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TECHNICAL ARTICLE

To Remediate or Not? Source Identification in an Acid Mine Drainage Stream, Warden Gulch, Colorado

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Abstract

A synoptic water quality study was implemented in Warden Gulch, a headwater stream affected by metals that are contributed by both natural and mining-impacted sources. Warden Gulch is a tributary to Peru Creek (Colorado, USA), where emplacement of a mine tunnel bulkhead and other remedial actions have improved water quality upstream of Warden Gulch. The goal of this study was to identify individual source contributions to Warden Gulch and determine if additional remedial actions were warranted. To this end, trace metal loading was quantified from various sources including an actively draining mine. Although highly concentrated waste streams from mining-impacted sites degrade water quality, natural contributions from unmined areas within the Warden Gulch watershed are the dominant sources of metal loading. Further, some mining-impacted sources are associated with diffuse groundwater inflows that may not be amenable to clean up, due to the diffuse nature of the sources and the associated cost. Mining-impacted sources that are amenable to clean up may therefore represent a small portion of the overall metal loading to Warden Gulch. Remedial measures directed at these sources may not substantially improve the water quality of Peru Creek and the larger Snake River watershed.

Keywords Acid mine drainage · Natural acid rock drainage · Tracer injection · Synoptic sampling · Metals · Water quality

Introduction

Abandoned mines degrade water quality, impair terrestrial and aquatic ecosystems, and pose human health concerns throughout the world (Li 2018; Wolkersdorfer and Bowell 2004). Abandoned mines often produce acid mine drainage when pyrite (FeS_2) and other sulfide-rich minerals are exposed to oxygen and water, resulting in their oxidation and dissolution. These processes produce elevated SO_4 concentrations, increased acidity, and elevated trace metal concentrations that can be toxic to aquatic life (McKnight and Bencala 1990; Nordstrom 2011). In the State of Colorado, these water quality challenges are particularly serious due to the presence of the Colorado Mineral Belt, a stretch of mineral-rich deposits that bands across the Colorado Front Range and through the middle of the state (Lovering 1935). The Colorado Mineral Belt has extensive igneous intrusions throughout, including hydrothermally altered, metal-rich veins that have long been subject to mining efforts (Chapin 2012). The Colorado Department of Public Health and Environment estimates ≈ 23,000 abandoned mines can be found in Colorado alone, which have degraded ≈ 2600 km of surface streams (CDPHE 2017) and caused substantial economic losses (Todd et al. 2003).

Most of the abandoned mine sites in the Colorado Mineral Belt are in mineralized watersheds that are affected by both natural and mining-impacted sources. The terms Acid Rock Drainage (ARD) and Acid Mine Drianage (AMD) are used herein to refer to natural and mining-impacted sources, respectively. Although ARD can result in similar environmental impacts, ARD often results in diffuse groundwater inflows as opposed to concentrated point sources often seen with AMD (e.g. flowing mine adits). In many cases, limited information regarding pre-mining watershed conditions

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poses challenges in differentiating between AMD and ARD impacts (Alpers and Nordstrom 2000; Runkel et al. 2018). Mast et al. (2007), for example, were unable to differentiate between AMD and ARD for some sampling locations during a field investigation in southwestern Colorado and devised a numerical ranking scheme to reflect their uncertainty. Natural background water quality (pre-mining) within mineralized watersheds often possess trace metal concentrations and pH values that exceed generic water quality standards (Runnells et al. 1992).

Extensive mining activities were conducted within the Colorado Mineral Belt during the late 1800's and early 1900's (Lovering 1935). These activities often occurred on public lands managed by the federal government, and most of the small mining companies that conducted the work are no longer in existence. Federal, state, and local agencies are thus responsible for the reclamation of these lands, and the associated cleanup can be costly because of the need to access remote locations in the rugged terrain near the Continental Divide. Further, a given watershed may include numerous mine shafts, mine tunnels, mine dumps, and mill tailing deposits that potentially degrade water quality. Natural sources are also present, with mineralized host rock producing ARD that is a source of metals and acidity. Given the magnitude of the problem, it may not be feasible to address all of these sources (Gustavson et al. 2007). There may therefore be a need to focus resources on large mining-impacted sources that are amenable to remediation. Remediation of natural ARD sources, small mining-related sources, and sources that are difficult to treat (e.g. diffuse groundwater) may be impractical or cost prohibitive. Additionally, variability in hydrologic regimes and ongoing remedial efforts coupled with spatial and temporal variability in water quality at mining-impacted sites (Petach et al. 2021) make generalized remedial efforts difficult.

In the case of watersheds with multiple AMD/ARD sources, a high degree of spatial resolution is required to accurately characterize the effects of individual sources. The synoptic mass balance approach can be used to quantify and rank sources of contamination at a fine spatial scale, with changes in water quality attributed to discrete source areas (Bencala and McKnight 1987; Kimball et al. 2002; Runkel et al. 2009). Under the synoptic approach, spatial profiles of constituent load (mass/time) are developed, where load estimates are the simple product of constituent concentration and streamflow. Constituent concentrations are obtained through synoptic sampling, where numerous instream sites that bracket source areas are sampled for the constituents of interest. Streamflow estimates may be developed using various techniques (e.g. conventional stream gaging, flumes, etc.), but the tracer-dilution method is often used in headwater streams to accurately quantify small additions of water such as diffuse groundwater inflow (Bencala et al. 1987; Kilpatrick and Cobb 1985). Synoptic studies are typically conducted in late summer/early fall when temporal variability in streamflow due to snowmelt and/or rainfall is negligible. Given steady flow conditions, the estimated loading profiles provide a steady-state snapshot of water quality (Grayson et al. 1997) that is used for source identification (Kimball et al. 2002; Runkel et al. 2013).

