Creek Superfund Site above North Fork Clear Creek neutralize upon mixing with the North Fork, where stream pH ranges between 6.5 to 8 (Butler *et al*., 2008).

Water hardness in the Upper Arkansas River Basin is greater during times of lower discharge (Figure 5). This is to be expected as there is less dilution of constituents in solution with low flow (Stednick, 2012). It may also be expected that a lower pH could result in harder water as many metals tend to have higher solubility at lower pH, so the divalent cations remain in solution at lower pH. Specific conductivity has a similar correlation to pH and metal concentrations as hardness because specific conductivity and hardness in the study area have a positive linear correlation with r^2 equal to 0.85 (Figure 6). Data in the Upper Arkansas River Basin show that increased hydrogen activity and higher metal concentrations both contribute to increased electric current carrying capacity of a solution. In instances where a sample from any site is missing hardness or conductivity components, it may be possible to glean a general understanding of water quality conditions with the use of available components given the different correlations shown.

Mean annual hardness decreases downstream from treatment at the LMDT Water Treatment Plant unlike at the Yak Tunnel Water Treatment Plant where treatment causes an increase in hardness (Table 4). Both of these plants are active treatment sites where chemical dosing occurs. While metals are removed during the process thus decreasing the associated divalent cations, the addition of basic compounds like calcium carbonate, calcium hydroxide, ammonia, sodium hydroxide, etc. alter the water chemistry and increase hardness with the addition of different divalent cations (Yadav, H.L. and A. Jamal, 2015). In addition to this, the sampling site above the LMDT plant is near the intake of the Leadville Mine Drainage Tunnel itself with very low discharge while the LMDT plant outlet is in the East Fork with much higher discharge. It is possible that hardness increases with treatment at the LMDT Water Treatment Plant but is not represented due to the dilution that occurs downstream treatment plant.

Hardness data are not available for SL Up and SL Down, so it is not entirely possible to describe how the wetland system affects water hardness, but the relationship between hardness and electrical conductivity (Figure 6) can provide insight. Electrical conductivity increases downstream from the Dinero Wetland Complex though, as do electrical conductivity and hardness up- and downstream from the Yak Tunnel plant, suggesting an increase in hardness downstream from the Dinero Wetland Complex (Table 4). However, given the overall decrease in dissolved metal concentrations downstream from treatment in the Dinero Wetland Complex (Table 6), hardness may slightly decrease as divalent cations have been removed from the system without the addition of pH raising chemicals. These two factors combined suggest that hardness may not be significantly affected as waters move through the wetland complex.

4.2. Metal Concentrations

Water quality standards for impaired streams are often established by regulatory agencies on a site-specific basis. Determination of these standards, especially in mineralized watersheds with previous mining history, can be difficult as background water quality data rarely exist for the time before mining activity began. General water quality standards used for unmineralized sites can be problematic when applied to mineralized areas as the geology of these regions affects most watersheds with or without mining activity (Runkel *et al*., 2007).   Due to these complications, water quality standards at impaired streams may differ from standards for surrounding streams (Apodaca *et al*., 2000 and Johnson, per. comm., 2013). This may explain why California Gulch has no metal standards (CDPHE 2014b), and is not the only case of a change in water quality standards compared with surrounding streams.

The Colorado Water Quality Control Commission has established temporary in-stream water quality standards for French Gulch, a headwater stream of the Blue River in the Breckenridge mining district (Apodaca *et al*., 2000). During periods of low flow there is little dilution of metals in French Gulch; and while increased discharge during periods of high flow should alleviate these concentrations, acidic groundwater flow then influences stream composition (Apodaca *et al*., 2000). Metal concentrations upstream from treatment complexes in this study are higher than those seen in French Gulch, with mean annual concentrations even exceeding the temporary standards set for French Gulch. The East Fork and Lake Fork tributaries to the Arkansas River maintain water quality standards even though zinc, iron, and manganese concentrations exceed the range observed at French Gulch.

It is difficult to compare metal concentrations between mine drainage sites as these vary dramatically depending upon the geology and mining processes at each site. In many instances, metal concentrations observed upstream from treatment sites of this study exceed those observed around other mine land affected waters in Colorado (Apodaca *et al*., 2000; Smith *et al*., 2000; SAIC, 1994 as reported by Hazen *et al*., 2002; Kimball *et al*., 2002; Runkel *et al*., 2007; Butler *et al*., 2008). But there are studies that show metal concentrations upstream from treatment in this study are comparable or even lower than those found in other mine-affected waters (Kimball *et al*., 2002; Runkel *et al*., 2007). There are also times when waters immediately downstream from studied treatment complexes exceed average values from other untreated mine land affected waters (SAIC, 1994 as reported by Hazen *et al*., 2002; Kimball *et al*., 2002), or when metal concentrations of treated waters in this study are equivalent to those of untreated waters from different mine site (Runkel *et al*., 2007). In most cases, metal concentrations seen in the main channel of the Arkansas River are lower than concentrations seen at other affected mine drainage sites (Smith *et al*., 2000; SAIC, 1994 as reported by Hazen *et al*., 2002; Kimball *et al*., 2002; Butler *et al*., 2008).

4.3. Treatment Removal Efficiency

The Leadville Mine Drainage Tunnel Water Treatment Plant, Yak Tunnel Water Treatment Plant, and Dinero Wetland Complex effectively treat water in East Fork, California Gulch, and Lake Fork by reducing metal concentrations and in some instances increasing pH, although waters immediately downstream from treatment facilities do not always meet water quality standards for the respective tributary system during the period of record. Downstream from treatment, waters downstream from the Leadville Mine Drainage Tunnel at EF-2/3 are in compliance with Arkansas River standards below the East Fork confluence at AR-1 (Table 7). In California Gulch, waters immediately downstream from Yak Tunnel at CG-2 are still out of compliance with Arkansas River standards at AR-3A for all metals of concern (Table 7). There are no hardness data available at SL Up and SL Down, but waters downstream from Dinero Tunnel and Dinero Wetland Complex are out of compliance for all Arkansas River standards at AR-4 (Table 7).

Removal efficiency varies depending on the degree of contamination of the influent water to be treated as well as the treatment methods in place. Metal removal efficiency is greater at the LMDT Water Treatment Plant than at Yak Tunnel Water Treatment Plant or the Dinero Wetland Complex. However, there are some metals for which the Dinero Wetland Complex has higher removal efficiency than the Yak Tunnel Water Treatment Plant, and others where the active plant outperforms the passive system. The active plant at Yak Tunnel removes more dissolved copper, lead, and manganese than the wetland system, but the Dinero Wetland Complex removes more cadmium, iron, and zinc than the Yak Tunnel Water Treatment Plant (Table 6, Figure 14).

Given the relative ease of alteration to active chemical treatment regiments when compared with the ease of altering passive systems, greater emphasis is given to comparing efficiency of different passive treatment systems in the literature than to different active treatment plants. A previous study on the same wetland area of this study was done by Arati Neopane in 1997. She studied dissolved metal concentrations at the inlet and outlet of Sugarloaf Gulch and the Dinero Wetland. In 1997, waters at the outlet of the Dinero Wetland had higher dissolved metal concentrations than those entering the wetland for cadmium and copper; the wetland had no retention of these dissolved metals and even released these metals into effluent water (Neopane, 1997). The Dinero Wetland Complex did not share the problem of releasing cadmium and copper into effluent waters during the paired-date removal analysis from this study, it retained 50 percent of dissolved Cd and 61 percent of dissolved Cu entering the system (Table 6). However, given the use of a database for this study versus collecting samples from the actual inlet and outlet of the wetland, the assumption that SL Up sites, many of which are below tailings piles, accurately represent the water at the inlet to the wetland may be at fault. Neopane did find positive metal removal for iron, lead, manganese and zinc, this study found the same with the exception of 0 percent removal for lead. Neopane had iron removal of 90 percent compared to 84 percent in this study, 100 percent removal for lead compared with 0 percent in this study due to data reported below the method detection limit, 19 percent for manganese versus 26 percent in this study, and 20 percent removal of dissolved zinc compared with 42 percent in this study (Neopane, 1997 and Table 6). The similarity between high iron and lower manganese and zinc removal efficiencies suggests that error in the SL Up assumption may be the culprit for this difference. In any case the wetlands were less effective at treating mine water for most dissolved metals than the active treatment systems studied.

The Lick Run wetland is constructed to treat water contaminated by mine seeps in the Lick Run tributary to the Hocking River in Athens County, Ohio. This wetland also found successful retention of dissolved iron and manganese; other metals of this study were not studied by Mitsch and Wise. Dissolved iron removal was 82 percent in the Lick Run wetland, and manganese was 5.9 percent (Mitsch and Wise, 1998). Like the Dinero Wetland, iron removal is greater than manganese removal in the wetland system, with the efficiency of dissolved iron removal being comparable to dissolved iron removal at the LMDT and Yak Tunnel active treatment facilities.

