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Water-quality change following remediation using structural bulkheads in abandoned draining mines, upper Arkansas River and upper Animas River, Colorado USA

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ABSTRACT

Water-quality effects after remediating abandoned draining mine tunnels using structural bulkheads were examined in two study areas in Colorado, USA. A bulkhead was installed in the Dinero mine tunnel in 2009 to improve water quality in Lake Fork Creek, a tributary to the upper Arkansas River. Although bulkhead installation improved pH, and manganese and zinc concentrations and loads at the Dinero mine tunnel, water-quality degradation was observed at the nearby Nelson tunnel. Only manganese concentrations improved in Lake Fork Creek downstream from the tunnel. To improve water quality in Cement Creek, a tributary of the Animas River, multiple bulkheads were installed in mine tunnels during 1996–2003 and a water treatment plant operated from 1989 to 2003 to treat drainage from several draining tunnels. After bulkhead installation and cessation of active water treatment (about 2003), water quality (pH and dissolved copper, manganese, and zinc concentrations) degraded at the mouth of Cement Creek. The patterns and timing were similar to post-bulkhead increased discharge and trace-metal loads at non-bulkheaded tunnels indicating the bulkheads might have been the cause. Pre-1989 water-quality data for Cement Creek are scarce, although limited historical data indicate possible, slight improvement in only manganese concentrations after bulkhead installation. Increased zinc loads in Lake Fork Creek and decreased pH through time in Cement Creek may indicate increased groundwater discharge to the streams after bulkhead installation. In these two study areas, bulkheads did not substantially improve downstream water quality.

1. Introduction

Abandoned draining mine features including adits and tunnels (horizontal access to mine workings), shafts (vertical access to mine workings), and seeps and runoff from mine waste and tailings are a persistent water-quality problem worldwide (Blowes et al., 2003; 2014; Sheoran and Sheoran, 2006, p. 61 in Wolkersdorfer, 2008). Water interacts with mineralized rock containing pyrite and other sulfides in these features and generates mining-impaired water (mine drainage) that is sometimes acidic and may contain elevated concentrations of various trace metals and metalloids (Nordstrom et al., 2015). In the State of Colorado, over 23,000 abandoned mines impair water quality in about 2,900 stream kilometers (km) (Colorado Department of Public Health and Environment, 2019).

Remediation of mine drainage remains a challenge. Recommended technologies for solid wastes include removal, consolidation, or capping to minimize percolation or generation of mine drainage from the wastes (Colorado Department of Natural Resources Division of Minerals and Geology, 2002; International Network for Acid Prevention, 2014). Remediation alternatives for draining adits and shafts include operation of water-treatment plants to chemically treat the drainage (Walton-Day, 2003), installation of structural bulkheads to physically limit water discharge from mine workings (Colorado Department of Natural Resources Division of Minerals and Geology, 2002; Johnson and Hallberg, 2005) and combinations of bulkheads and engineering controls to limit infiltration of surface water into underground mine workings (Marks et al., 2008).

Installation of structural bulkheads to reduce discharge from mines is often cited as a preferred alternative because this approach avoids long-term operation and maintenance costs associated with water-treatment plants (Bureau of Land Management, 2006; Younger et al., 2002). A structural bulkhead is an engineered concrete structure extending from

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floor to ceiling in a mine tunnel with enough thickness to withstand lithostatic pressure of overlying rocks, hydrostatic pressure of the mine pool formed when the bulkhead is sealed, and additional pressure that could occur during a mine blowout (Einarson and Abel, 1990; Sorenson and Brown, 2015). Mine blowout occurs when water impounded behind a collapse or debris in an upgradient part of the mine is abruptly released. Although bulkheads physically limit mine discharge, they are known to leak (p. 24 in Gusek and Figueroa, 2009) and generally do not completely stop discharge from draining mine tunnels.

There are three primary goals associated with installation of a structural bulkhead in a draining mine tunnel: (1) to limit the discharge of poor-quality water from the tunnel (Bureau of Land Management, 2006; Sorenson and Brown, 2015); (2) to protect existing or future infrastructure in front of the mine-tunnel opening and (or) downstream water bodies from the effects of blowouts from the mine workings (Bureau of Land Management, 2006; Stratus Consulting, 2009); and (3) to improve water quality by limiting some of the physical and chemical changes that degrade water quality in underground mine tunnels.

Underground mining and drainage tunnels lower the elevation of the water table thereby increasing contact of pyrite-bearing mineralization to atmospheric oxygen (Fig. 1a). Oxygen, infiltrating water from precipitation and snowmelt, and micro-organisms, fuel generation of acid mine drainage (Nordstrom et al., 2015) through the overall reaction (Blowes et al., 2014):

$$FeS_2 + \frac{15}{4}O_2(aq) + \frac{7}{2}H_2O(aq) \rightarrow 2SO_4^{2-} + Fe(OH)_3(s) + 4H^+(aq) \quad (1)$$

The products of this reaction drive dissolution of metal-sulfide minerals and formation of secondary, variably soluble sulfate minerals, degrading water quality in the mine and its discharge to the surface (Fig. 1a) (Alpers et al., 1994; Blowes et al., 2003, 2014; Jambor et al., 2000; Nordstrom, 2011). Seasonal wetting and drying in underground workings exacerbate acid mine drainage and formation of secondary sulfate minerals. During the dry season, secondary sulfate minerals accumulate underground; during the wet season, infiltrating water promotes forward progress of reaction (1), and soluble secondary sulfate minerals that accumulated during the dry season dissolve, causing a wet-season flush of more degraded water compared to other times of year (Alpers et al., 1994; Blowes et al., 2003, 2014; Nordstrom and Alpers, 1999; Nordstrom et al., 2015; U.S. Environmental Protection Agency, 1994). Groundwater backed up behind bulkheads may re-submerge mineralized bedrock, greatly decreasing dissolved-oxygen influx and limiting the acid mine drainage reaction, thereby potentially improving water quality of the impounded mine pool water and bulkhead leakage (Sorenson and Brown, 2015; Walton-Day and Mills, 2015; Wolkersdorfer, 2008) (Fig. 1b). Saturation of mine workings also may decrease or eliminate seasonal wetting and drying (4 in Fig. 1b), limiting formation and dissolution of secondary sulfate minerals, further improving water quality. Though where accumulations of soluble sulfate minerals are extreme, their dissolution upon flooding could greatly degrade water quality (Jambor et al., 2000; Nordstrom and Alpers, 1999). Water-quality improvement may also be limited by the relation between the elevation of the final water table and pyrite-bearing rock in the mine workings. The elevated post-bulkhead water table may reroute water from the mine pool through permeable fractures and strata to non-bulkheaded workings, and may increase flow in existing springs or cause emergence of new springs (6 in Fig. 1b) potentially off setting bulkhead-related water-quality improvement (Cowie and Roberts, 2020). Water-quality and discharge monitoring at the tunnel outflow and surrounding area before and after bulkhead installation documents the effects of the bulkhead.

In Colorado, USA, at least 26 structural bulkheads had been installed in mines as of 2015 (Appendix B; Bureau of Reclamation, 2015). Monitoring data documenting water-quality effects of bulkheads are not always readily or publicly available. Lake Fork Creek located in the upper Arkansas River watershed (Fig. 2) and Cement Creek, in the upper Animas River watershed (Fig. 3), are two areas having available data. In the Lake Fork Creek watershed, the Bureau of Land Management (2006) installed a bulkhead in the Dinero mine tunnel (hereinafter Dinero tunnel) in 2009. In the Cement Creek watershed, four bulkheads were installed in two tunnels from 1996 to 2003. Three were installed in the American tunnel between 1996 and 2002 by Sunnyside Gold Corporation (Sunnyside Gold Corporation, 2003), and one was installed in the Mogul mine tunnel in 2003 by the Gold King Mining Corporation (Bonita Peak Community Advisory Group, 2019a; Bureau of Reclamation, 2015) (Fig. 4).

The objective of this paper is to examine water-quality changes in the two mining districts to assess whether bulkhead installation improved downstream water quality. For the Dinero tunnel, which drains into Lake Fork Creek, water-quality and discharge data for four sampling sites are discussed for the period 2006–2017 (Fig. 2). To evaluate the American and Mogul tunnel bulkheads, water-quality and discharge data collected near the mouth of Cement Creek from 1971, 1981, and 1995–2015 are presented. Discussion includes discharge and water-quality data compiled from multiple sources (Walton-Day et al., 2020) from 1988 to 2015 for five mine tunnels including the American tunnel and the Mogul, Red and Bonita, Black Hawk, and Gold King mine tunnels. Herein, all are referred to simply as tunnels (e.g. Mogul tunnel).

2. Study areas and methods

2.1. Upper Arkansas River watershed, Dinero tunnel

The Dinero tunnel is one of five mining tunnels in the Sugar Loaf mining district in the upper Arkansas River watershed (Fig. 2). Elevation ranges from about 2,920 meters (m) at the confluence of Colorado Gulch with Lake Fork Creek to over 3,400 m on the ridge comprising the watershed boundary (Fig. 2). Mean annual precipitation (1981–2010) is 48 centimeters (cm) of which at least half occurs as snow (Sugarloaf RSVR Colorado at https://wrcc.dri.edu/cgi-bin/cliMAIN.pl?co8064 accessed 30 Nov 2020). Surface hydrology is dominated by snowmelt with 70% of runoff occurring in May through July (Walton-Day and

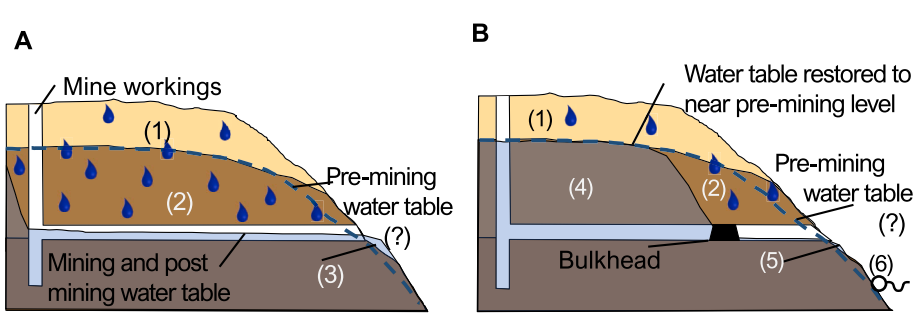

Fig. 1. Diagram showing (A) schematic cross section of mineralized rock and mine workings during and after mining. Notable features are (1) leached, mineralized rock above the historical water table; the lower post-mining water table caused by mine workings and tunnels that (2) exposes pyrite in mineralized rock to oxygen and infiltrating water and generates acid mine drainage (3) that flows to and may degrade surface water. (B) After bulkhead emplacement the water-table elevation increases behind the bulkhead and (4) some of the mineralized rock is re-submerged beneath the water table limiting the extent of acid mine drainage generation potentially causing (5) decreased flow of degraded water from the tunnel and rerouting some flow to other non-bulkheaded mine tunnels and existing or new springs (6). After Schmidt (2007).