Warden Gulch is a headwater stream in the Snake River watershed, which is a major inflow to Dillon Reservoir (Fig. 1), a water supply for the Denver metropolitan area. Previous studies have indicated that Warden Gulch is a significant contributor to water quality degradation in Peru Creek, a major tributary of the Snake River (Duren 2004; O'Shea 2007). These findings suggest that additional investigations to determine the relative impacts of AMD/ARD to the stream are warranted (i.e. how much of the metal loading from Warden Gulch is attributable to natural sources and how much is attributable to mining). The primary metals and parameters of concern in Peru Creek and the Snake River are Al, Cd, Cu, Fe, Mn, Pb, Zn, pH, and SO_4. The overall goal of this study was to use the synoptic mass balance approach to: (a) quantify and rank sources of metals and acidity within Warden Gulch; (b) distinguish between mining (AMD) and non-mining (ARD) sources; and (c) separate groundwater and surface water contributions. In addition, data from this study are compared to a previous study (O'Shea 2007) to assess temporal changes in water quality that are potentially related to climate change. Results of this work may be used to determine whether remedial actions in Warden Gulch are likely to substantially improve water quality.

Study Site

The Snake River watershed is located on the western slope of the Continental Divide in Summit County, Colorado (Fig. 1). Elevations in the watershed range from ≈ 3700 m in the headwaters near the Continental Divide to ≈ 2750 m at the mouth of the Snake River where it empties into Dillon Reservoir (watershed area 155 km^2, Crouch et al. 2013). Land cover in most of the lower watershed is comprised of forest, while the upper reaches extend into alpine and subalpine regions. The hydrologic regime of the Snake River watershed is dominated by spring snowmelt (Rodhe 1998), with large volumes of snowmelt runoff leading to orders of magnitude increases in streamflow during the spring and early summer (Supplemental Fig. S-1.1). Streamflow typically returns to baseflow in August following the summer monsoon season.

The underlying subsurface within the Snake River watershed is subject to significant hydrothermal alterations. The Montezuma Mining District, located in the Snake River watershed, was established in 1879 when the discovery of

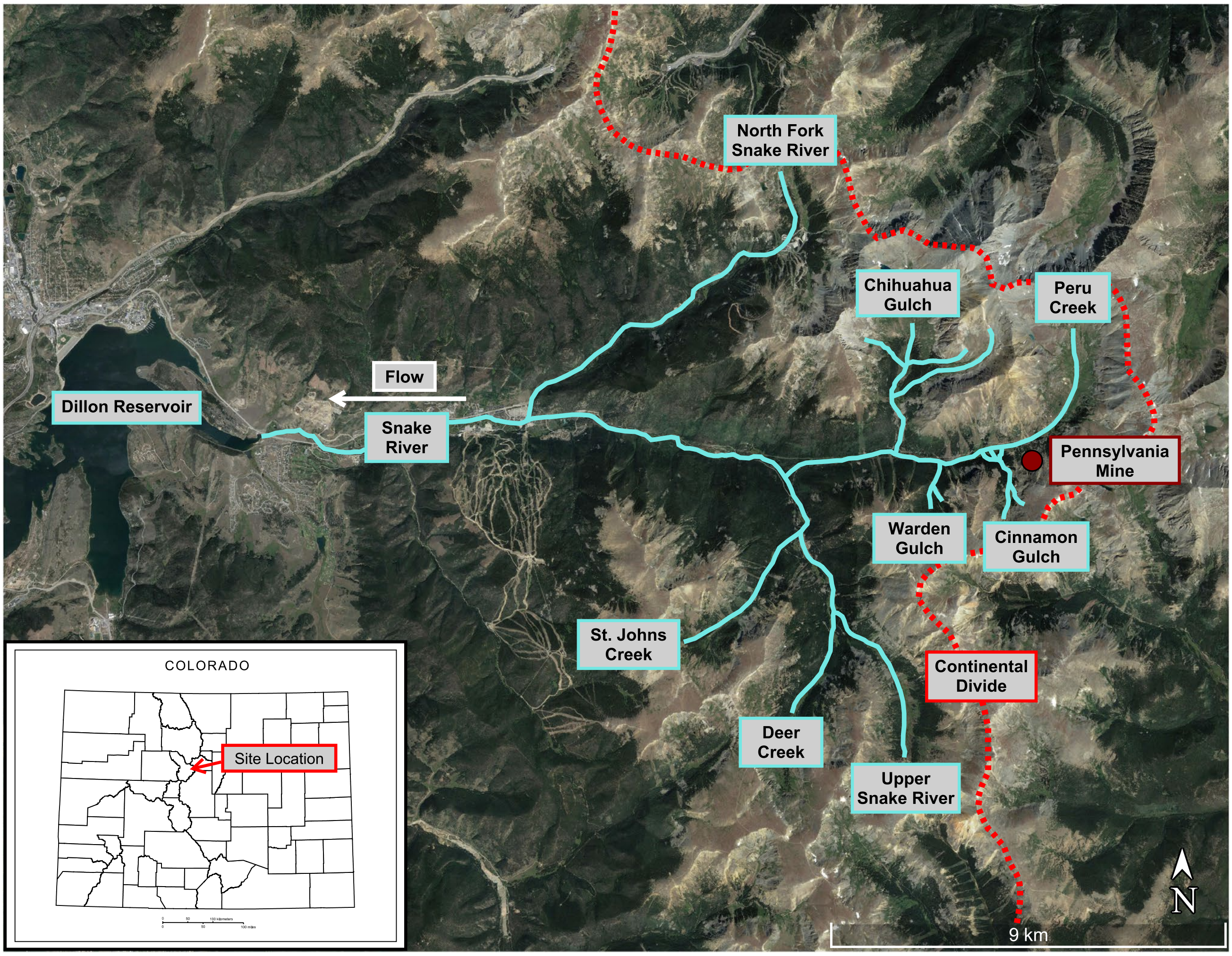

Fig. 1 Geographic setting of the Snake River watershed, Summit County Colorado (Basemap from Google Earth)

precious metals, particularly gold, resulted in extensive mining across the state. Mining continued within the district throughout the 1880s; however, much of the large-scale mining ceased due to limited production. Smaller mining operations continued off and on for decades before eventually halting completely in the 1930s (Lovering 1935).