P.L. Younger compiled data from many different mine water passive treatment systems in the United Kingdom and provides typical dissolved influent and effluent metal concentrations (2000). Data are not available for all metals of interest for this study, but removal efficiencies can be calculated at several different aerobic wetland sites across the United Kingdom. At the Wheal Jane passive treatment system, dissolved copper retention in a three tiered aerobic pilot system was found to be 50 percent (Younger, 2000). The Dinero Wetland retains 61 percent of dissolved copper. Many of the different aerobic wetlands in the Younger study include dissolved iron data. The removal efficiency ranged between 68 and 99 percent for the passive aerobic wetlands with an average removal efficiency of 85 percent (Younger, 2000). The average and range of removal efficiencies for dissolved iron across the 16 different aerobic wetlands provided is comparable to iron removal in this study. These wetland systems in the UK have higher average dissolved iron removal than both the Dinero Wetland Complex at 84 percent and the

Yak Tunnel Water Treatment Plant at 57 percent, but iron removal at the LMDT Water Treatment Plant is greater than these aerobic wetlands at 99.8 percent, though only 42 percent if dilution adjustment is taken into consideration for the LMDT plant (Table 6). One of the provided wetlands showed retention of 17 percent for dissolved manganese, following trends seen in this study and by others that wetlands seem poorly suited for manganese retention (Neopane, 1997 and Mitsch and Wise, 1998). Finally, two of the wetlands in the UK present dissolved zinc reductions between 43 and 88 percent, an average of 66 percent zinc removal (Younger, 2000). Zinc removal from these two aerobic wetlands in the United Kingdom is greater than that found in this study or Neopane's study of the Dinero Wetland Complex or the Yak Tunnel Water Treatment Plant. The LMDT Water Treatment Plant proves best at dissolved zinc removal at 100 percent, or 91 percent when adjusted for dilution. Overall, when comparing efficiency of dissolved metal removal, it appears active treatment is better suited for the removal of the variety of metals found in acid mine drainage, though passive treatment systems can still remove comparable quantities of some metals found in acid mine drainage.

4.4. <u>Mine Drainage Longevity</u>

Exceptionally high metal concentrations at an abandoned mine were previously not expected to continue very long into the future; after the initial filling of mine voids and seepage of highly metal laden water, the first flush stage would not last more than 40 years according to studies on all available mine data from Scotland (Wood *et al*., 1999 as cited by Younger and Bantwart, 2002). While the initial seepage from an abandoned or decommissioned mine is of great concern because of the extremely high metal concentrations and low pH that occur, this tends to improve over time (Younger and Bantwart, 2002). After the initial exponential decay, metal concentrations are maintained at lower to near asymptotic levels—this is most commonly seen where there is an abundance of neutralizing minerals in the mining area (Younger, 2000). However where neutralizing mineral abundance is exceeded by pyrite, metal concentrations tend to remain at higher levels and may even increase as time progresses (Younger, 2000). At California Gulch, there is a limited period of record which does not adequately capture what final metal concentrations can be expected in Leadville mine drainage. The exponential decay projection for each metal at this site helps to provide a frame of reference for how long water quality may remain out of compliance with standards, but a longer period of record and more in depth study of mineralogy at the site could help confirm these results.

The time range determined for mine discharges in California Gulch to be in compliance with water quality standards is between 115 to 2017 years (Table 8). This same analysis performed on data from two metal mines in Sardinia show a minimum time to compliance between 103 to 131 years (manipulation of data from Cidu, 2011). Maximum times to compliance ranged between 233 and 429 years. Not all data are provided for iron at one of these two mine sites in Sardinia, but the decay constant from the site with available data projected onto the other it showed a maximum time for iron compliance up to 950 years. The mines in Sardinia closed in the late 1990s (Cidu, 2011) and mining activities in the study area at Leadville, Colorado ended between the 1920s and 1950s (Bureau of Reclamation, 2008). Compliance since closure at these sites has not yet occurred for nearly 100 years, though there is a chance metal concentrations may be in compliance within the next few years. However with concentrations still exceeding water quality standards on a regular basis at many of these sites, it is likely substantially impaired water quality from mine drainage will continue further into the future.

5. CONCLUSIONS

5.1. Water Quality Characterization

Waters in the study area of the Upper Arkansas River Basin show characteristically low pH and high dissolved metal concentrations similar to what is seen in other regions impacted by acid mine drainage. Acidic degradation is greatest upstream from the studied treatment sites where mean annual pH ranges between 3.76 and 4.97, but there is improvement downstream from treatment sites. pH rises downstream from treatment and mean annual values remain circumneutral at each tributary mouth and in the main channel of the Arkansas River. Waters in the main channel of the Arkansas River downstream from the tributary associated with each treatment site have a circumneutral mean annual pH ranging between 7.43 and 7.57, although pH was still acidic at times during the period of record with a minimum 5.0 in the main channel of the Arkansas River and minimums between 3.1 and 6.3 at tributaries mouths. Discharge increases with distance downstream from tributary source in each tributary system with the lowest flows occurring at sites upstream from treatment complexes. Although hardness has an inverse relationship with discharge in the UARB system (Figure 5), it is not always the case that hardness decreases downstream from treatment even though discharge may increase due to the chemical additives used during the active treatment process.

5.2. Metal Concentrations

Waters upstream from the LMDT Water Treatment Plant, Yak Tunnel Water Treatment Plant, and Dinero Wetland Complex have dissolved metal concentrations exceeding state water quality standards for the designated uses of these streams. High dissolved metal concentrations are seen upstream from treatment sites throughout the study area for cadmium (0-4.8 mg/L), copper (0-9.4 mg/L), iron (0.01-1100 mg/L), lead (0-5.2 mg/L), manganese (0.01-281 mg/L), and zinc (0-617 mg/L). Metal concentrations in the Leadville area are generally lower downstream from active or passive treatment, but are still not always in compliance with state water quality standards.

5.3. Treatment Removal Efficiency

The three treatment systems studied were all effective at reducing dissolved metal concentrations in acid mine drainage impacted waters. The true effectiveness of treatment at each of these sites and how they compare to one another may come into question when dilution is taken into consideration. Dilution aside, waters impacted by mining in Leadville, Colorado have dissolved metal concentration reduction between 33 and 100 percent with active treatment and 0 to 84 percent with passive treatment. Comparison between the Yak Tunnel Water Treatment Plant, which removed less dissolved metals than the LMDT Water Treatment Plant, and the Dinero Wetland Complex shows that metal removal efficiencies for passive treatment systems could be comparable to active treatment systems for effluent water of this type.

5.4. Mine Drainage Longevity

The need for treatment systems in the Upper Arkansas River Basin is not only shown by the excessive metal concentrations that occur, but also by the time period in which contaminated drainage may persist. The average time needed for mine drainage waters in California Gulch to be in compliance with Arkansas River water quality standards is 353 years, but could exceed 2000 years given the 10 percent error bounds applied in this study. In the Upper Arkansas River

Basin, stream flow is greatest during spring snow melt; water supply in both surface water sources and groundwater sources is depleted during the remainder of the year until spring when the previous winter's snowpack begins to melt again. This fluctuation in the water table causes different mineral surfaces in underground mines to be exposed year round. This fluctuation does not allow for the depletion of sulfide ores that would occur with a steady water table and causes the prolonging of degraded water quality from mine drainage.

In conclusion, this study characterizes water quality along the tributary systems of three acid mine treatment systems in the Upper Arkansas River Basin. A degradation of water quality in the Upper Arkansas River Basin occurs from acidic and metal rich waters of the Leadville and Sugarloaf mining districts. Treatment of impaired water quality in these waters shows a reduction in dissolved metal concentration, though waters in the basin still exceed state standards on occasion. Based on the timeline which this study found impaired water quality from mine discharge to continue, it may be necessary for additional treatment in the area to bring Upper Arkansas River Basin waters into compliance with state water quality standards.

5.5. Recommendations

Acid mine drainage continues to impact the Upper Arkansas River Basin after several treatment processes occur, as seen in elevated metal concentrations downstream from water treatment and in the main channel of the Arkansas River. This may indicate there are other sources of metal contamination in the Arkansas River that are not accounted for in this study. This coupled with the lack of long term data at each of the three treatment sites leads to the recommendation of additional monitoring in the Upper Arkansas River Basin. Monitoring sites should be established upstream and downstream of all treatment facilities as well maintaining the monitoring that occurs along each tributary and main channel of the Arkansas River. Once this is established, it may become evident that groundwater monitoring may also be needed in the basin.

More extensive monitoring sites may clarify the impact of dilution for each of these treatment sites, but additional treatment may still be required along East Fork, Yak Tunnel, and Lake Fork. Each treatment system prevented significant metal concentrations from continuing along their respective tributary systems, though not always immediately downstream from treatment. It may be necessary for amended treatment plants at each of these sites. Some options for increased treatment at active sites would include increasing chemical dosage at treatment plants to improve metal colloid formation and settling, expansion of existing settling basins to allow for increased residence time of treated waters, or the installation of up- and/or downstream from treatment wetland systems. Increased treatment at the Dinero Wetland Complex may include the construction of additional wetlands to expand the area for metal precipitation, absorption, or uptake to occur, increasing the frequency of waste sediment removal from the wetlands to improve metal retention by increasing residence time, or the addition of more refined limestone lined beds that deliver water from Dinero Tunnel to the wetland. Increasing monitoring in the Upper Arkansas River Basin will provide the information necessary to determine if there are unaccounted sources of acid and metal contamination to the system, and will help establish plans for remediated or additional treatment facilities.