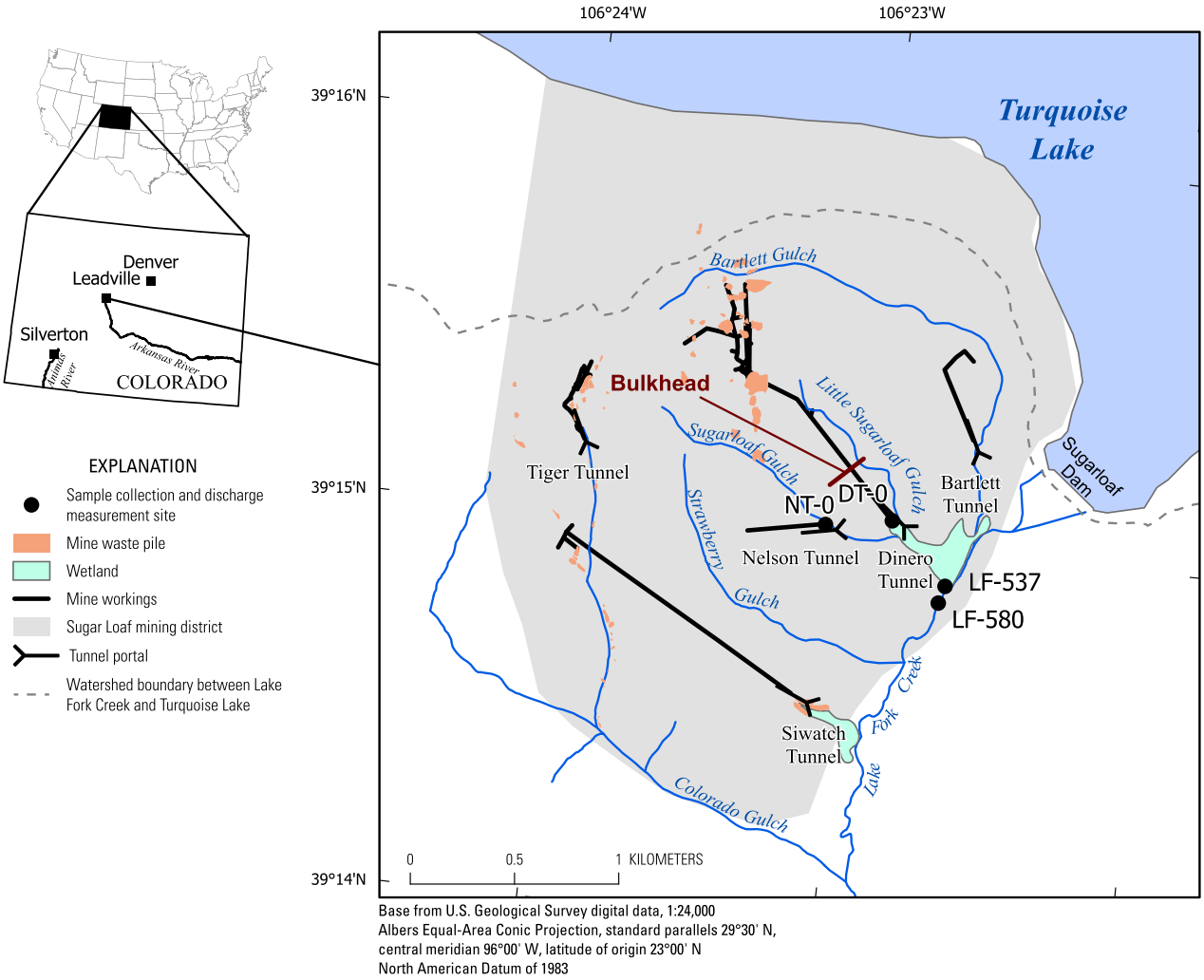

Fig. 2. Map showing location of upper Arkansas River watershed study area in Colorado, USA, Sugar Loaf mining district, mine-waste piles, mine tunnels, and sampling sites at the Dinero tunnel (DT-0), Nelson tunnel (NT-0), channel draining wetland downstream from Dinero tunnel (LF-537), and Lake Fork Creek downstream from Dinero tunnel (LF-580). The extent of tunnels was digitized from published maps (Singewald, 1955) and by compilation from mineral surveys (e.g. U.S. Surveyor General's Office, 1912).

Mills, 2015). Annual mean streamflow at the U.S. Geological Survey (USGS) streamgage Arkansas River at Leadville, located about 3 km directly east of Dinero tunnel, varied from about 1 to 3 cubic meters per second (m^3/s), was punctuated by wet (2011 and 2014) and dry (2012) years, but showed no trend during the study period (Supplemental Fig. S1a).

In the Sugar Loaf mining district, silver and some gold, lead, and zinc were mined from Tertiary quartz-sulfide veins in crystalline, Precambrian bedrock (schist, gneiss, and granite) mostly from 1880 until the 1920s (Singewald, 1955). The primary mine tunnels (Fig. 2) total approximately 6 km in length. The Dinero tunnel provided drainage and access to higher elevation mine workings at its northwest end, and is a major contributor to degraded water quality, primarily elevated manganese and zinc concentrations in Lake Fork Creek (Walton-Day et al., 2005; Bureau of Land Management, 2006), a tributary to the upper Arkansas River. A bulkhead for Dinero tunnel was chosen as the preferred remediation approach and was installed and closed in 2009 (Bureau of Land Management, 2006). The bulkhead is located approximately 390 m into the tunnel at an elevation of 2,984 m. Elevation of ground surface above the bulkhead is 3,049 m.

Controls on groundwater occurrence and flow in the Dinero area are not well understood. Groundwater flow likely is dominantly fracture controlled in the Precambrian rocks. In general, snowmelt likely provides high rates of seasonal recharge to a shallow, active groundwater system that exists over a deeper, inactive groundwater system (Johnson and Yager, 2006; Manning and Caine, 2007; Mayo et al., 2003; Snow, 1968; Walton-Day and Poeter, 2009). There is a groundwater divide near the watershed divide between the area containing most of the mine workings and Turquoise Lake (Fig. 2) (Walton-Day and Poeter, 2009). Some groundwater in the Sugar Loaf mining district likely discharges to surface streams (Bartlett, Little Sugarloaf, Sugarloaf, Strawberry, and Colorado Gulches (Fig. 2), and also directly to Lake Fork Creek between Sugarloaf Dam and LF-580 where previous work indicated inflow of trace-metal rich groundwater to Lake Fork Creek (p. 45 in Walton-Day et al., 2005). Underground mine workings provide preferential pathways for groundwater flow.

Water-quality data were collected near the Dinero tunnel as part of an extensive monitoring program to understand the water-quality effects of bulkhead installation (Walton-Day et al., 2013; Walton-Day and Mills, 2015). Herein, discussion includes data collected in 2006 (four times between May and October) and from 2010 to 2014 and 2016–2017 (in spring and autumn each year) at sites DT-0 (Dinero tunnel), LF-537, LF-580, and NT-0 (Nelson mine tunnel) (Fig. 2). Raw data are stored in the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2019a and can be retrieved using USGS site IDs (see "Data Availability" section). Water from DT-0 discharges into the

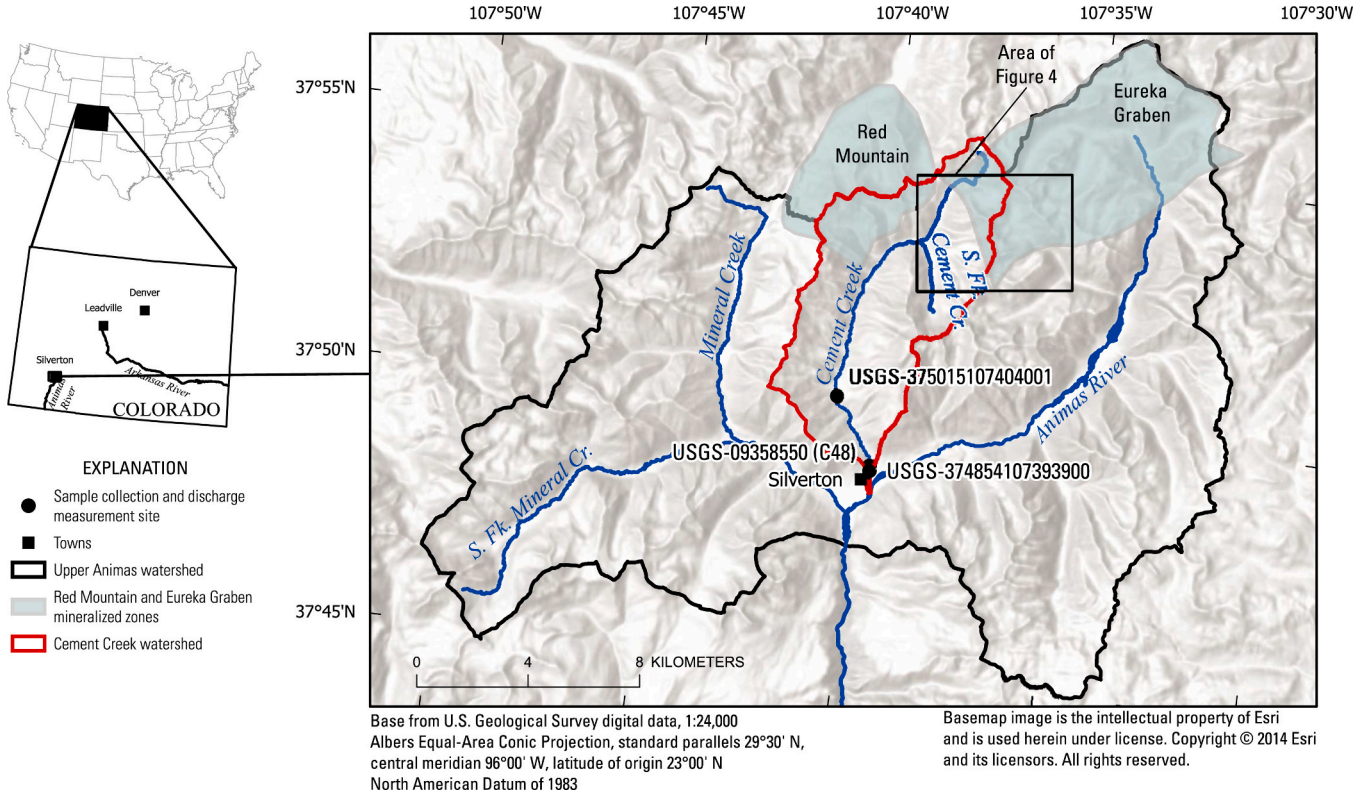

Fig. 3. Map showing location of upper Animas River and Cement Creek watersheds in southwestern Colorado, USA, sample monitoring sites, and mineralized areas.