Impacts from AMD/ARD are widespread throughout the Snake River watershed resulting in low pH and elevated constituent concentrations, including toxic trace metals. Numerous studies have characterized water quality issues in the watershed identifying AMD/ARD sources (Carroll 2017; McKnight and Bencala 1990; Sullivan and Drever 2001). The Colorado Department of Public Health and the Environment 303(d) List of Impaired Waters cites the main stem of the Snake River as impaired for Zn and has established total maximum daily loads (TMDL’s) for Cd, Cu, Pb, and pH (CDPHE 2008, 2021a). The largest tributary to the Snake River is Peru Creek, an alpine stream originating at the Continental Divide and flowing for ≈ 11 km before discharging into the Snake River (Fig. 1). Peru Creek has established TMDL’s for Cd, Cu, Mn, Pb, Zn, and pH (CDPHE 2008, 2021a) and is the setting of multiple abandoned mines (Lovering 1935; Wood et al. 2005).

The major hydrologic features within the Peru Creek catchment, from upstream to downstream, include the Pennsylvania Mine, Cinnamon Gulch, Warden Gulch, and Chihuahua Gulch (Fig. 1). The Pennsylvania Mine consists of several crosscuts that accessed the main vein, and mining occurred on six levels (Wood et al. 2005). Discharge from the lowest level was determined to be the greatest contributor of metals to Peru Creek, with highly acidic pH (3.5) (Runkel et al. 2013). From 2013 to 2015, the US Environmental Protection Agency and the State of Colorado conducted full-scale remediation of the Pennsylvania Mine, installing several bulkheads to reduce flows from the mine workings and re-establish reducing conditions in the subsurface (Keystone Policy Center 2020). Downstream water quality improved substantially near the Pennsylvania Mine, with post-bulkhead decreases in concentration and increases in pH (Supplemental Fig. S-2.1). However, this improvement is not sustained further downstream, as tributary inflows from Cinnamon Gulch and Warden Gulch cause Peru Creek to approach pre-remediation levels above the confluence with Chihuahua Gulch (Fig. S-2.2). A recent study of Cinnamon Gulch indicates that most of the constituent loading is attributable to natural ARD (Runkel et al. 2018), and that most mining-impacted sources in Cinnamon Gulch have been addressed. The present study therefore focused on Warden Gulch, as part of an effort to improve conditions in Peru Creek and the greater Snake River watershed.

The Warden Gulch headwaters originate on the west slope of the Continental Divide (Fig. 1). Within the high elevations of the catchment, several abandoned mine adits are present, including the Allan Emory, and Orphan Boy Mines. One actively-discharging mine is located within the lower reaches of Warden Gulch and is known herein as "the Warden Gulch Mine" (Fig. 2). The streambed within Warden Gulch is coated with Fe-rich precipitates (Jones 2020). In October 2006, a similar synoptic study was conducted in Warden Gulch to assess metal loading contributions (O'Shea 2007); the results indicated that loads to Warden Gulch were well distributed and not significantly linked to AMD sources. However, a large early-season snowfall limited the extent of the study to the lower reaches of Warden Gulch. Additionally, snowmelt throughout the study resulted in variable streamflow, increasing uncertainty in the interpretation of results.

Since the 2006 study, no intervening changes (e.g. remediation, mining, road construction) have been conducted in the Warden Gulch watershed. Although previous studies have cited installation of bulkheads as a driver on changes in hydrology and water quality (Walton-Day et al. 2021), the installation of bulkheads at the Pennsylvania Mine is not believed to affect water quality within Warden Gulch due to