6. FIGURES

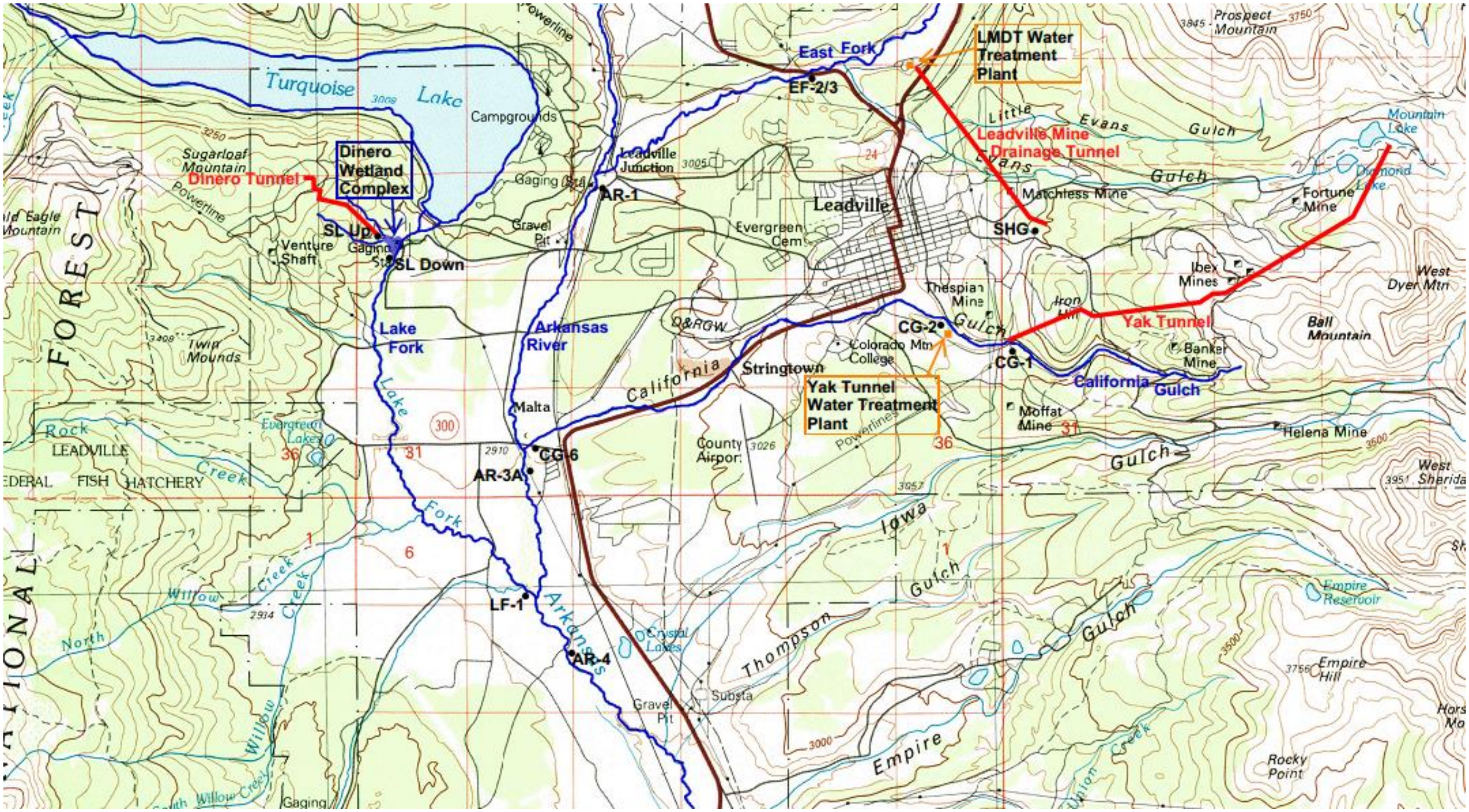


Figure 1: Location of study sites in the Upper Arkansas River Basin (modified from U.S. Geological Survey).

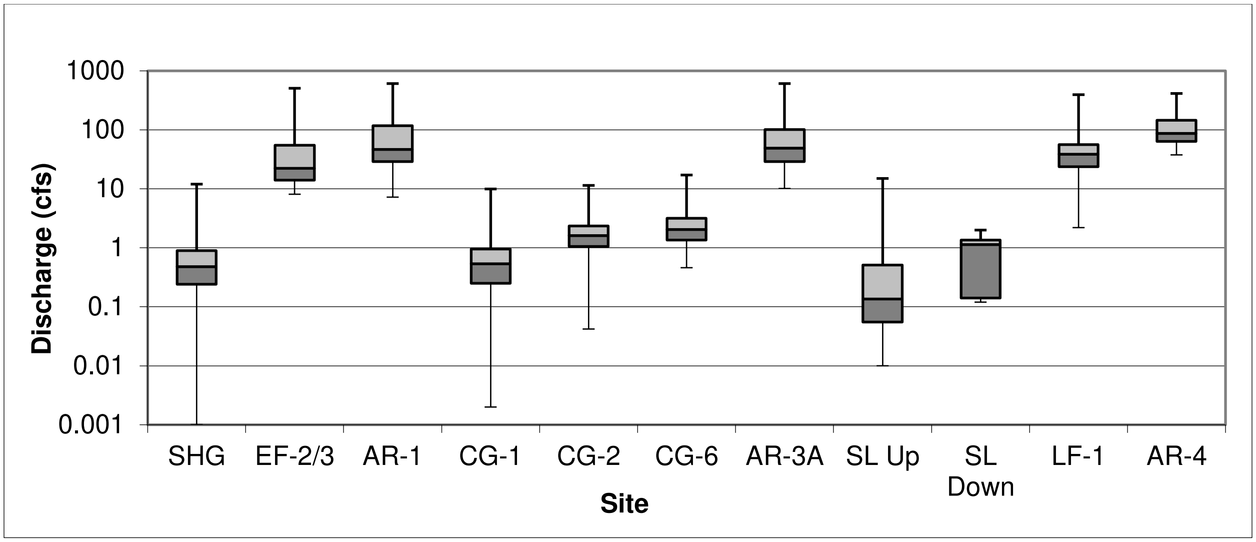


Figure 2: Box and whisker plot of discharge in the Upper Arkansas River system. Sites are shown from up- to downstream on each tributary in the order as they appear along the Arkansas River. For this and all following box and whisker plots, the box midline represents the median, the bottom and top of the box represent the first and third quartiles, and the end points of the whiskers represent minimum (lower whisker) and maximum (upper whisker) values.

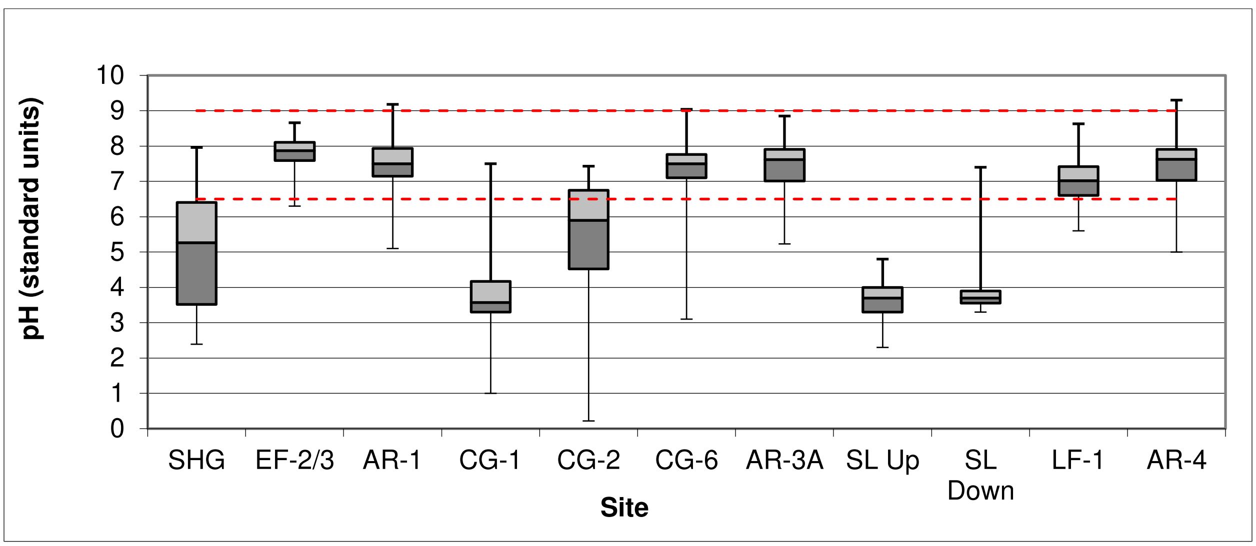


Figure 3: Box and whisker plot of pH in the Upper Arkansas River system. pH is in compliance with water quality standards when measurements fall between the dashed red lines.

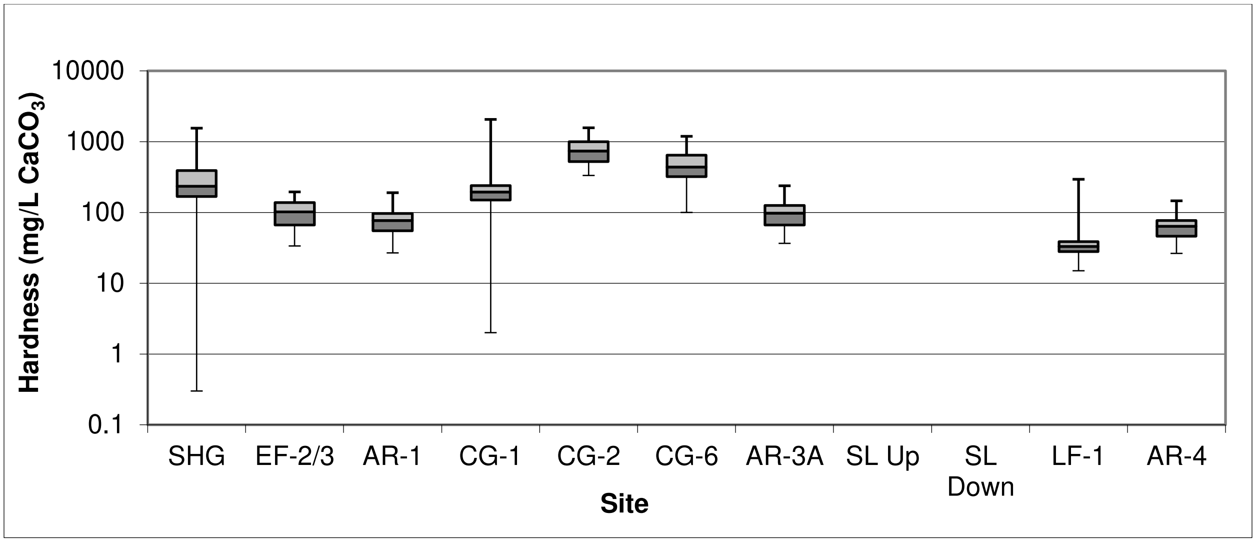


Figure 4: Box and whisker plot of hardness in the Upper Arkansas River system. Note that hardness data are not available for SL Up and SL Down sites.