wetland located between the Dinero tunnel and Lake Fork Creek (Fig. 2). Site NT-0 discharges to Little Sugarloaf Gulch that flows into the same wetland, which is also fed by Sugarloaf Gulch, near Dinero tunnel. The wetland drains to Lake Fork Creek upstream from site LF-580 via surface flow at LF-537 and via seeps and groundwater on the eastern edge of the wetland (Fig. 2). Data presented are discharge, pH, and dissolved (<0.45 μm) manganese and zinc concentrations. Sample collection, analytical methods, and quality-assurance information are presented in Walton-Day and Mills (2015). Metal loads were calculated by multiplying instantaneous discharge measured at the time of sample collection by metal concentration and are presented as kilograms per day (kg/day). Discharge, hydrogen ion (from pH), and manganese and zinc concentrations and loads were compared before and after the Dinero bulkhead closure using a two-sample permutation test with the R package 'perm' (https://www.rdocumentation.org/packages/perm/versions/1.0-0.0). For p-values $\leq$ 0.05, the difference in the means for the two groups were considered statistically significant.

2.2. Upper Animas River watershed, Cement Creek

Cement Creek is tributary to the upper Animas River, upstream from Silverton, Colorado (Figs. 3 and 4). Elevation ranges from about 2,860 m at C48 to more than 4,000 m on the ridge comprising the watershed boundary. Mean annual precipitation (from 1981 to 2010) is 67 cm (Silverton Colorado at https://wrcc.dri.edu/cgi-bin/cliMAIN.pl?co7656, accessed 30 Nov 2020). Similar to the Dinero area, most precipitation occurs as snow, and surface hydrology is dominated by melting of the seasonal snowpack. Annual mean streamflow at USGS streamgage Cement Creek at Silverton, Colorado (station 09358550, C48) varied from about 0.5 to 1.6 m^3/s, was punctuated by wet (1995, 1997, 1999, 2005, 2008, 2011, and 2014–2015) and dry years (2002 and 2012–2013), but showed no trend during the study period (Supplemental Fig. S1b).

Cement Creek drains the central part of the collapsed and mineralized Silverton volcanic caldera consisting of Tertiary-age extrusive and intrusive volcanic rocks (von Guerard et al., 2007). Extensive hydrothermal alternation and mineralization associated with the caldera and its collapse form the basis for historical mining in the region. Mining in the upper Animas River watershed occurred from the early 1870s through 1991 and was extensive with over 300 mine, mill, mill tailing, and smelter sites documented (Church, 2007, Figs. 2 and 5 in Church et al., 2007a; Jones, 2007). Polymetallic (silver, lead, zinc, copper, ± gold) sulfide veins in fractures and fissures in the Eureka Graben area were the target of the mines in upper Cement Creek (Figs. 3–4) (Bove et al., 2007). Mine tunnels (Fig. 4) total over 60 km in length (Bonita Peak Community Advisory Group, 2019b). Cement Creek is influenced by both acid mine drainage from mined and mineralized areas (Eureka Graben and Red Mountain areas, Figs. 3–4), and acid rock drainage from acid-generating hydrothermally altered areas resulting in low pH stream water (pH = 4–5) having elevated metal concentrations (Bove et al., 2007; Mast et al., 2007).

In the Cement Creek area, groundwater flow is likely fracture controlled (Simon Hydro-Search, 1992, 1993). Similar to the Dinero study area, snowmelt recharge provides most groundwater recharge (Caine and Wilson, 2011). Prior to mining, groundwater is estimated to primarily have moved southwest from the Sunnyside basin to discharge along Cement Creek (Fig. 4) (Simon Hydro-Search, 1992).

Remediation and reclamation in the Cement Creek watershed have been ongoing since the early 1980s and include consolidation and capping of mine-waste deposits, passive treatment, and hydrologic controls (Bonita Peak Community Advisory Group, 2019a, table 5 in Church et al., 2007b; Lange, 2019). Water treatment of American tunnel discharge started in the early 1980s and consisted of addition of hydrated lime ($Ca(OH)_2$) and flocculant, precipitation of solids, and settling in a series of four settling ponds in the Gladstone area (Fig. 4) (Colorado Department of Health, 1988; Standard Metals Corporation, 1981). From 1996 to 2003, water treatment expanded to include Cement Creek upstream from Gladstone (upper Cement Creek, including

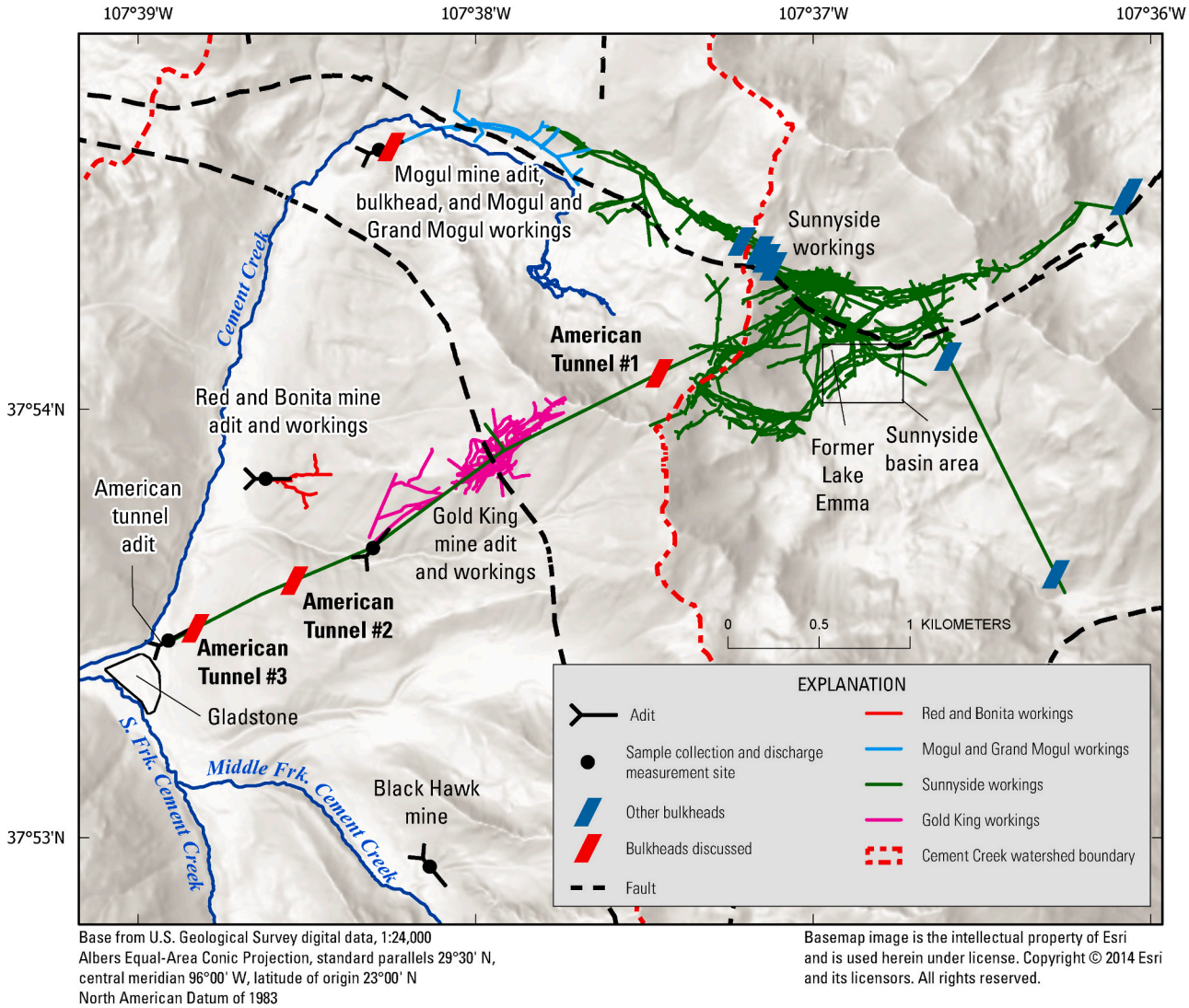

Fig. 4. Map showing mine workings for Mogul and Grand Mogul, Red and Bonita, Gold King, and Sunnyside mines, the Black Hawk mine, bulkhead locations, and surface drainage. Water from the American tunnel, Mogul, Red and Bonita, and Gold King tunnels discharges towards Cement Creek upstream from Gladstone. Faults represented as black dashed lines are from Yager and Bove (2007).

discharge from the Mogul, Red and Bonita, and Gold King tunnels) (Fig. 4), up to the capacity of the treatment plant; during 2003–2004 Gold King effluent was sometimes treated (Bonita Peak Community Advisory Group, 2019a). All active treatment of these sources ceased by July 2004 (Bonita Peak Community Advisory Group, 2019a). In summary, *most importantly, nearly continuous, active treatment of the American tunnel occurred from 1989 through 2003 with upper Cement Creek (upstream from Gladstone) being wholly (low discharge) or partially (high discharge) treated from 1996-2003, and the Gold King tunnel discharge discontinuously treated during 2003 and 2004.*

The focus herein is on Cement Creek and the four bulkheads installed into tunnels draining into Cement Creek: (1) American tunnel #1 (AT#1) bulkhead, the most upgradient bulkhead in the tunnel between the overlying Sunnyside and Gold King mine workings, closed in September 1996; (2) American tunnel #2 (AT#2) bulkhead, located downgradient from the overlying Gold King mine workings, closed in August 2001; (3) American tunnel #3 (AT#3), the most downgradient bulkhead, closed in December 2002; and (4) Mogul tunnel bulkhead closed in August 2003 (Bonita Peak Community Advisory Group, 2019a; Sorenson and Brown, 2015). The American tunnel extends northeast from its mouth (elevation about 3,240 m) near Gladstone upgradient to the Sunnyside mine workings (Fig. 4) and was completed as a development and exploration tunnel in 1961 (Burbank and Luedke, 1969; Sorenson and Brown, 2015). Additional draining mine tunnels discussed include the Red and Bonita (portal at 3,340 m) and Gold King (portal at 3,487m), that drain into Cement Creek, and the Black Hawk (portal at 3,535 m) that drains into the South Fork Cement Creek via the Middle Fork (Fig. 4) (Sorenson and Brown, 2015). The AT#1 bulkhead and multiple bulkheads to the east in the Sunnyside mine workings (Fig. 4) were designed to promote groundwater flow towards Cement Creek. The expectation was that groundwater would discharge along Cement Creek in a reach between the Mogul mine and 4–5 km south, rather than to the upper Animas River watershed east of the Cement Creek watershed divide (Lange, 2019; Simon Hydro-Search, 1992, 1993).