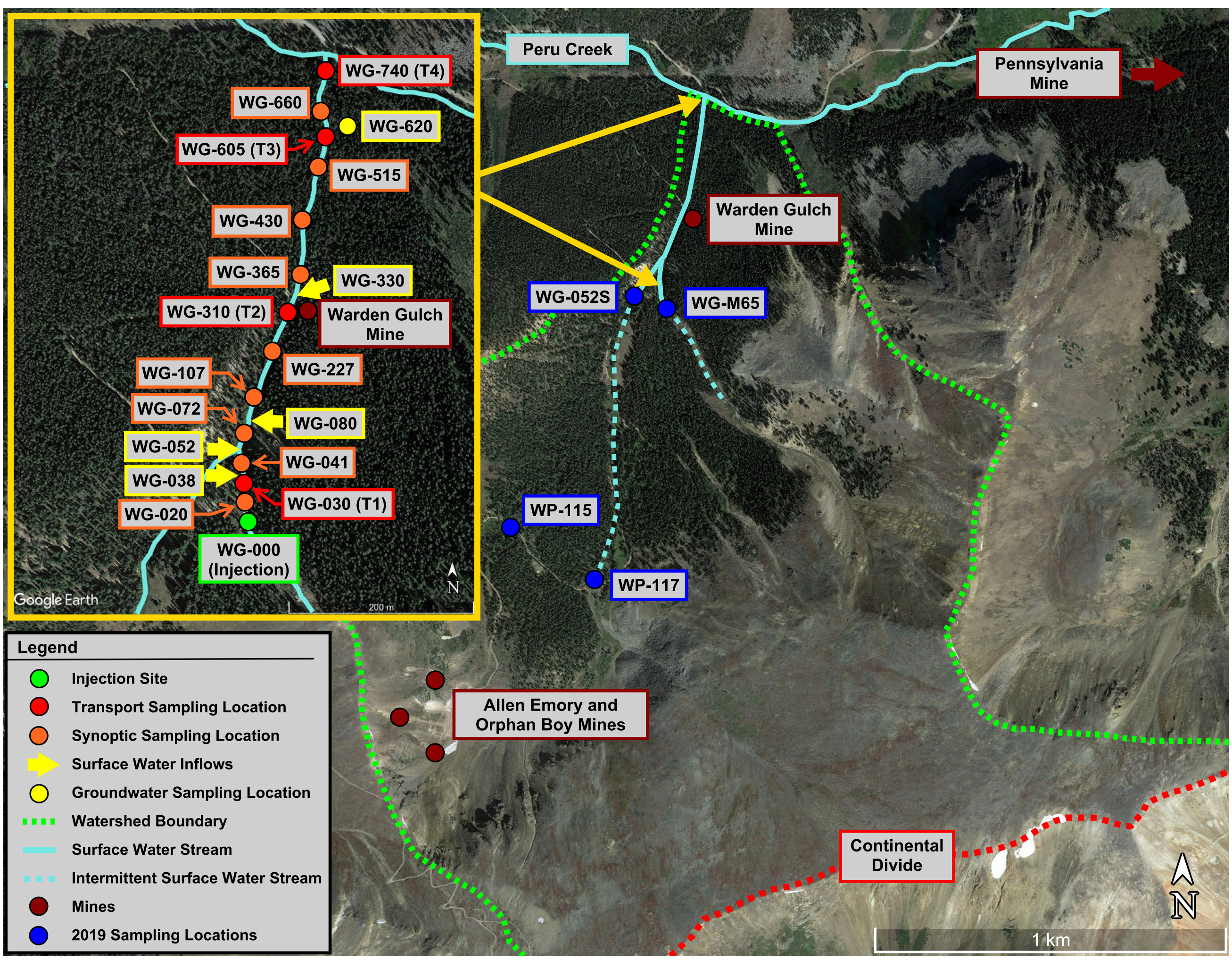

Fig. 2 Inset map of sampling locations within Warden Gulch for the September 29th, 2018 synoptic sampling study and larger map showing new sampling locations from the September 30, 2019 site visit (Jones 2020; Basemap from Google Earth)

hydrologic separation by the Cinnamon Gulch catchment (Fig. 1). Furthermore, although this study was not intended to determine the impacts of climate change on water quality to Warden Gulch, recent studies have documented increasing Zn concentrations over time in mineralized headwater streams (Petach 2022). Additionally, linkages between climate change and increasing Zn concentrations have been documented in nearby watersheds (Crouch et al. 2013; Rue and McKnight 2021; Todd et al. 2012) with similar impacts potentially occurring within Warden Gulch due to changing climate. Based on these factors, a reinvestigation of ARD/AMD sources within Warden Gulch and their impact to Peru Creek is presented herein.

Methods

The following subsections detail methodological aspects of the field work conducted by the authors and the subsequent data analysis. Additional information and data are presented in Jones (2020).

Tracer Injection and Synoptic Sampling, September 2018

On September 28, 2018, an initial reconnaissance of Warden Gulch was conducted to locate the origins of continuous flow in the stream (Supplemental Table S-3). Sampling locations were selected throughout the study reach to isolate surface water flows into the stream, as shown in Fig. 2 (inset). Site IDs corresponding to the various sampling locations are given by a "WG-" prefix followed by a numeric value representing the distance downstream, in meters, from the continuous tracer injection. Sampling locations extended from the injection site (WG-000) on the Right Fork of Warden Gulch to the confluence with Peru Creek (WG-740).

On September 29, 2018, a solution of NaBr was mixed using stream water to a concentration of 30,056 mg L^{-1}. This solution was injected into Warden Gulch at site WG-000 at a constant rate of 64 mL min^{-1} beginning at 10:12 h and was terminated at 16:37 h. Injectate flow rate was checked at 10:12 h, 11:07 h, 13:30 h, and was confirmed to be constant throughout the tracer injection.

Synoptic samples were collected at 13 stream sites and four inflow locations using a simple grab technique. Pairs of adjacent stream sites define the stream segments used in the loading analysis that follows. The synoptic sampling event was initiated at 14:57 h beginning at site WG-740, the most downstream site. Samples were collected in downstream-to-upstream order (starting at WG-740 and ending at WG-000) to prevent cross-contamination of samples by resuspended streambed materials. Synoptic sampling of the stream sites was completed at 16:04 h, after which inflow samples were collected. These stream and inflow samples are referred to as synoptic samples. A subsampling event was conducted from 16:45 to 17:02 h, shortly after the injection was terminated. During this time, samples were collected at sites WG-310, WG-605, and WG-740 to confirm that steady-state conditions had been reached. These samples are referred to as sweep samples.

During sample collection, stream temperature was measured in situ at each site. Bulk synoptic and sweep samples were collected and partitioned into aliquots for various analyses in the field at a filtering station. Specific conductivity and pH were measured using water from the bulk samples with a sonde (Yellow Springs Instruments XLM). For anion analysis, 50 mL of sample was filtered through a 0.45-µm high-capacity capsule filters using a peristaltic pump. For dissolved cation analysis, 50 mL of sample was filtered through the same high-capacity filter and acidified to pH < 2.0 on-site via ultra-pure trace metal grade HNO_3. For total recoverable cation analysis, 50 mL of unfiltered sample was acidified to pH < 2.0 on-site via ultra-pure trace metal grade HNO_3. All samples were stored at 4 °C in the dark to limit (bio)chemical or photochemical transformations until analysis.