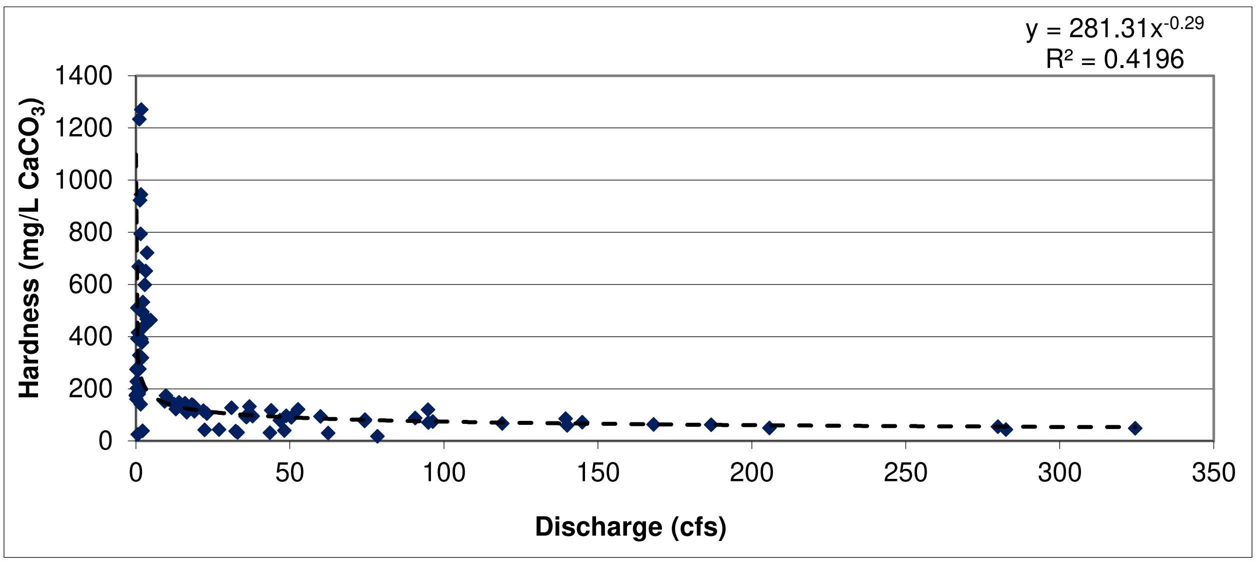


Figure 5: Mean annual hardness versus mean annual discharge for all sampling sites in the Upper Arkansas River Basin.

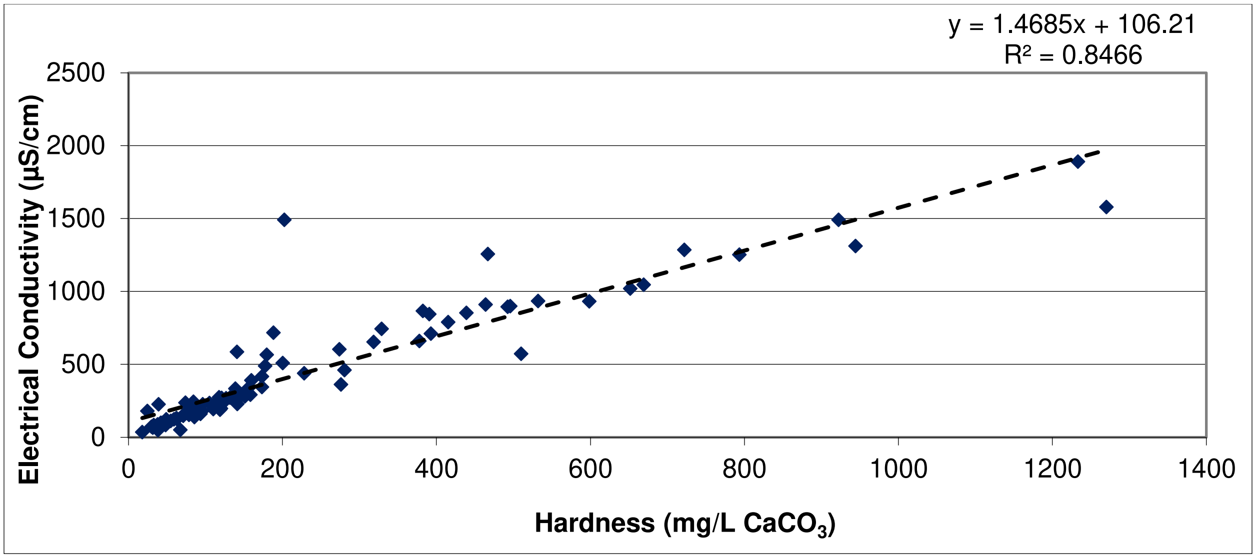


Figure 6: Mean annual electrical conductivity versus mean annual hardness for all sites in the Upper Arkansas River Basin.

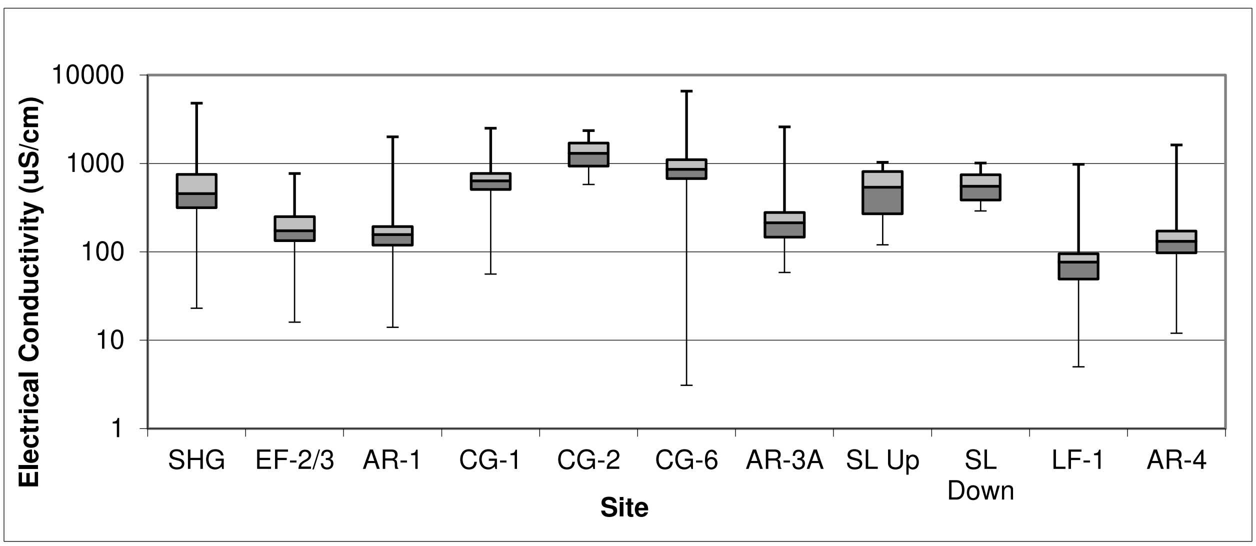


Figure 7: Box and whisker plot of electrical conductivity in the Upper Arkansas River System. Note that given electrical conductivity and hardness correlation, hardness and water quality standards for sites with no hardness data may be estimated given similar electrical conductivities with other sites.

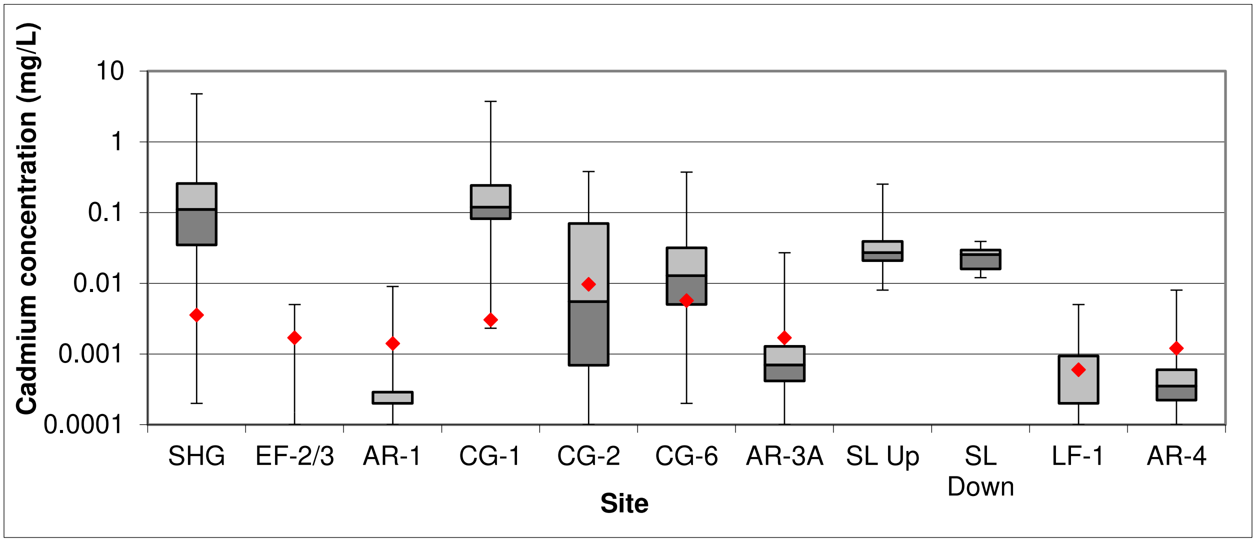


Figure 8: Box and whisker plot of cadmium concentration at all sites. Red diamonds indicate the water quality standard for each site.