Water-quality data were compiled for samples collected at five sites in the vicinity of the USGS streamgage near the mouth of Cement Creek (USGS station 09358550 and site C48 on Fig. 3). Data including dissolved (<0.45 μm) copper, manganese, and zinc concentrations and pH were retrieved from the Water Quality Portal (WQP) (https://www.waterqualitydata.us/data retrieved April 2019; see "Data Availability" section). Mast (2018) describes data aggregation and quality assurance for this data set. Data for two additional samples were retrieved from NWIS including a sample collected on October 4, 1971, at USGS site ID

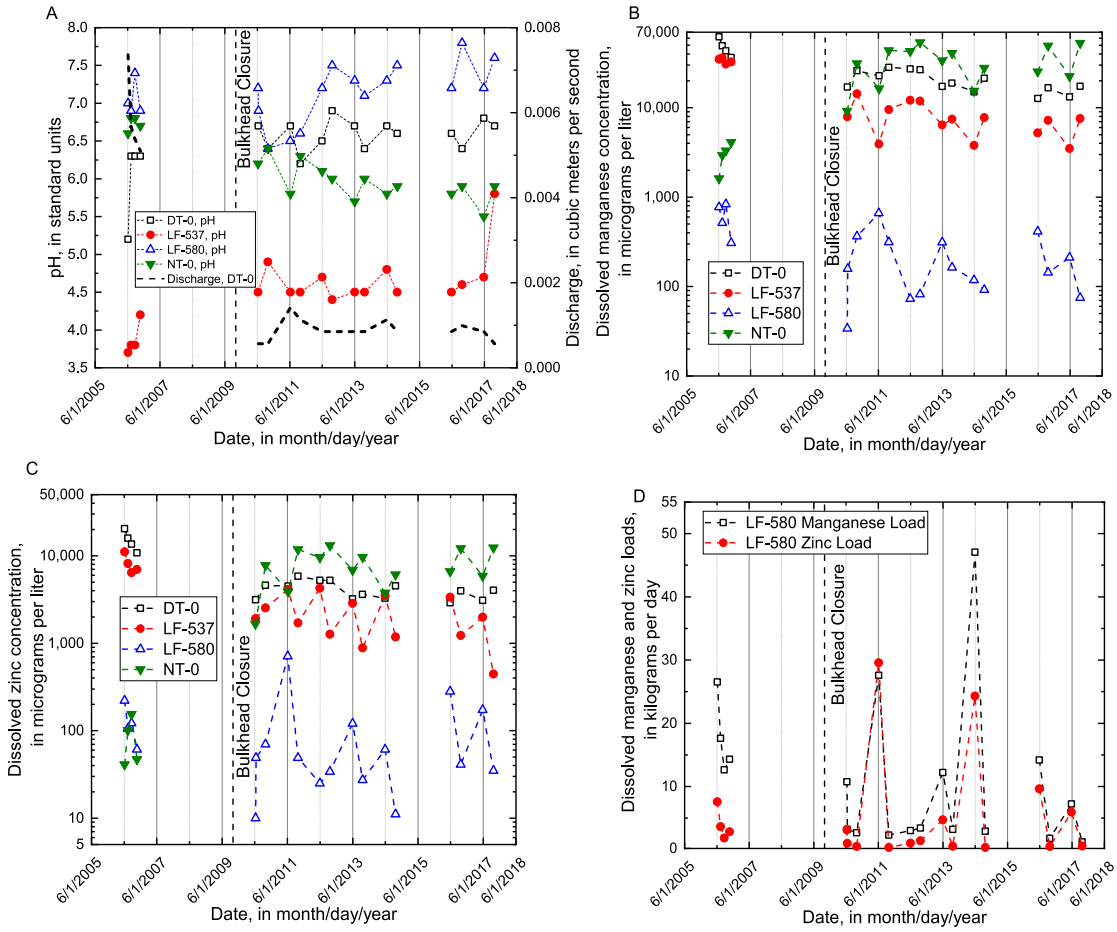

Fig. 5. Graphs showing variation in (A) in pH and discharge, (B) dissolved manganese concentrations, (C) dissolved zinc concentrations, and (D) dissolved zinc and manganese loads for sites at the Dinero tunnel (DT-0), LF-537 draining the Dinero wetland, LF-580 on Lake Fork Creek, and Nelson tunnel (NT-0).

374854107393900 located 0.5 km downstream from C48, and a sample collected on September 24, 1981, at USGS site ID 375015107404001, 2 km upstream from C48 (Fig. 3). Daily mean streamflow values for station 09358550 (C48) also were retrieved from NWIS. This analysis excluded samples collected after the Gold King mine spill occurred in August 2015 (Bureau of Reclamation, 2015).

Annual discharge-weighted-mean (DWM) concentrations of copper, manganese, zinc, and pH for these data in Cement Creek were estimated for 1995–2015. Discharge weighting of concentrations helps to remove the influence of year-to-year streamflow variability on underlying concentration trends. DWMs were computed using a period-weighted approach, which interpolates concentrations between sampling events to estimate solute loads (Aulenbach et al., 2016). In high-elevation streams, the period-weighted approach works well because solute concentrations exhibit a pronounced annual pattern of dilution during snowmelt that minimizes changes in solute concentrations between sampling events. In addition, metal concentrations in Cement Creek changed dramatically over the study period, complicating development of regression equations to predict concentrations based on streamflow. To estimate DWM concentrations, daily concentrations were computed by linear interpolation of concentrations between sampling events, which averaged 18 samples per year and ranged from 10 to 38. The estimated daily concentrations were multiplied by the daily mean discharge (providing loads), which were then summed over the year and divided by the sum of the daily discharge values to yield an annual DWM concentration in micrograms per liter (μg/L). Time-series graphs of the DWM concentrations reproduced the overall trends in the discrete sample data (Supplemental Fig. S2). Loads were calculated for samples collected during 2004–2015 to help provide context for the loads at the mine tunnels. Average daily loads were calculated by multiplying the raw data concentration times the mean daily discharge for the day of sample collection, converting to kg/day, and averaging over the total number of samples.

Discharge and dissolved concentrations of copper, manganese, and zinc for the American tunnel (1988–2015), the Mogul tunnel (1992–2015), the Red and Bonita tunnel (1997–2015), the Gold King tunnel (1993–2015), and the Black Hawk tunnel (1991–2005) were compiled from multiple sources (Walton-Day et al., 2020). Metal loads were calculated as described for the Dinero tunnel.

3. Results and discussion

3.1. Discharge and water-quality responses to bulkhead closure

3.1.1. Upper Arkansas River watershed, Dinero tunnel

The discharge and water-quality responses to closure of the Dinero tunnel bulkhead were mixed. After bulkhead closure, mean discharge decreased at DT-0 by 85% and increased at LF-537, LF-580, and NT-0 by as much as 200% (Fig. 5, Table 1, Supplemental Table S1). Mean pH values increased after bulkhead closure at DT-0 and LF-537 but decreased at LF-580 and NT-0 (Fig. 5, Table 1, Supplemental Table S1). Mean dissolved manganese concentrations decreased after bulkhead

Table 1
Statistical comparison of pre- and post-bulkhead discharge and water quality, Dinero study area. Percent change is the difference in mean concentration or load between periods and p-value is from the 2-sample permutation test comparing the 2 periods. Values in bold are significant at 95% confidence. Before closure, n = 4. After closure n = 14 except at LF-580 where n = 15. [DT-0, Dinero tunnel; LF-537, sample site draining wetland downstream from DT-0; LF-580, sample site on Lake Fork Creek downstream from DT-0 and LF-537; NT-0, Nelson tunnel; Dis., dissolved; Conc., concentration; %, percent; <, less than].

Site	Discharge		pH as hydrogen ion concentration		Mean Dis. Manganese Conc.		Mean Dis. Zinc Conc.		Mean Dis. Manganese Load		Mean Dis. Zinc Load	
	% change	p-value	% change	p-value	% change	p-value	% change	p-value	% change	p-value	% change	p-value
DT-0	**−85**	**< 0.05**	**−85**	**< 0.05**	**−58**	**< 0.05**	**−73**	**< 0.05**	**−94**	**< 0.05**	**−96**	**< 0.05**
LF-537	66	0.68	**−82**	**< 0.05**	**−77**	**< 0.05**	**−73**	**< 0.05**	**−75**	**< 0.05**	−32	0.64
LF-580	120	0.85	11	0.91	**−65**	**< 0.05**	−12	0.88	−47	0.20	40	0.90
NT-0	**200**	**0.05**	**580**	**< 0.05**	**1,000**	**< 0.05**	**9,200**	**< 0.05**	**3,100**	**< 0.05**	**23,000**	**< 0.05**

closure by as much as 77% at DT-0, LF-537, and LF-580 but increased at NT-0 by 1,000% (Fig. 5, Table 1, Supplemental Table S1). Similarly, mean dissolved zinc concentrations decreased after bulkhead closure by as much as 73% at DT-0, LF-537, and LF-580, but increased at NT-0 by 9,200% (Fig. 5, Table 1, Supplemental Table S1). Mean dissolved manganese loads decreased by as much as 94% at DT-0, LF-537, and LF-580, but increased at NT-0 by 3,100% (Fig. 5, Table 1, Supplemental Table S1). Finally, mean dissolved zinc loads decreased by up to 96% at DT-0 and LF-537, but increased at LF-580 and NT-0 by 40% and 23,000% (Fig. 5, Table 1, Supplemental Table S1).

At the Dinero tunnel portal (DT-0), water quality improved after bulkhead closure evidenced by statistically significant ($p < 0.05$) decreases in discharge, manganese and zinc concentrations and loads, and increases in pH (Table 1; Fig. 5a–c). In addition, bulkhead installation seems to have reversed seasonal concentration patterns. Before bulkhead closure (2006 values), the lowest pH and greatest manganese and zinc concentrations occurred during spring runoff coincident with the greatest discharge. The highest pH and lowest metal concentrations occurred during low flow in summer and fall (Fig. 5a-c). In contrast, after bulkhead closure (2010–2017), pH values were higher, and metal concentrations were lower during high flow than during base flow (Fig. 5a-c). Higher concentrations during snowmelt prior to bulkhead installation may indicate that seasonal wetting and drying in exposed mine workings was likely contributing to a spring flush of low pH, metal-rich water (Fig. 1a). After bulkhead closure, water levels and chemistry were more stable, limiting pyrite oxidation as mine workings and rocks became submerged (Fig. 1b).