Temporal samples were collected at a subset of synoptic stream sites throughout the day to document the breakthrough of the bromide tracer and the attainment of a steady-state tracer plateau (Runkel et al. 2013; supplemental Table S-4). These "Transport Sites" were located at WG-030 (T1), WG-310 (T2), WG-605 (T3), and WG-740 (T4) (Fig. 2), corresponding to locations above major hydrodynamic changes in Warden Gulch. A 40-mL sample was collected for bromide analysis and filtered immediately on-site using 50-mL polypropylene syringes and 0.45-µm polypropylene disposable disc filters into 50-mL trace metal free centrifuge tubes.

Reconnaissance and Sampling of the Warden Gulch Headwaters, September 2019

A follow up site visit was conducted on Sept. 30, 2019, to perform additional reconnaissance and collect additional samples. The primary goals were to: (1) collect a sample from WG-080, an inflow within the 2018 study reach that was not sampled at the time, (2) assess the impacts of the Allen Emory and Orphan Boy Mines within the upper reaches of Warden Gulch and determine if surface flows were draining from the mine adits, and (3) evaluate the topography of upper Warden Gulch and determine the likely direction of groundwater flow from the Allen Emory and Orphan Boy mine areas. Bulk samples of the WG-080 inflow and samples upstream (WG-072) and downstream (WG-107) from the WG-080 inflow were collected to compare instream conditions from 2018 to 2019.

Additionally, several sites were sampled outside of the 2018 study reach (Fig. 2). Sample WG-M65 was collected at the emergence of the stream, ≈ 65 m upstream from WG-000. Sample WG-52S was collected at the emergence of the WG-052 inflow, ≈ 70 m upstream from the discharge to Warden Gulch. Sites WP-115 and WP-117 are both located in the upper drainages of the WG-052 inflow and are denoted by their waypoint numbers. Site WP-117 in particular appeared to be within the main drainage way of the WG-052 catchment and could contain any drainage from the Allen Emory and Orphan Boy Mines. Although there were no direct drainages from these mine workings that could be sampled, WP-117 provided a potential insight into the impact of these mine workings. All new samples collected were processed identically to the 2018 synoptic samples.

Analytical Methods

Total-recoverable and dissolved cation concentrations were determined from unfiltered and filtered samples, respectively, using inductively coupled argon plasma-mass spectrometry (ICP–MS). ICP–MS analyses were performed at the Center for Trace Analysis at the University of Southern Mississippi. Dissolved anion concentrations (Br, Cl, F, and SO_4) were determined from filtered, unacidified samples by ion chromatography (IC). IC analyses were performed at the U.S. Geological Survey in Boulder, Colorado. Cation and anion concentrations are reported in Supplemental Tables S-3.1–3.6. Additional details are provided in Jones (2020).

Streamflow and Loading Calculations

Streamflow was calculated using the tracer-dilution method with Eq. 1 (Kimball et al. 2002):

$$Q_i = \frac{Q_{Inj}\left(C_{Inj} - C_0\right)}{C_i - C_0} \quad (1)$$

where Q_i is the flow rate at site i, Q_{inj} is the flow rate of the injection, C_{inj} is the injectate tracer concentration, C_i is the plateau tracer concentration at site i, and C_o is the background tracer concentration.

The streamflow estimates calculated using the bromide concentrations observed during synoptic sampling were deemed to be erroneously high due to failure to reach plateau prior to sampling (Supplemental Information SI-5). Streamflow estimates developed using sweep bromide concentrations were therefore used to adjust the synoptic streamflow profile downward, as discussed in SI-5. The final adjusted profile is nearly identical to the original synoptic profile at the upper locations where bromide concentrations had plateaued, and ≈ 4% less at the downstream end of the study reach where the synoptic concentration was the farthest from plateau (SI-5.2).

Instream load is given by the simple product of concentration and streamflow. The final adjusted streamflow profile was used with the observed concentration profiles to generate spatial profiles of instream load. Increases in instream load with distance reflect the addition of constituent mass due to sources, whereas decreases in load are attributable to reactive processes, such as mineral precipitation or sorption (Kimball et al. 2002). Spatial profiles of constituent load therefore represent the net amount of loading after chemical reaction. Cumulative instream load, in contrast, is equal to the sum of all increases in constituent load (Kimball et al. 2002) and reflects the total amount of loading due to sources. For a given stream segment, the cumulative instream load was increased if the constituent load had increased or held constant if the constituent load had decreased. Stream segments in which the cumulative instream load increased are considered sources of constituent mass, with the percent contribution given by:

$$Percent\ contribution = 100 * \left(\Delta load / L_{740,cum}\right) \quad (2)$$

where $L_{740,cum}$ is the cumulative instream load at the downstream end of the study reach (WG-740).

Results

Streamflow

Based on inflow characteristics, several distinct reaches can be identified in Warden Gulch as summarized in Table 1 and presented in Fig. 3. Streamflow immediately downstream from the injection on the Right Fork (WG-030) was ≈ 1.7 L sec^{-1}, and increased by an order of magnitude over the next 77 m (10.3 L sec^{-1}, WG-107). This sharp increase is attributable to a spring that emerges between the Right and Left Forks (1.5 L sec^{-1}, WG-038), the Left Fork (6.0 L sec^{-1}, WG-052), and the Mn Seep (1.2 L sec^{-1}, WG-080) (Fig. 3). Streamflow increased more gradually in the remainder of Warden Gulch, reaching 12.9 L sec^{-1} near the mouth (WG-740). This gradual increase is attributable to groundwater inflow along the Middle Reach (1.3 L sec^{-1}, WG-107 to WG-310), surface flow from the Warden Gulch Mine (0.4 L sec^{-1}, WG-330), and groundwater inflow along the Lower Reach (0.9 L sec^{-1}, WG-365 to WG-740) (Fig. 3). Within the Lower Reach, 87% of the flow increase occurred below WG-605. Flow at WP-117 during the 2019 site visit was 0.25 L sec^{-1}, an estimate obtained by recording the length of time required to fill a sample jug to a known volume.