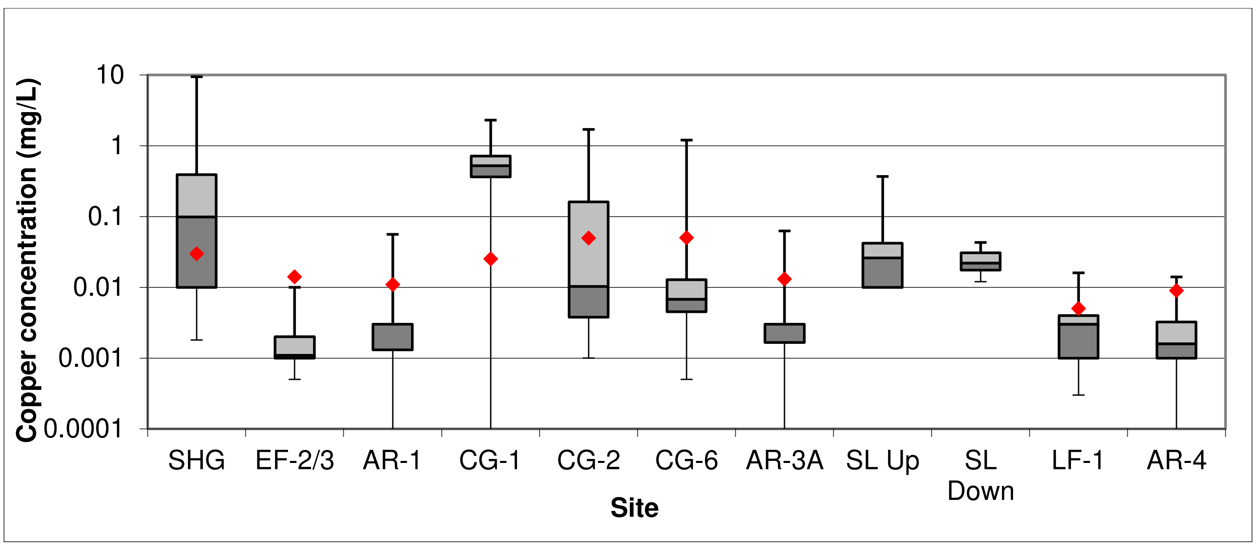


Figure 9: Box and whisker plot of copper concentration at all sites. Red diamonds indicate the water quality standard for each site.

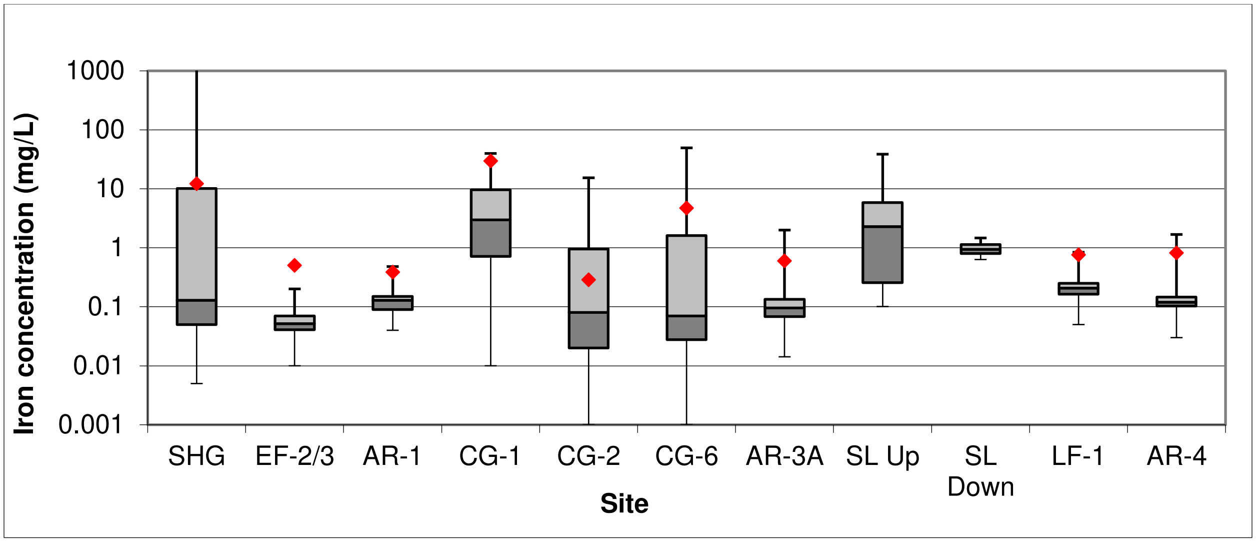


Figure 10: Box and whisker plot of iron concentration at all sites. Red diamonds indicate the water quality standard for each site.

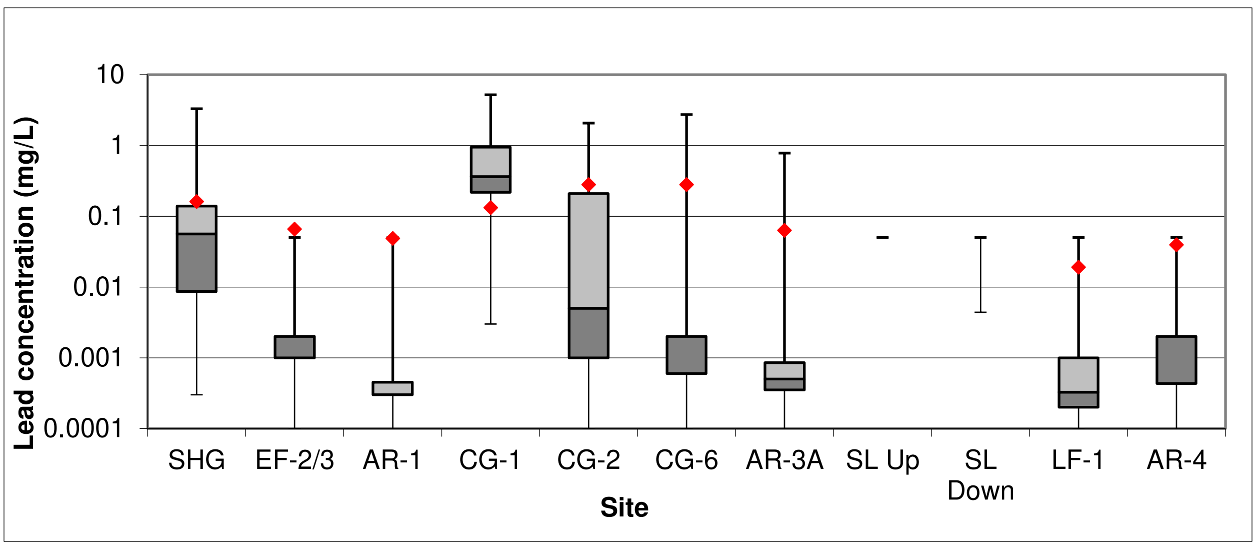


Figure 11: Box and whisker plot of lead concentration at all sites. Red diamonds indicate the water quality standard for each site.

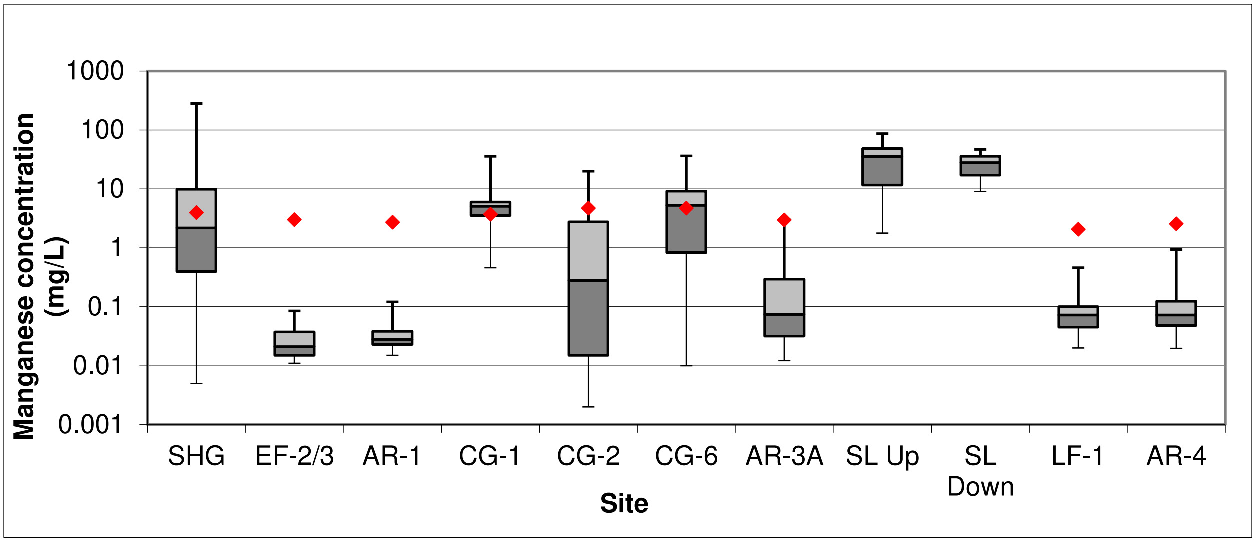


Figure 12: Box and whisker plot of manganese concentration at all sites. Red diamonds indicate the water quality standard for each site.