Water quality also improved after bulkhead closure at LF-537, the wetland outflow, though not as dramatically as at DT-0. At LF-537, significant ($p < 0.05$, Table 1) water-quality improvement included increased pH and decreased manganese and zinc concentrations and manganese loads (Fig. 5a-c). The pH at LF-537 is less than at Dinero tunnel because other acid sources, primarily Sugarloaf Gulch and Little Sugarloaf Gulch, discharge into the wetland. Further, precipitation of iron oxyhydroxides is a reaction that generates acidity (Walton-Day and Mills, 2015) that likely occurs in the wetland. Overall, the bulkhead appeared to improve water quality at LF-537.

Farther downstream, Lake Fork Creek (LF-580) exhibited mixed results with pH decreasing, manganese and zinc concentrations and manganese load decreasing, but mean zinc load increasing (Table 1, Fig. 5a-d). Only the decrease in manganese concentration was statistically significant (Table 1).

Despite decreases in zinc concentrations, zinc loads actually increased at LF-580 after the bulkhead due to interannual variability in runoff. For example, the greatest elevated zinc and manganese concentrations and loads occurred during the spring of 2011 (concentrations and loads) and 2014 (loads) (Fig. 5c and d), years that were characterized by above average snowfall and spring and annual runoff (Supplemental Fig. S1a; Walton-Day et al., 2013; Walton-Day and Mills, 2015; U.S. Geological Survey, 2019b). In addition, post-bulkhead mean zinc loads (5.57 kg/d) were greater than the sum of loads from DT-0, LF-537, and NT-0 (about 1.7 kg/d) indicating other sources are contributing zinc to LF-580 (Supplemental Table S1). Manganese loads show a similar pattern (Supplemental Table S1). The source of this additional loading at LF-580 is not definitively known but is likely related to additional groundwater and trace-metal input along the west side of Lake Fork Creek upstream from LF-580 where previous studies noted groundwater inflow (p. 45 in Walton-Day et al., 2005), and/or additional runoff of acid-mine drainage from upstream mining features into the wetland after bulkhead closure.

Manganese concentrations from all samples (pre- and post-bulkhead) at site LF-580 met both chronic and acute hardness-based water-quality standards for protection of aquatic life in segment COARUA05a, which includes Lake Fork Creek (p. 174 in Colorado Department of Public Health and Environment Water Quality Control Commission, 2020). Zinc concentrations for almost all samples exceeded both the acute and chronic hardness-based standards, and only two samples in the post bulkhead period (10.0 μg/L on 10 June 2010 and 11.1 μg/L on 30 September 2014) (Fig. 5c) met both the acute and chronic zinc standards. Together these data indicate statistically significant ($p < 0.05$) improvement only in manganese concentrations and attainment of zinc water-quality standards for two of 15 samples at Lake Fork Creek monitoring site LF-580 after bulkhead closure.

After bulkhead closure, the Nelson tunnel (NT-0) exhibited stastically significant decreases in pH and increases in discharge and dissolved manganese and zinc concentrations and loads (Table 1; Fig. 5a-c) indicating water-quality degradation. The Nelson tunnel is a collapsed draining mine tunnel having more limited workings than Dinero tunnel (Fig. 2). Previous work concluded that a fracture and associated vein connect the Nelson tunnel to the mine pool behind the Dinero bulkhead, which caused impounded water from Dinero to reroute to NT-0 after bulkhead closure (Fig. 2 in Walton-Day and Mills, 2015). Over the entire study period, seasonal concentration patterns at NT-0 (Fig. 5b and c) did not show first-flush effects. The absence of a seasonal first flush may indicate that material generating mine drainage in the Nelson tunnel is submerged within the mine pool, minimizing the annual wetting and drying cycles common in open mine workings.

3.1.2. *Cement Creek, upper Animas River watershed*

3.1.2.1. Pre- and post-bulkhead water quality at the mouth of Cement Creek. Interpreting effects of bulkhead installation in Cement Creek is complicated by overlap between the timing of bulkhead installation (1996–2003) and active water treatment (1989–2003). Two pre-treatment samples collected near or at the mouth of Cement Creek during September and October before treatment and bulkhead closure (1971 and 1981) were compared to samples collected in September and October, 2004–2015, after treatment ceased and bulkheads were closed (Fig. 6a–d). After bulkhead closure, these data showed decreased mean pH values (from about 4 to about 3.2), mean manganese concentrations (from about 5,000 to 3,800 μg/L), and mean zinc concentrations (from about 2,500 to 2,100 μg/L). Mean copper concentrations increased (from about 120 to 170 μg/L). The decrease in stream pH indicates no improvement from the bulkheads. The greater pre-bulkhead manganese

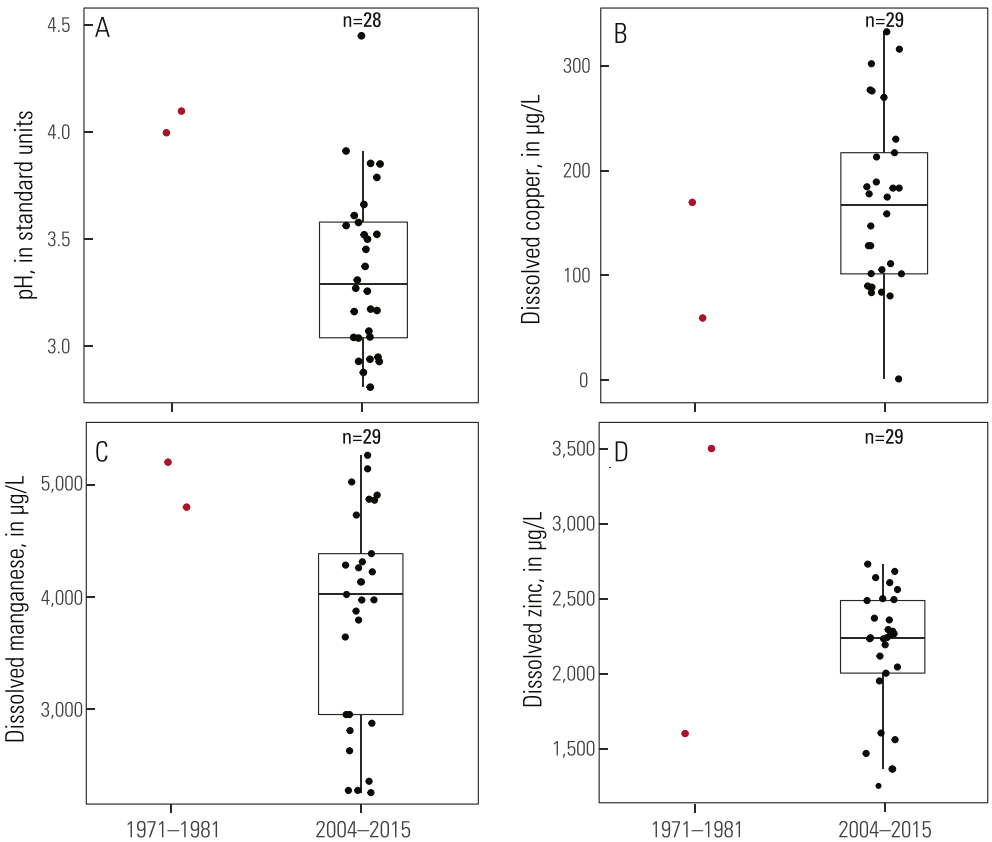

Fig. 6. Graphs comparing (A) pH, and dissolved (B) copper, (C), manganese, and (D) zinc concentrations (in micrograms per liter [µg/L]) at the mouth of Cement Creek in samples collected before active water treatment and bulkhead installation (1971 and 1981) to samples collected after cessation of water treatment and after bulkhead installation (2004–2015). The number of samples (n) indicated for each boxplot. Central line in boxplot is median, lower and upper boundaries of box are 25th and 75th percentiles (inter-quartile range) of the data, and lower and upper whiskers extend to the largest and smallest values no further than 1.5 times the interquartile range. Values beyond this range are shown beyond the whisker. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

concentrations (Fig. 6c) are clearly separated from lower post-bulkhead values, evidence that the bulkheads improved water quality with respect to manganese. In contrast, pre-bulkhead zinc and copper mean concentrations generally fall within the range of data from 2004 to 2015, indicating no substantial change in concentration after bulkhead installation (Fig. 6b). These results indicate the difficulty of drawing any firm conclusions from only two pre-treatment data points, but generally indicate that pH decreased through time and manganese concentrations may have improved slightly after bulkhead installation. Results are inconclusive for copper and zinc.

3.1.2.2. Mine tunnel hydrographs. Mine tunnel hydrographs indicate the range and timing of discharge changes at the tunnels as bulkheads were closed. At the American tunnel, closure of bulkhead AT#1 in 1996 decreased discharge from values greater than 0.1 to about 0.03 m^3/s (Fig. 7). Discharge slowly increased to less than 0.06 m^3/s in late 2002 when closure of AT#2 decreased discharge to less than 0.01 m^3/s (Fig. 7). Subsequently, discharge increased and seemed to stabilize near 0.02 m^3/s in late 2003 when closure of AT#3 decreased discharge to between 0.005 and about 0.01 m^3/s for the remainder of the study period, representing as much as a 95% decrease from initial conditions (Fig. 7). At the Mogul mine portal, discharge increased by almost 100 times (9,100%) from 1992 to 2001 (Table 2, Fig. 7), and decreased after closure of the Mogul bulkhead in 2003 to 0.003 m^3/s in 2008 (still more than 1,000% greater than in 1992) (Table 2, Fig. 7, Walton-Day et al., 2020). At Red and Bonita, discharge increased from no flow (1997–2001) to a maximum of about 0.03 m^3/s in July 2015 (Table 2, Fig. 7). Increasing discharge is most notable starting in 2005 after closure of all four bulkheads (Table 2, Fig. 7), though increased discharge was noted as early as July 2003 (Bonita Peak Community Advisory Group, 2019a). At Gold King tunnel, discharge increased from no flow in 1994 to about 0.02 m^3/s in 2006, generally decreasing after 2006 to values less than 0.005 m^3/s in 2015. At Black Hawk tunnel,