Table 1 Stream reaches based on source water inflows and major hydrologic changes

Stream reach	Inflow source	Distance (m)	Flow contribution (L sec^{-1})	Flow contribution (%)
Warden Gulch	SW/GW	0–740 m	12.9	100
Right Fork	SW	< 30 m	1.71	13.2
Spring	SW	30–41 m	1.46	11.3
Left Fork	SW	41–72 m	5.98	46.3
Mn Seep	SW	72–107 m	1.17	9.0
Middle Reach	GW	107–310 m	1.30	10.1
Warden Gulch Mine	SW	310–365 m	0.366	2.8
Lower Reach	GW	365–740 m	0.935	7.2

SW surface water inflow, *GW* groundwater inflow

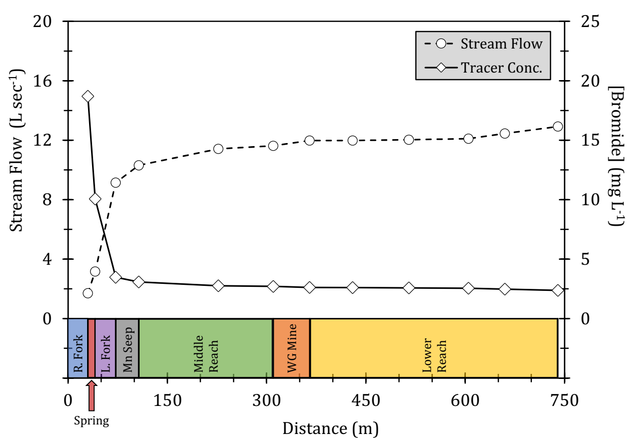

Fig. 3 Flow profile determined from synoptic samples and the tracer-dilution method

pH and Metal Concentrations

Spatial profiles of dissolved and total recoverable concentrations were nominally equivalent, indicating that most metals were in dissolved form under the acidic conditions observed in Warden Gulch (Jones 2020). As such, only dissolved concentrations are presented herein. This paper focuses on the primary metals of concern in Peru Creek and the Snake River (Al, Cd, Cu, Fe, Mn, Pb, and Zn) in addition to pH and SO_4. Discussion of additional constituents and total recoverable concentrations can be found in Jones (2020) and Supplemental Tables S-3.1–3.6.

Chronic aquatic life standards have been developed by the Colorado Department of Public Health and the Environment for a variety of trace metals (CDPHE 2021b). Warden Gulch had instream concentrations greater than the referenced standards for Al, Cd, Cu, Mn, and Zn throughout the entire study reach. Instream concentrations in excess of the standard for Fe were measured downstream from WG-227 to the confluence with Peru Creek (Fig. 4). However, instream concentrations in Warden Gulch for additional trace metals [Ag, Cr(VI), Ni, Pb, U] and metalloids (As), were less than the referenced chronic aquatic life standards. Spatial concentration profiles and aquatic life standards in Warden Gulch are presented in Fig. 4.

The pH within the Right Fork was initially low (≈ 3.8) and increased to 4.05 as contributions from both the Spring and Left Fork entered the stream, both of which were characterized by inflow pH greater than instream pH (Fig. 4). The pH steadily decreased below the confluence of the Right and Left Forks with substantial decreases attributed to the Mn Seep and Warden Gulch Mine inflows. The pH decreased immediately following the Warden Gulch Mine inflow (WG-365) and subsequently increased before continuing to decline throughout the Lower Reach, discharging to Peru Creek at a pH of ≈ 3.7.

Spatial concentration profiles for most constituents (Al, Cd, Cu, Mn, SO_4, Zn) showed similar characteristics within Warden Gulch (Fig. 4). Initially, the Right Fork was characterized by elevated concentrations. As contributions from both the Spring and Left Fork characterized by lower concentrations entered the stream, instream concentrations declined. As surface inflows from the Mn Seep (WG-080) characterized by high concentrations and groundwater inflows through the Middle Reach entered the stream, instream concentrations gradually rose. The Warden Gulch Mine inflow (WG-330), characterized by high concentrations, caused instream concentrations to increase. Through the upper part of the Lower Reach (WG-365 through WG-605), concentrations remained relatively unchanged due to minimal groundwater inflow. Following WG-605, instream concentrations sharply increased as groundwater inflows, assumed to be represented by WG-620 and characterized by high concentrations, entered Warden Gulch (Fig. 4). Sweep samples for all constituents discussed above showed nearly identical concentrations to