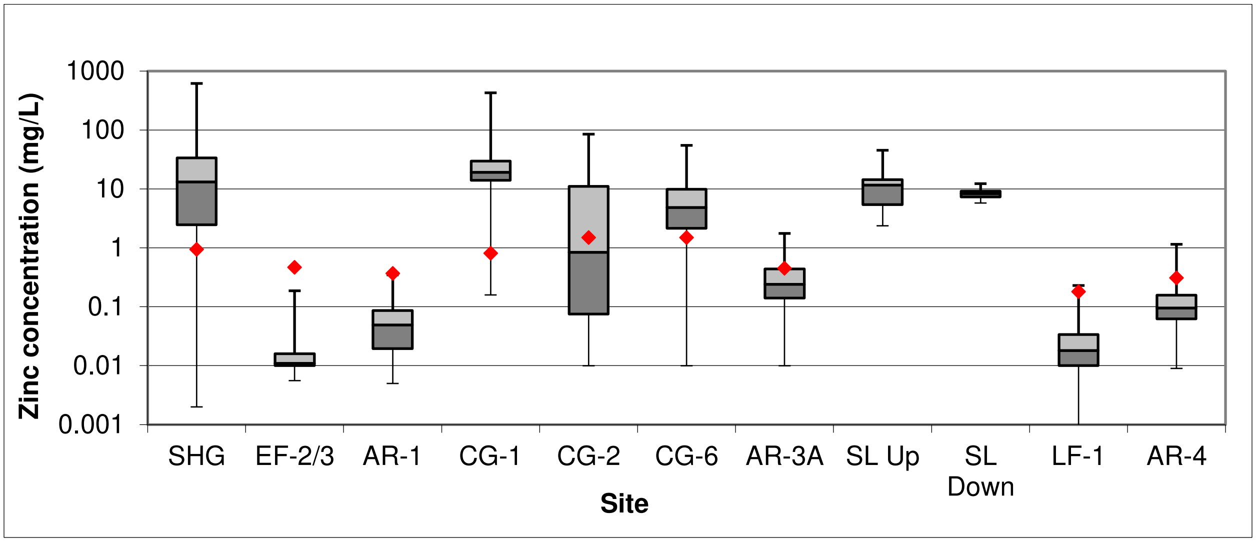


Figure 13: Box and whisker plot of zinc concentration at all sites. Red diamonds indicate the water quality standard for each site.

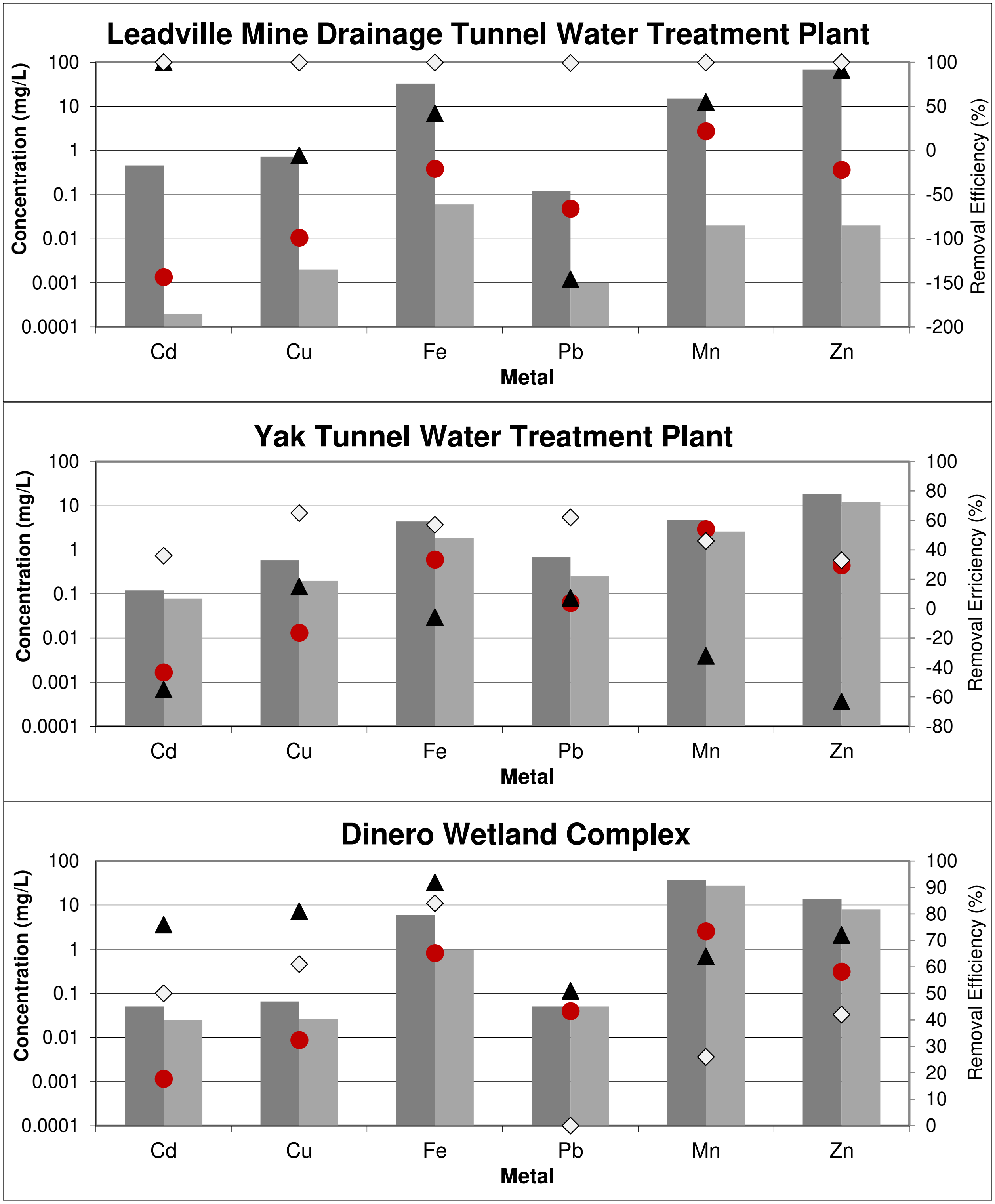
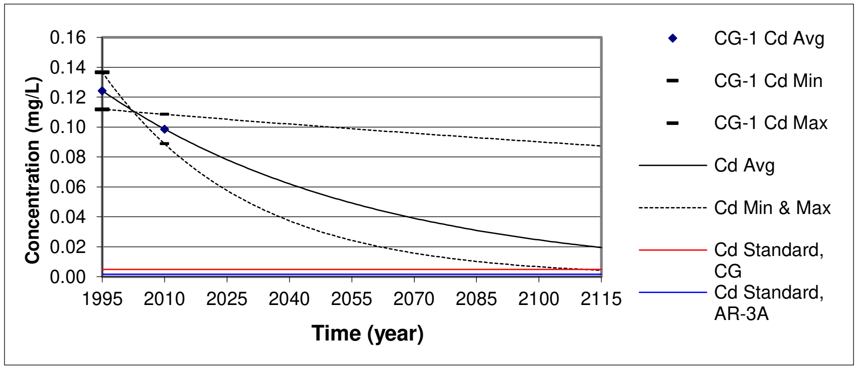
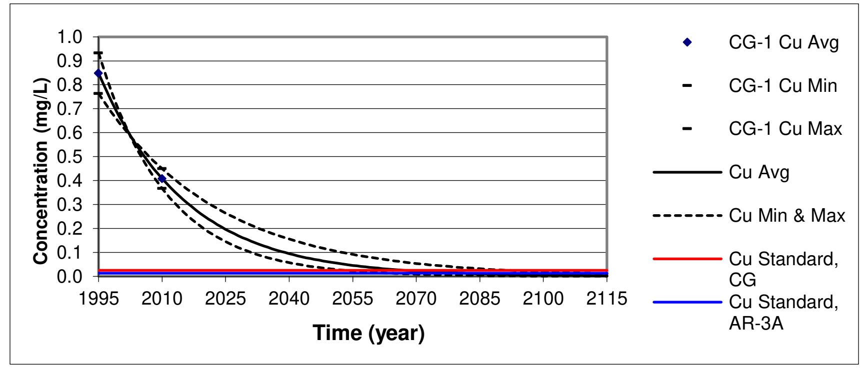
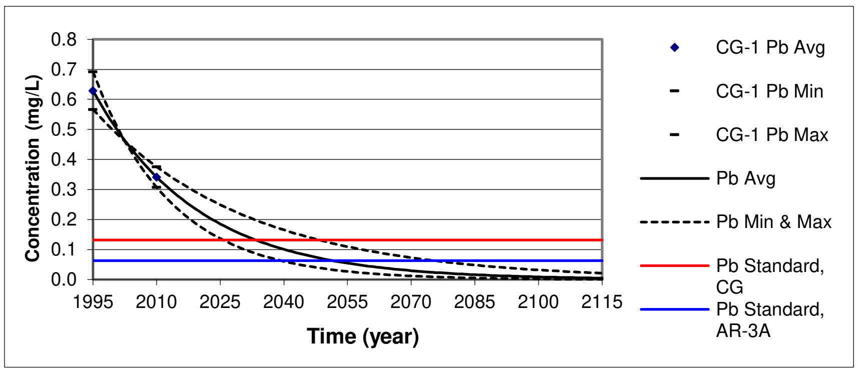
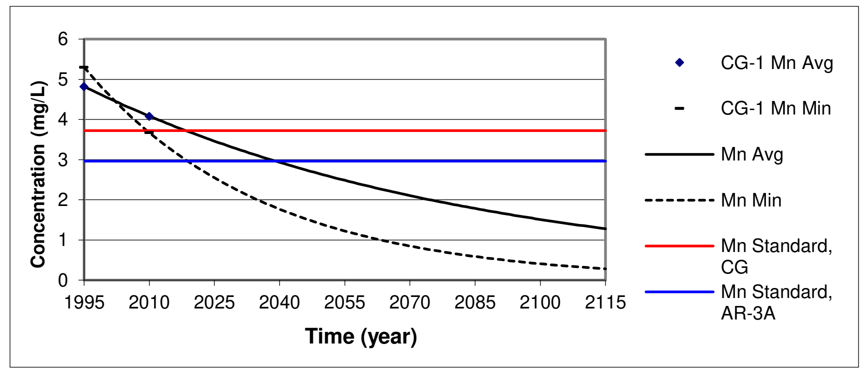