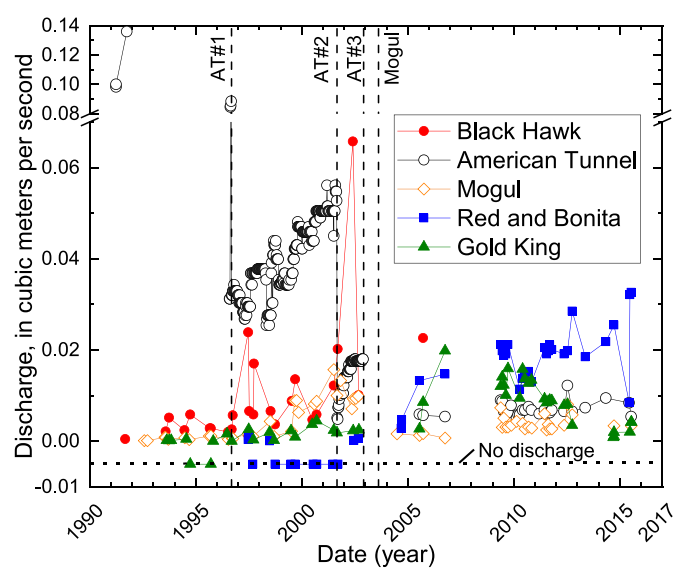

Fig. 7. Graph showing variation in discharge from the American tunnel and the Black Hawk, Mogul, Red and Bonita, and Gold King mine tunnels. Vertical lines represent closure of the American tunnel #1 bulkhead (AT#1), American tunnel #2 bulkhead (AT#2), American tunnel #3 bulkhead (AT#3), and the Mogul bulkhead (Mogul). Horizontal line near bottom of graph indicates data points where no discharge was specifically noted in original data records. Data from Walton-Day et al., (2020).

discharge increased 4,000% from 1991 to 2005 with one greater but unrepeated measurement during 2002 (Table 2, Fig. 7).

The discharge responses of non-bulkheaded flowing mine tunnels in Cement Creek relate to the timing of bulkhead closure at the American

Table 2
Portal elevations, and minimum and maximum values and dates of occurrence for discharge, pH, and copper, manganese, and zinc loads in the American tunnel and Black Hawk, Gold King, Mogul, and Red and Bonita mine tunnels, 1988–2015. Discharge, pH, and load data from Walton-Day et al. (2020), elevation data from Sorenson and Brown (2015) and Google Earth (Black Hawk) [PE, portal elevation; m, meters; m^3/s, cubic meters per second; Min, minimum; Mult., multiple; Max., maximum; kg/d, kilograms per day].

	American Tunnel PE = 3,236 m	Red and Bonita PE = 3,340 m	Mogul PE = 3,475 m	Gold King PE = 3,487 m	Black Hawk PE = 3,536 m
Discharge (m3/s)					
Min. value	0.0048	No flow	0.00017	No Flow	0.000481
Date of min.	14 Sep 2001	Mult. 1997–2001	30 July 1992	29 Sep 1994	7 Sep 1991
Max. value	0.136	0.0326	0.0157	0.0198	0.0657
Date of max.	2 Oct 1991	15 July 2015	9 July 2001	3 Oct 2006	31 May 2002
pH **(standard units)**					
Min. value	3.8	1.7	1.1	0.9	5.6
Date of min.	29 June 1998	29 June 1998	7 July 1998	29 June 1998	19 Sep 1997
Max. value	9.12	6.5	4.8	5.13	7.64
Date of max.	18 Nov 1988	14 July 2009	19 July 2002	14 Apr 2010	7 Sep 1991
Copper load (kg/d)					
Min. value	0.00248	0.00569	0.0024	0.00739	0.00036
Date of min.	17 Feb 2010	14 July 2009	4 Oct 2006	3 Nov 1993	3 Aug 1993
Max. value	0.732	0.0999	13.2	22.0	0.0388
Date of max.	15 Oct 1997	21 July 2005	3 Sep 1999	2 July 1997	10 Sep 1999
Manganese load (kg/d)					
Min. value	1.5	0.117	0.128	0.0921	0.0749
Date of min.	4 Sep 2001	26 June 1997	30 July 1992	3 Nov 1993	7 Sep 1991
Max. value	228	83.0	28.5	88.9	11.1
Date of max.	2 Aug 2001	2 Oct 2012	9 July 2001	3 Oct 2006	20 Sep 2005
Zinc load (kg/d)					
Min. value	0.87	0.22	0.434	0.0809	0.0237
Date of min.	4 Sep 2001	20 June 2002	23 Sep 1992	3 Nov 1993	7 Sep 1991
Max. value	140	39.5	83.5	57	1.81
Date of max.	2 Aug 2001	2 Oct 2012	1 Oct 1999	1 July 1999	20 Sep 2005

tunnel and Mogul mine and indicate the hydrologic effects of the bulkhead closures. Most of this discussion is derived from Sorenson and Brown (2015) though other data presented herein (Black Hawk) are also interpreted. Three primary sources of water to American tunnel were the basis for locations of the American tunnel bulkheads: (1) the veins and fractures associated with the Sunnyside mine workings and located east of AT#1; (2) water bearing fractures and faults located between AT#1 and AT#2; and (3) diffuse seepage located between AT#2 and the portal (Fig. 4) (Sorenson and Brown, 2015). AT#1 was intended to back up and impound fracture-related groundwater within the Sunnyside workings. Bulkheads located in the Sunnyside workings east of the watershed divide (Fig. 4) were intended to prevent groundwater impounded in the Sunnyside workings by AT#1 from discharging at the Mogul mine or into the upper Animas River downstream from the Sunnyside basin (Sorenson and Brown, 2015). Final recorded elevation of the water behind the AT#1 bulkhead was 3,557 m measured 14 May 2001 (Sorenson and Brown, 2015). This water level is greater than elevation of all other tunnels (Table 2). Black Hawk tunnel (having the highest portal elevation = 3,536 m) and Mogul tunnel (3,475 m) showed marked increases in discharge after 2001 with minor increases shown for Gold King tunnel (3,487 m) (Fig. 7). This increased discharge from the Mogul and Gold King tunnels has been attributed to the mine pool impounded behind AT#1 (Sorenson and Brown, 2015). The elevation and timing of discharge from Black Hawk tunnel indicate that increased discharge at that tunnel is also likely related to water impounded behind AT#1. Even though Red and Bonita portal elevation (3,340 m) is lower than the AT#1 water level, Red and Bonita tunnel remained dry before AT#2 was closed and is likely not hydrologically connected to the Sunnyside mine pool.

Bulkhead AT#2 was designed to limit water draining into American tunnel between AT#1 and AT#2 and closed in August 2001. Groundwater impounded behind the bulkhead equilibrated at an elevation of 3,357 m, recorded in August 2002, greater than the elevation of Red and Bonita mine tunnel portal (3,340 m); water impounded behind AT#2 is responsible for the increased Red and Bonita mine-tunnel discharge observed starting in 2003 (Sorenson and Brown, 2015). Because the water elevation behind AT#2 (3,357 m) is less than that at Mogul (3,475 m) (Sorenson and Brown, 2015), discharge at the Mogul mine was relatively constant after closure of AT#2 (Fig. 7, Walton-Day et al., 2020).

Closure of AT#3 (December 2002) was designed to limit diffuse seepage between AT#2 and AT#3 from discharging at the American tunnel portal (Sorenson and Brown, 2015). Closure of the Mogul tunnel bulkhead (2003) was designed to limit discharge at the mouth of the Mogul mine. There were no discharge data for the tunnels in the period between installation of these two bulkheads (most of 2003). After these two bulkheads were installed, discharge decreased at American tunnel and Mogul tunnel, but continued increasing at both the Gold King and Red and Bonita tunnels (Fig. 7) (Sorenson and Brown, 2015).

A possible alternate explanation for changing discharge in the tunnels is short-term climate variation of wet years versus dry years. However, climate is likely not the cause of discharge variations because if it were a controlling factor, the hydrographs at different non-bulkheaded tunnels would be showing similar patterns through time, which is generally not the case. In addition, none of the peak discharge years for the tunnels shown on Table 2, for which there is discharge record at USGS station 09358550 (2001, 2002, 2006, 2015; Supplemental Fig. S1b), are wet years on the hydrograph; 2002 was notably a dry year.

3.1.2.3. Water quality at Cement Creek during and after active treatment and bulkhead installation. Water quality at the mouth of Cement Creek exhibited large changes in the period from 1996 through 2015 (Fig. 8). Metal loads at some of the tunnels also exhibited large changes during the same time period (Table 2, Fig. 8). Raw and DWM values for pH, and dissolved copper, manganese, and zinc generally show similar long-term