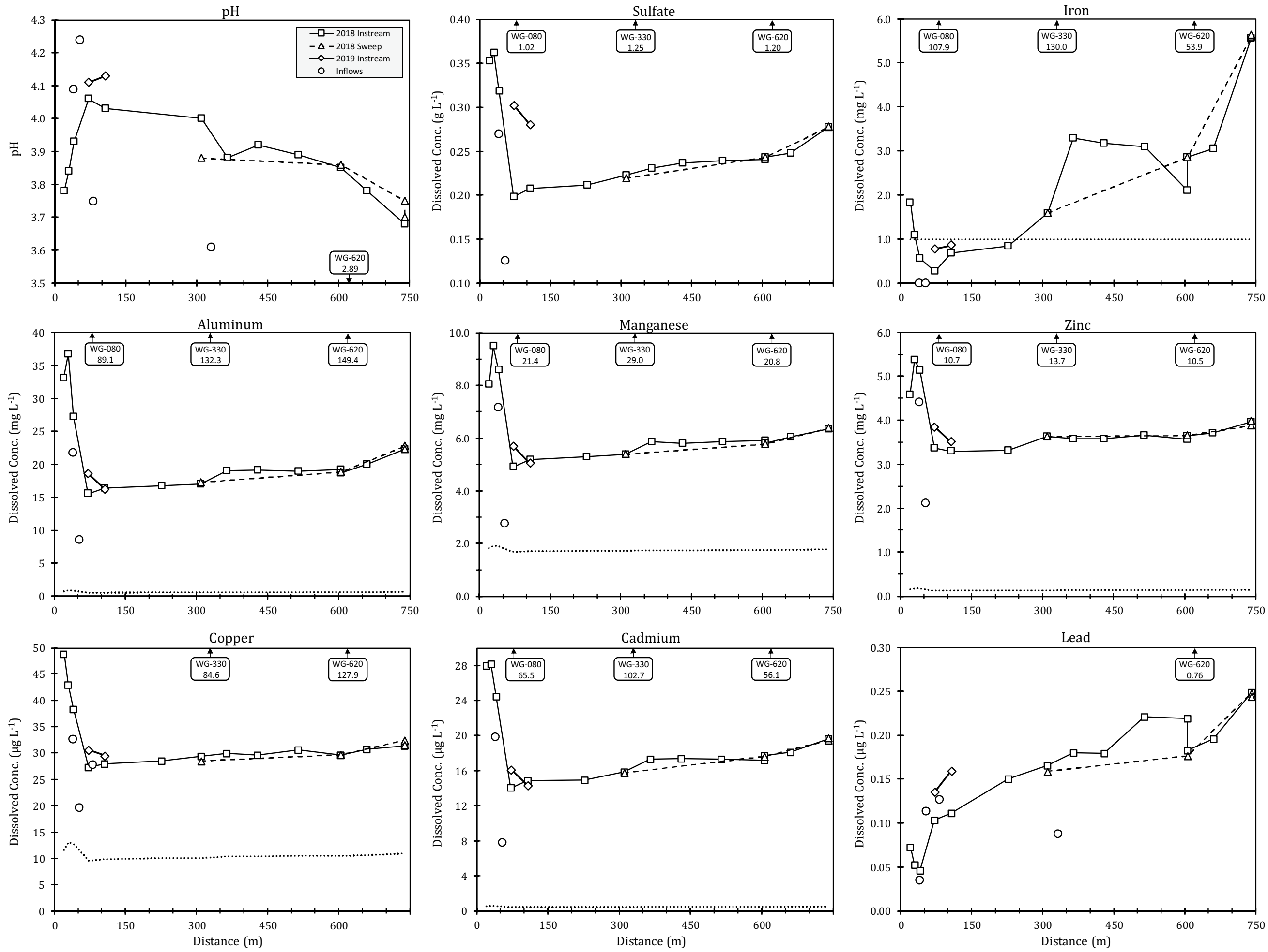

Fig. 4 Concentration plots from Warden Gulch synoptic sampling study. 2018 instream samples are represented by squares, 2018 instream sweep samples are represented by triangles, 2019 instream samples are represented by diamonds, and inflow samples are represented by circles. Additional inflow samples with values off the scale of plots are indicated by labels. Water quality standards (if within presented concentration range) are indicated by dotted lines

the synoptic samples, indicating steady-state concentrations throughout the sampling event.

The main exceptions to the general concentration trends discussed above were observed for Fe and Pb (Fig. 4). Like the aforementioned constituents, Fe concentrations near the injection site were diluted by the Spring and Left Fork. The Fe concentration profile in the downstream part of the study reach differed from the other constituents, however, with a sharp concentration increase following inflow from the Warden Gulch Mine, a decrease in the upper part of the Lower Reach, and a second sharp increase at the end of the Lower Reach (> WG-605). The Pb concentrations near the injection site on the Right Fork were initially low and abruptly increased downstream from the Left Fork (WG-072, Fig. 4). Pb concentrations increased linearly from the top of the Middle Reach to the Warden Gulch Mine. Pb concentrations decreased in the upper part of the Lower Reach and then increased downstream from WG-605, mirroring the behavior of Fe in the Lower Reach. The similar behavior of Fe and Pb in the Lower Reach is likely due to the precipitation of Fe oxides after the Fe-rich inflow from the Warden Gulch Mine enters the stream, and the subsequent sorption of Pb onto iron oxides. Sweep samples for Fe and Pb showed nearly identical concentrations to the synoptic samples at sites WG-310 and WG-740, and one of the two sequential replicates at WG-605 (Fig. 4).

The WP-115 sample collected in the upper Warden Gulch watershed was found to have low concentrations and did not reflect the effects of ARD/AMD. The WP-117 sample also had low concentrations, despite occurring downgradient from the Allen Emory and Orphan Boy Mines. Instream samples collected during the 2019 sampling event at WG-072 and WG-107 had dissolved constituent concentrations that were similar in magnitude to the 2018 instream samples (Fig. 4). Based on these results, the inflow sample collected at WG-080 during the 2019 sampling event (Sect. 3.2) is expected to be representative of the inflow waters that were present during the 2018 synoptic sampling event.

Loading Analysis

Spatial profiles of instream and cumulative instream load are presented in Fig. 5 and summarized in Table 2. For loading profiles with continuously increasing instream concentrations (e.g. SO_4, Cd) or minor instream concentration decreases (Al, Mn, Zn) resulting in < 1.0% difference between instream and cumulative instream loads, the instream and cumulative instream loads were nearly identical, and so cumulative instream loads are not plotted. All percentages presented herein are relative to the total cumulative instream load observed at WG-740 (Eq. 2; Fig. 6).