Figure 14: Upstream from treatment (dark gray bars) and downstream from treatment (light gray bars) metal concentrations at each treatment study site with Arkansas River water quality standards shown for sites downstream from treatment complex (red circles). Standard removal efficiency is shown as empty diamonds and dilution adjusted removal efficiency as black triangles.









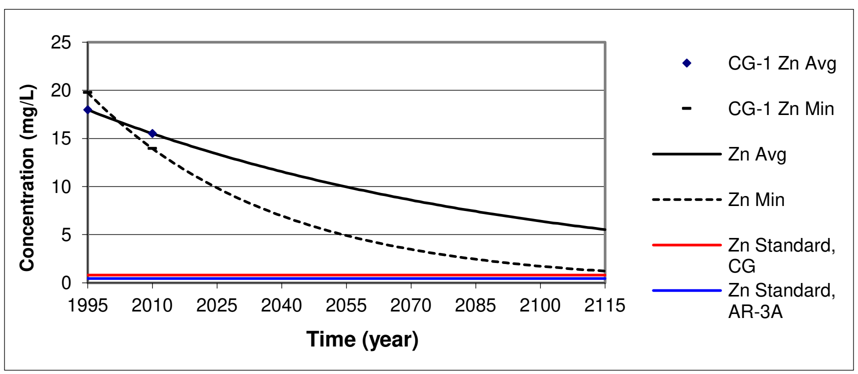


Figure 15: Mine drainage longevity predictions by metal at CG-1. Solid black line indicates average decay projection while dashed lines indicate ±10 percent error range. Solid red line shows acute water quality standard for CG-1 using median hardness at CG-1. Solid blue line shows acute water quality standard for AR-3A using AR-3A hardness.

7. TABLES

Table 1: Listing of lab qualifiers used for analytical analysis. These qualifiers may be found next to the reported value for each of the analytes in the provided database.

Interpreted Lab Qualifier	Qualifier Description
B	Analyte concentration detected between MDL[1] and PQL[2]
BJ	Analyte concentration detected at an estimated value between MDL and PQL
J	Estimated value
U	Analyte was analyzed but not detected above MDL
UJ	Analyte was analyzed for but not detected above MDL with estimated value

[1] MDL is method detection limit, "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the true value is greater than zero" (50 FR 46902 as cited by Cooper *et al*., 1999)
[2] PQL is practical quantitation limit, "[t]he lowest level that can be reliably achieved within the specified limits of precision and accuracy during routine laboratory operating conditions" (50 FR 46902 as cited by Cooper *et al*., 1999)

Table 2: List of Table Value Standard equations for metals in the Upper Arkansas River Basin (CDPHE 2014b) and associated water quality standard for each studied treatment system. Where median hardness exceeds 400 mg/L $CaCO_3$ (maximum allowed per TVS) standards are calculated at a hardness of 400 mg/L $CaCO_3$ Note that only the metals of concern are shown although additional metals must also be in compliance.

Metal	Table Value Standard Equation
Cd	Acute Trout: $(1.136672-[\ln(hardness)*0.041838])*e^{0.9151*[\ln(hardness)]-3.6236}$
	Chronic[1]: $(1.101672-[\ln(hardness)*0.041838])*e^{0.7998*[\ln(hardness)])-4.4451}$
	Chronic[2]: $(1.101672-[\ln(hardness)*0.041838])*e^{0.7998*[\ln(hardness)]-3.1725}$
Cu	Acute: $e^{0.9422*[\ln(hardness)]-1.7408}$
	Chronic: $e^{0.8545*[\ln(hardness)]-1.7428}$
Fe	Chronic: 1000*Trec
Pb	Acute: $(1.46203-[\ln(hardness)*0.145712])*e^{1.273*[\ln(hardness)]-1.46}$
	Chronic: $(1.46203-[\ln(hardness)*0.145712])*e^{1.273*[\ln(hardness)]-4.705}$
Mn	Acute: $e^{0.3331*[\ln(hardness)]+6.4676}$
	Chronic: $e^{0.3331*[\ln(hardness)]+5.8743}$
Zn	Acute: $0.978*e^{0.8537*[\ln(hardness)]+2.2178}$
	Chronic: $0.986*e^{0.8537*[\ln(hardness)]+2.0469}$

		Table Value Standard in mg/L by Site*								
Metal		SHG	EF-2/3	AR-1	CG-1	CG-2	CG-6	AR-3A	LF-1	AR-4
Cd	Chronic	0.0029	0.0015	0.0012	0.0025	0.0043	0.0043	0.0015	0.0007	0.0011
	Acute	0.0036	0.0017	0.0014	0.0030	0.0057	0.0057	0.0017	0.0006	0.0012
Cu	Chronic	0.018	0.009	0.007	0.016	0.029	0.029	0.009	0.003	0.006
	Acute	0.030	0.014	0.011	0.025	0.050	0.050	0.013	0.005	0.009
Fe	Chronic	12	0.51	0.39	30	0.29	4.7	0.60	0.76	0.83
Pb	Chronic	0.006	0.003	0.002	0.005	0.011	0.011	0.003	0.001	0.002
	Acute	0.160	0.066	0.049	0.132	0.281	0.281	0.063	0.019	0.040
Mn	Chronic	2.19	1.66	1.51	2.06	2.62	2.62	1.64	1.14	1.42
	Acute	3.96	3.00	2.74	3.72	4.74	4.74	2.96	2.06	2.57
Zn	Chronic	0.80	0.40	0.31	0.68	1.27	1.27	0.38	0.15	0.27
	Acute	0.95	0.47	0.37	0.81	1.50	1.50	0.45	0.18	0.31

[1] for the main stem of East Fork of the Arkansas River from above confluence with Birdseye Gulch to immediately above confluence with California Gulch and tributaries to the Arkansas River

[2] for the main stem of the Arkansas River from immediately above confluence with California Gulch to immediately above confluence with Lake Creek

*Table Value Standards not provided for SL Up and SL Down as hardness data are not available for these sites.

Table 3: Code and description of location for all sampling sites

Site Code	Site Description
SHG	Combination of sites in Stray Horse Gulch associated with mine drainage upstream of the Leadville Mine Drainage Tunnel
EF-2/3	East Fork Arkansas River at Highway 24 Bridge/Highway 24 USGS gage
AR-1	Arkansas River upstream of confluence with California Gulch
CG-1	California Gulch immediately upstream of the Yak Tunnel Portal
CG-2	California Gulch just downstream of Yak Tunnel Treatment Plant discharge pipe
CG-6	California Gulch immediately upstream of confluence with Arkansas River
AR-3A	Arkansas River approximately 0.5 miles downstream from confluence with California Gulch
SL Up	Combination of sites along Sugarloaf Gulch and surrounding mine tailings piles
SL Down	Sugarloaf Gulch at Lake Fork
LF-1	Lake Fork immediately upstream of the confluence with Arkansas River
AR-4	Arkansas River approximately 0.5 miles downstream from confluence with Lake Fork

Table 4: General water quality characterization at each sample site. Statistical analyses for discharge, pH, hardness, and electrical conductivity from upstream to downstream. Please note: n, range, and median represent all data in the period of record for a given site while mean is the mean of monthly data for each site.