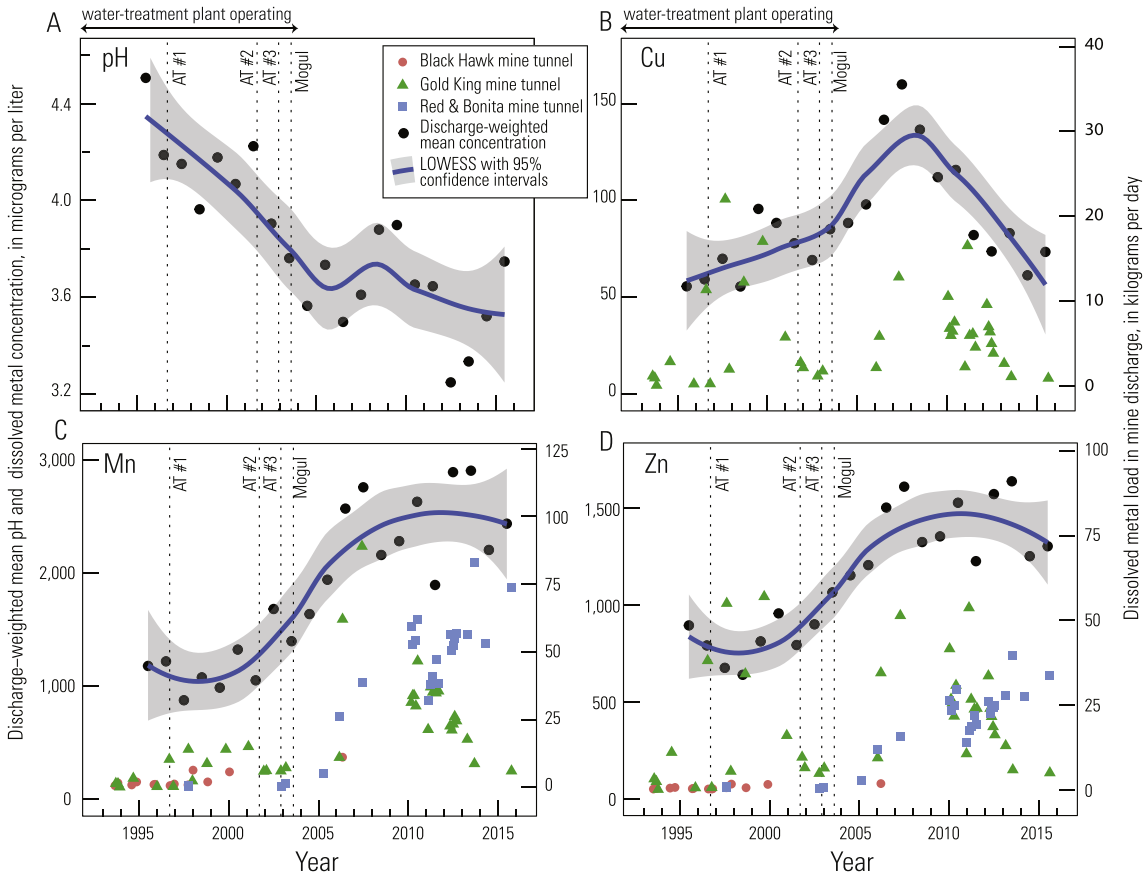

Fig. 8. Graphs showing variation in (A) discharge-weighted-mean (DWM) pH at the mouth of Cement Creek, (B) DWM concentrations of copper (Cu) at the mouth of Cement Creek and copper loads from the Gold King mine, (C) DWM concentrations of manganese (Mn) at the mouth of Cement Creek and manganese loads from the Black Hawk, Red and Bonita, and Gold King mine tunnels, (D) DWM concentrations of zinc (Zn) at the mouth of Cement Creek and zinc loads from the Black Hawk, Red and Bonita, and Gold King mine tunnels. All annual average DWM values are represented individually as black dots and as a LOWESS (locally weighted scatter plot smoothing) line with 95% confidence intervals. Vertical lines represent closure of the American tunnel #1 bulkhead (AT#1), American tunnel #2 bulkhead (AT#2), American tunnel #3 bulkhead (AT#3), and the Mogul bulkhead (Mogul).

patterns, although the DWM curves have lower values than the raw data (Supplemental Fig. S2, Fig. 8). Discharge weighting gives more weight to higher flow, more dilute concentration samples, resulting in lower DWM concentrations compared to the raw-data mean concentrations.

The DWM pH of Cement Creek decreased from about 4.5 to 3.6 during 1996–2015 (Fig. 8). Mine tunnel pH varied from as low as 0.9 at the Gold King tunnel in June 1998 (a year when all tunnels except Black Hawk tunnel demonstrated minimum pH) to 9.12 in November 1988 at the American tunnel. The high value may be related to water-treatment adjustments (Walton-Day et al., 2020 and sources therein). The DWM dissolved copper concentrations increased from about 50 to 150 μg/L between 1996 and 2009, decreasing to about 50 μg/L in 2015 (Fig. 8b). Maximum dissolved copper loads from mine tunnels ranged from less than 0.1 kg/d to about 22 kg/d (at Gold King in 1997) (Table 2). The DWM dissolved manganese concentrations increased from about 1,000 to 3,000 μg/L from 1996 to 2012–2013 (Fig. 8c). Maximum dissolved manganese loads from mine tunnels ranged from about 11 to 89 kg/d with as much as 228 kg/d at American tunnel in 2001 (Table 2). The DWM dissolved zinc concentrations increased from about 900 to 1,600 μg/L from 1996 to 2013 (Fig. 8d). Maximum dissolved zinc loads from mine tunnels ranged from about 2 to 84 kg/d with as much as 140 kg/d at American tunnel in 2001 (Table 2). DWM manganese and zinc concentrations show similar concentration patterns through time with slight decreases from 1996 to 2000, followed by increases in DWM concentrations (and raw data) from about 2000 through 2012–2013 (Fig. 8, Supplemental Fig. S2). Average daily metal loads at the mouth of Cement Creek for the period 2004–2015 were about 10 kg/d for copper, 200 kg/d for manganese, and 120 kg/d for zinc.

The timing of pH decreases in Cement Creek is not obviously related to patterns and timing of changes in discharge or pH values at the various mine tunnels (Fig. 7, Table 2). In addition to the mine tunnels, there are numerous sources of low pH water in Cement Creek related to mining. As well, naturally occurring low pH water also derives from unmined mineralization and hydrothermal alteration in the watershed (Mast et al., 2007; Yager and Bove, 2007; Wirt et al., 2007). The decreased pH through time might indicate increased unsampled groundwater discharge occurred in South Fork after bulkhead installation, as also evidenced by increased discharge at the Black Hawk tunnel during this time. This idea warrants additional investigation.

Increased mine-tunnel discharge in non-bulkheaded tunnels caused increased metal loads from the mine tunnels that coincide with, and likely contributed to, some of the changes in water quality at the mouth of Cement Creek (Fig. 8b-d). Loads from the mine tunnels, rather than their concentrations are presented because loads quantify the most important sources of metals to the receiving stream (Kimball et al., 2002; Walton-Day et al., 2005). As previously described, active water treatment removed most of the metal load from the American tunnel during 1989–2003, and some of the load from the Mogul, Red and Bonita, and Gold King tunnels when Cement Creek (1996–2003) and Gold King were being treated (2003–2004). The increased discharge at the Black Hawk tunnel (1996–2002) that drains to the South Fork of Cement Creek (Figs. 4 and 7) was not treated. The increased loads of manganese and less strongly zinc that occurred with increased Black Hawk tunnel discharge (Figs. 7 and 8c-d) coincide with the onset of gradual increases

in DWM manganese and zinc at the mouth of Cement Creek that started around 2000 and are a possible cause for some of these increases (Fig. 8c-d). Elevated copper loads at Gold King tunnel during this period were not consistently captured at the treatment plant, and likely contributed to increasing DWM copper concentrations at the mouth of Cement Creek as did minor (untreated) copper loads at the Black Hawk tunnel (Table 2).

After water treatment ended in 2004, untreated discharge and metal loads from the American, Mogul, Red and Bonita, and Gold King tunnels moved downstream and appear to influence water quality at the mouth of Cement Creek. After 2003, the pattern of copper load from the Gold King tunnel closely mimicked the pattern of DWM copper concentrations at the mouth of Cement Creek, which increased until 2009 but then decreased to values similar to those in 1995 (Fig. 8b). The other four tunnels (American, Black Hawk, Mogul, and Red and Bonita) had copper loads that were less than 5 percent of the Gold King tunnel during this time (2003–2015) and are not shown (Table 2, and data in Walton-Day et al., 2020). The post-2003 patterns of manganese and zinc DWM concentrations at the mouth of Cement Creek are coincident with increasing loads at the Red and Bonita and Gold King tunnels (Fig. 8c-d). The American and Mogul tunnels have zinc and manganese loads that are generally less than 50% of the loads at the Red and Bonita and Gold King tunnels at this time and are not shown (data in Walton-Day et al., 2020). Slight decreases in DWM manganese and zinc concentrations from 2013 to 2015 may have been caused by decreased loading from the Gold King tunnel during this time (Fig. 8c-d). During this time, the DWM manganese and zinc concentration decreases are not as steep as the decrease in the DWM copper because the Red and Bonita tunnel provides manganese and zinc load, but minimal copper load (Fig. 8b-d).

The coincidence in the timing of load increases starting in 2003 from the Gold King and Red and Bonita tunnels with increases in DWM metal concentrations at the mouth of Cement Creek provides evidence that the changes in discharge and loads from these tunnels contributed to the observed increases in copper, manganese, and zinc DWM concentrations at the mouth of Cement Creek. Additional evidence is provided by the large copper and zinc loads at the Gold King tunnel during 1996–2000, that are of similar magnitude to those that occurred during 2004–2015 (Fig. 8b and d). Because of partial treatment of upper Cement Creek in the 1990s, these loads did not fully contribute to water quality at the mouth of Cement Creek. When treatment ceased by 2004, the loads from this tunnel were transported downstream and were partly responsible for increasing copper and zinc DWM concentrations observed at the mouth of Cement Creek (Fig. 8b and d). Finally, the mean daily metal loads calculated for 2004–2015 at the mouth of Cement Creek (copper, 10 kg/d; manganese, 200 kg/d; zinc, 120 kg/d) are in the range of metal-load values for the tunnels, particularly Gold King and Red and Bonita (Fig. 8b-d) indicating that the loads from the tunnels substantially contributed to the loads and thus the concentration increases observed at the mouth of Cement Creek. The lower copper load at the mouth of Cement Creek compared to some tunnel loads likely indicates copper attenuation between upper Cement Creek and the mouth of Cement Creek (Kimball et al., 2002).

4. Summary and conclusions

The water-quality response in two different study areas in Colorado after bulkhead installation for remediation of abandoned draining mines indicated mixed water-quality responses, with only limited improvement in receiving waters. In Lake Fork Creek (upper Arkansas River watershed), a bulkhead installed in Dinero tunnel in 2009 caused significant water-quality improvement (pH and zinc and manganese concentrations and loads) at the Dinero tunnel mouth (DT-0) but significant water-quality degradation at the nearby Nelson tunnel (NT-0). At the downstream-most site on Lake Fork Creek, LF-580, limited water-quality improvement included statistically significant decreased manganese concentrations and attainment of zinc water-quality standards for two of 15 samples after bulkhead closure. At LF-580, increased post-bulkhead zinc loads may indicate increased post-bulkhead, unsampled groundwater contributions from multiple sources upstream from LF-580.

In Cement Creek (upper Animas River watershed) four bulkheads were installed and closed between 1996 and 2003. Water treatment (1989–2003) overlapped with the period of bulkhead installation and complicated interpretation of bulkhead effects. Comparison of limited pre-treatment data with post-bulkhead data from near the mouth of Cement Creek indicates possible improvement in manganese concentrations, decreasing pH through time, and is inconclusive for copper and zinc concentrations. There is no consistent and robust evidence that bulkheads caused substantial positive or negative long-term changes in water quality. In contrast, the lowest concentrations of copper, manganese, and zinc occurred during active treatment (1989–2003). After bulkheads were installed, and active water treatment ceased (2004), water quality in Cement Creek degraded. The timing of water-quality degradation was similar to timing of increased discharge and metal loads from non-bulkheaded tunnels that occurred in response to bulkhead installation in other tunnels, evidence that increased loading from the tunnels contributed to water-quality degradation at the mouth of Cement Creek. In both study areas, data potentially indicate increased, unsampled groundwater discharge after bulkhead installation that caused increased zinc loads at site LF-580 after Dinero bulkhead installation, and decreased pH over time at Cement Creek. Greater understanding of this result could be a topic for future investigations. Overall, the lack of substantial water-quality improvement in these two areas from bulkhead installation indicates that other treatment techniques might warrant consideration.

Data availability

Data for the four sites discussed in the Dinero tunnel section are available from the National Water Information System (NWIS) (https://doi.org/10.5066/F7P55KJN) using USGS site identification numbers 391504106225200 (DT-0); 391454106224201 (LF-537); 391452106224201 (LF-580); and 391501106230601 (NT-0). Data for the mouth of Cement Creek are available from the Water Quality Portal (WQP) (https://www.waterqualitydata.us/) using site identifiers 21COL001_WQX-CEM49, ARSG-CC48, CORIVWCH_WQX-323, USEPA_REGION8-CC48, and USGS-09358550. Data for two additional samples, USGS site ID 374854107393900, October 4, 1971, and USGS site ID 375015107404001, September 24, 1981, are available from NWIS at https://doi.org/10.5066/F7P55KJN. Data for the five mine tunnels in Cement Creek are available from Walton-Day et al. (2020) at https://doi.org/10.5066/P9FE667O.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2021.104872.

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Water-quality change following remediation using structural bulkheads in abandoned draining mines, upper Arkansas River and upper Animas River, Colorado USA

Supplemental Information

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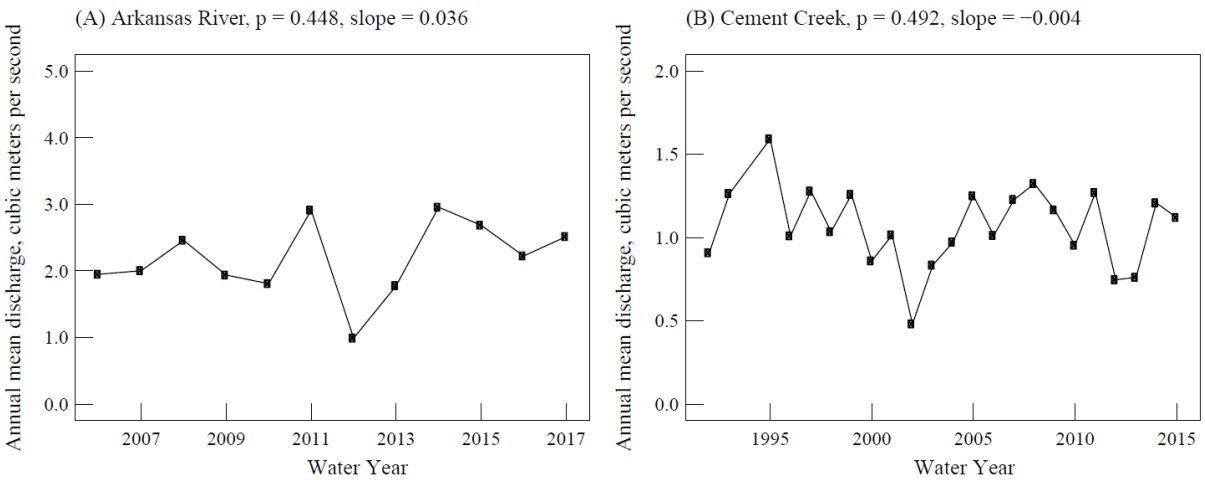
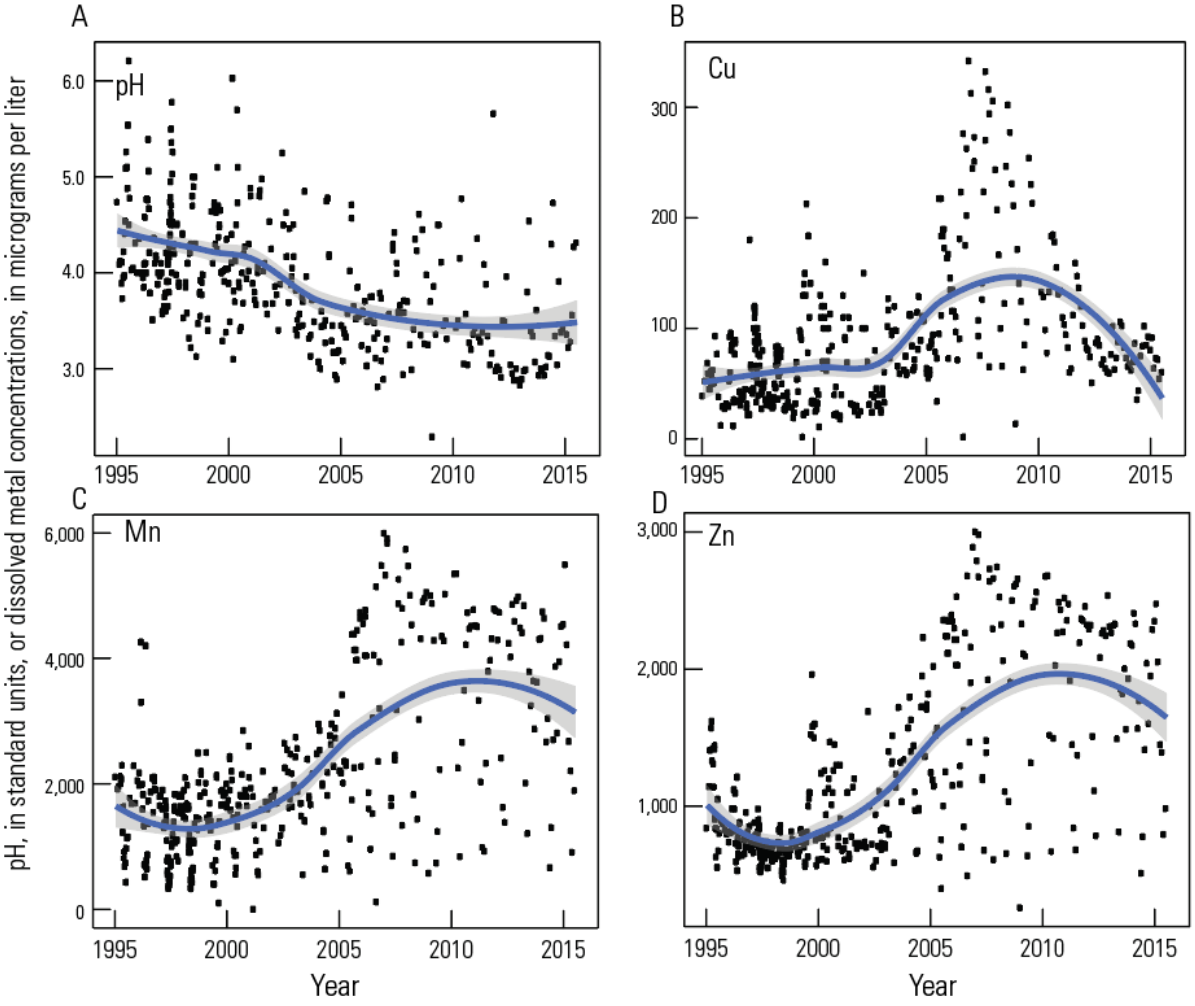


Supplemental Figure S1. Graphs showing (A) annual mean discharge (by water year, Oct. through Sept.) at the Arkansas River near Leadville, Colorado, U.S. Geological Survey (station 07081200) streamgage near the Dinero study area (data from https://waterdata.usgs.gov/co/nwis/annual/?referred_module=sw&site_no=07081200&por_07081200_17776=344903,00060,17776,1968,2020&start_dt=2006&end_dt=2017&year_type=W&format=html_table&date_format=YYYY-MM-DD&rdb_compression=file&submitted_form=parameter_selection_list) and (B) annual mean discharge (by water year, Oct. through Sept.) at the Cement Creek at Silverton, Colorado, U.S. Geological Survey (station 09358550) (data from https://waterdata.usgs.gov/co/nwis/annual/?referred_module=sw&site_no=09358550&por_09358550_19575=345987,00060,19575,1992,2020&start_dt=1993&end_dt=2015&year_type=W&format=html_table&date_format=YYYY-MM-DD&rdb_compression=file&submitted_form=parameter_selection_list). There are no data available prior to 1992 for this site, and record for 1992 is not for entire year, so it was omitted from the graph.

Supplemental Table S1. Mean discharge, pH, and dissolved manganese and zinc concentrations and loads before and after bulkhead closure in the Dinero tunnel at four sample sites, Lake Fork Creek, upper Arkansas River watershed, Colorado. Mean pH calculated from hydrogen ion concentration. **Bold** indicates post bulkhead value is less than pre-bulkhead value. Before closure, n=4. After closure n=14 except at LF-580 where n=15. [DT-0, Dinero tunnel sample site; LF-537, sample site draining wetland downstream from DT-0; LF-580, sample site on Lake Fork Creek downstream from DT-0 and LF-537; NT-0, Nelson tunnel sample site; Dis., dissolved; m^3/s, cubic meters per second; Conc., concentration; µg/L, micrograms per liter; kg/d, kilograms per day]

Site	**Mean discharge (m^3/s)**		**Mean pH (standard units)**		**Mean Dis. Manganese Conc. (µg/L)**		**Mean Dis. Zinc Conc. (µg/L)**		**Mean Dis. Manganese Load (kg/d)**		**Mean Dis. Zinc Load (kg/d)**	
	Pre-bulk-head	Post-bulk-head	Pre-bulk-head	Post-bulk-head	Pre-bulk-head	Post-bulk-head	Pre-bulk-head	Post-bulk-head	Pre-bulk-head	Post-bulk-head	Pre-bulk-head	Post-bulk-head
DT-0	0.0059	**0.00088**	5.71	6.55	47,800	**20,000**	15,200	**4,090**	24.9	**1.53**	7.96	**0.31**
LF-537	0.0020	0.0033	3.84	4.59	33,600	**7,760**	8,160	**2,230**	5.72	**1.45**	1.39	**0.95**
LF-580	0.38	0.82	7.01	**6.96**	608	**215**	128	**113**	17.8	**9.52**	3.97	5.57
NT-0	0.00021	0.00063	6.72	**5.89**	2,990	33,200	85.8	7,940	0.055	1.75	0.002	0.42



Supplemental Figure S2. Graphs showing variation in (A) pH at the mouth of Cement Creek, (B) dissolved copper (Cu) concentrations at the mouth of Cement Creek; (C) dissolved of manganese (Mn) concentrations at the mouth of Cement; and (D) dissolved zinc (Zn) concentrations at the mouth of Cement Creek. LOWESS (locally weighted scatter plot smoothing) line with 95% confidence intervals.