Site		Discharge (cfs)	pH (standard units)	Hardness (mg/L CaCO3)	Electrical Conductivity (µS/cm)
SHG	n	326	187	226	261
	mean annual	0.79	4.78	192	716
	median	0.48	5.26	234	456
	range	0-12	2.39-7.96	0.3-1550	23-4800
EF-2/3	n	106	176	141	188
	mean annual	41	7.75	125	235
	median	22.	7.87	101.8	173
	range	8.1-510	6.3-8.66	34-195	16-796
AR-1	n	650	197	614	660
	mean annual	72	7.57	95	181
	median	47	7.5	77	157
	range	7.2-610	5.1-9.18	27-190	14-2000
CG-1	n	311	167	277	315
	mean annual	0.6	4.97	236	538
	median	0.54	3.57	194	634
	range	0.002-10	1-7.5	2-2060	56-2500
CG-2	n	43	43	35	48
	mean annual	1.7	6.15	826	1291
	median	1.62	5.9	739	1298
	range	0.042-11	0.22-7.43	222-1570	578-2350
CG-6	n	922	823	764	912
	mean annual	2.4	7.32	456	852
	median	2.0	7.5	437	861
	range	0.46-17	3.1-9.04	100-1190	3-6570
AR-3A	n	636	308	648	782
	mean annual	80	7.43	121	259
	median	49	7.62	98	213
	range	10-610	5.23-8.85	37-238	58-2590
SL Up	n	16	21	NO DATA	21
	mean annual	0.91	3.76	NA	590
	median	0.14	3.7	NA	540
	range	0.01-15	2.3-4.8	NA	120-1030
SL Down	n	9	11	NO DATA	11
	mean annual	1.1	4.36	NA	688
	median	1.1	3.7	NA	550
	range	0.12-2	3.3-7.4	NA	290-1010
LF-1	n	67	74	55	81
	mean annual	47	7.01	38	87
	median	39	7.02	33	76.6
	range	2.2-400	5.6-8.63	15-294	5-977
AR-4	n	75	264	182	243
	mean annual	120	7.57	73	173
	median	87	7.63	64	132
	range	38-410	5-9.3	26-146	12-1620

Table 5: Characterization of metal sampling and concentrations at each sampling site in the Upper Arkansas River Basin. Concentrations below are manipulations of database values and are reported in mg/L. Please note: n, range, and median represent all data in the period of record for a given site while mean is the mean of monthly data for each site.

Site		Cd	Cu	Fe	Pb	Mn	Zn
SHG	n	372	351	159	350	161	371
	mean annual	0.38	1.01	73	0.21	16.3	46.5
	median	0.11	0.097	0.13	0.056	2.17	13.1
	range	0.0002-4.8	0.002-9.4	0.01-1100	0.000-3.3	0.01-281	0.00-617
EF-2/3	n	187	186	189	184	187	193
	mean annual	0.0003	0.002	0.05	0.002	0.03	0.01
	median	0.0002	0.001	0.05	0.002	0.02	0.01
	range	0.0001-0.005	0.001-0.01	0.01-0.20	0.000-0.05	0.01-0.09	0.01-0.19
AR-1	n	624	620	124	610	124	743
	mean annual	0.0003	0.003	0.12	0.001	0.03	0.03
	median	0.0002	0.003	0.13	0.000	0.03	0.05
	range	0-0.009	0.000-0.056	0.04-0.48	0.000-0.05	0.02-0.12	0.01-0.35
CG-1	n	299	295	84	293	84	347
	mean annual	0.27	0.34	3.6	0.72	5.56	33.9
	median	0.12	0.53	3.0	0.36	5.09	19.1
	range	0.0023-3.7	0-2.3	0.01-40	0.003-5.2	0.46-38.5	0.16-428
CG-2	n	51	48	49	48	50	51
	mean annual	0.019	0.057	0.53	0.075	0.63	2.99
	median	0.0055	0.010	0.08	0.005	0.28	0.84
	range	0.0001-0.38	0.001-1.7	0-15	0.000-2.1	0.00-20	0.01-85
CG-6	n	941	935	444	899	445	1138
	mean annual	0.017	0.023	1.2	0.020	4.75	5.06
	median	0.013	0.007	0.07	0.002	5.27	4.839
	range	0.0002-0.37	0.001-1.2	0-50	0.000-2.7	0.01-36.3	0.01-54.9
AR-3A	n	826	803	199	800	198	933
	mean annual	0.0011	0.004	0.10	0.001	0.33	0.35
	median	0.0007	0.003	0.10	0.001	0.07	0.24
	range	0.0001-0.027	0.001-0.063	0.01-2	0.000-0.78	0.012-3.05	0.01-1.76
SL Up	n	21	21	20	21	21	21
	mean annual	0.045	0.055	5.0	0.05	35.7	12.8
	median	0.027	0.026	2.3	0.05	35.3	11.6
	range	0.008-0.25	0.01-0.37	0.10-39	0.05-0.05	1.78-86.6	2.37-45.3
SL Down	n	12	12	12	12	12	12
	mean annual	0.022	0.024	1.0	0.041	33.5	8.82
	median	0.026	0.022	0.95	0.05	27.9	8.32
	range	0.012-0.039	0.012-0.043	0.63-1.5	0.004-0.05	9.09-46.9	5.77-12.3
LF-1	n	97	91	61	96	61	100
	mean annual	0.0007	0.003	0.21	0.003	0.09	0.03
	median	0.0002	0.003	0.21	0.000	0.07	0.02
	range	0.0001-0.005	0.000-0.016	0.05-0.84	0.000-0.05	0.02-0.46	0.00-0.23
AR-4	n	309	299	254	274	254	307
	mean annual	0.0005	0.003	0.12	0.002	0.11	0.11
	median	0.0004	0.002	0.12	0.002	0.07	0.10
	range	0.0001-0.008	0.000-0.014	0.03-1.7	0.000-0.05	0.02-0.94	0.01-1.15

Table 6: Mean discharge, pH, hardness, and metal concentrations upstream and downstream from treatment using mean values from dates with paired samples. Discharge is in cfs, pH is in standard units, hardness is in mg/L $CaCO_3$, all metals are in mg/L.

	Leadville Mine Drainage Tunnel Water Treatment Plant			
	SHG (upstream from treatment)	EF-2/3 (downstream from treatment)	Standard Removal (%)	Dilution Adjusted Removal (%)
Discharge	0.36	113	-31000	NA
pH	4.85	7.13	-47	NA
Hardness	233	79	66	NA
Cadmium	0.46	0.0002	100	99.9
Copper	0.72	0.002	99.7	-5.3
Iron	33	0.06	99.8	42
Lead	0.12	0.001	99.2	-146
Manganese	15	0.02	99.8	55
Zinc	66.8	0.02	100	91
	Yak Tunnel Water Treatment Plant			
	CG-1 (upstream from treatment)	CG-2 (downstream from treatment)	Standard Removal (%)	Dilution Adjusted Removal (%)
Discharge	1.36	3.32	-144	NA
pH	3.77	4.98	-32	NA
Hardness	139	765	-448	NA
Cadmium	0.12	0.079	36	-55
Copper	0.58	0.2	65	15
Iron	4.4	1.9	57	-5.7
Lead	0.67	0.25	62	7.4
Manganese	4.78	2.59	46	-32
Zinc	18.3	12.2	33	-63
	Dinero Wetland Complex			
	SL-U (upstream from treatment)	SL-D (downstream from treatment)	Standard Removal (%)	Dilution Adjusted Removal (%)
Discharge	1.6	0.78	51	NA
pH	3.65	3.59	1.7	NA
Hardness	ND	ND	NA	NA
Cadmium	0.05	0.025	50	76
Copper	0.066	0.026	61	81
Iron	5.97	0.95	84	92
Lead	0.05	0.05	0	51
Manganese	37.2	27.3	26	64
Zinc	13.7	8	42	72

ND = no data available

NA = not applicable

Table 7: Mean metal concentrations up- and downstream from treatment, using mean values from dates with paired sampling, compared with water quality standard of study site downstream from treatment site in the Arkansas River. Acute water quality standard is shown for each metal except iron in which the chronic standard is shown. All concentrations are shown in mg/L.

	Leadville Mine Drainage Tunnel Water Treatment Plant		
Metal	Upstream from treatment Concentration (SHG)	Water Quality Standard (AR-1)	Downstream from treatment Concentration (EF-2/3)
Cadmium	0.46	0.0014	0.0002
Copper	0.72	0.011	0.002
Iron	33	0.39	0.06
Lead	0.12	0.049	0.001
Manganese	15	2.74	0.02
Zinc	66.8	0.37	0.02
	Yak Tunnel Water Treatment Plant		
Metal	Upstream from ttreatment Concentration (CG-1)	Water Quality Standard (AR-3A)	Downstream from treatment Concentration (CG-2)
Cadmium	0.12	0.0017	0.079
Copper	0.58	0.013	0.2
Iron	4.4	0.60	1.9
Lead	0.67	0.063	0.25
Manganese	4.78	2.96	2.59
Zinc	18.3	0.45	12.2
	Dinero Wetland Complex		
Metal	Upstream from treatment Concentration (SL-U)	Water Quality Standard (AR-4)	Downstream from treatment Concentration (SL-D)
Cadmium	0.05	0.0012	0.025
Copper	0.066	0.009	0.026
Iron	5.97	0.83	0.95
Lead	0.05	0.040	0.05
Manganese	37.2	2.57	27.3
Zinc	13.7	0.31	8

Table 8: Time in years to CG-1 drainage compliance with median acute metal standards from present day (2018). Minimum and maximum times use the 10 percent error bounds on the predicted average exponential decay at the site.

		Metal				
		Cd	Cu	Pb	Mn	Zn
CG-1 Standards	Minimum	93	35	8	-9[1]	115
	Average	187	49	15	<1	293
	Maximum	1497	74	30	NA[2]	NA[2]
AR-3A Standards	Minimum	130	46	21	1	140
	Average	256	63	33	21	353
	Maximum	2017	92	57	NA[2]	NA[2]

[1] Negative value indicates the system has already come into compliance by 2018.
[2] Values could not be determined as k value (Equation 3) becomes negative from initial concentration becoming lower than final concentration with 10 percent maximum error.

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