The loading profile for pH, calculated as the concentration of the H^+ ion in mmol sec^{-1}, shows varying magnitudes of increase throughout Warden Gulch. The Right Fork of Warden Gulch, characterized by initially low pH (≈ 3.8) and moderate flow (≈ 13%), had a loading contribution of 9% (Fig. 6). Higher pH (≈ 4.1) and moderate flow (≈ 11%) from the Spring contributed the least loading to Warden Gulch (4%). The Left Fork (WG-052) had the highest pH (least H^+) of all samples collected (4.25) and contributed the greatest amount of flow (≈ 46%) to Warden Gulch. Despite the high pH (Fig. 4), the large amount of flow associated with the Left Fork contributed 15% of the H^+ load. The

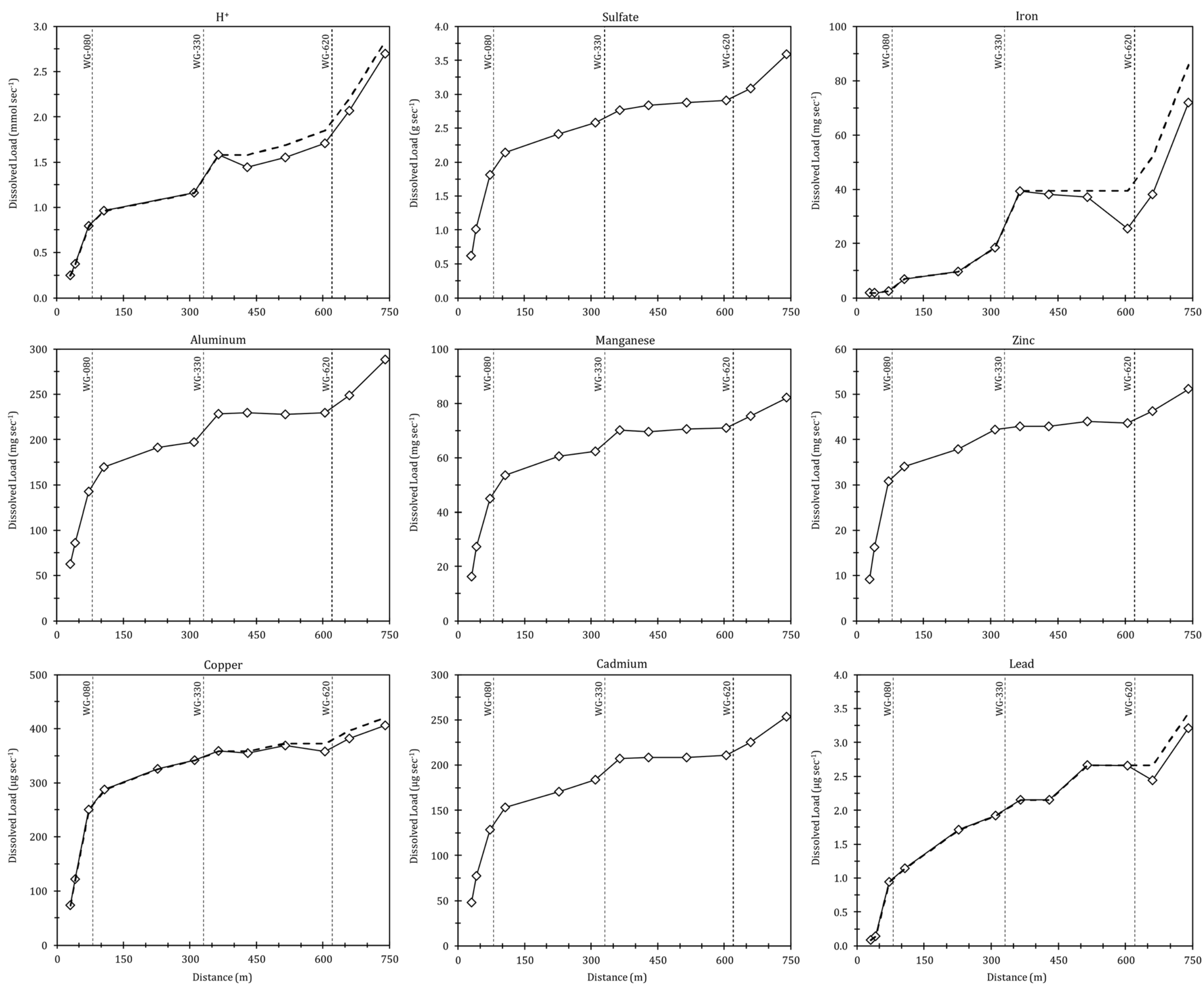

Fig. 5 Spatial loading plots throughout Warden Gluch calculated from the September 2018 synoptic sampling event. Cumulative loading profiles which do not differ from instream loading profiles are not presented (SO4, Al, Mn, Zn, Cd). Instream loads are represented by a solid line and cumulative instream loads are represented by a dashed line

Table 2 Cumulative instream load at the end of the study reach (WG-740), percent load contributions, and rank by stream segment

Stream reach	Rank	Al	Cd	Cu	Fe	H^+	Mn	Pb	SO_4	Zn
Warden Gulch, WG-740	–	290 mg sec^{-1}	254 µg sec^{-1}	421 µg sec^{-1}	81.3 mg sec^{-1}	2.84 mmol sec^{-1}	82.7 mg sec^{-1}	3.44 µg sec^{-1}	3.56 g sec^{-1}	51.5 mg sec^{-1}
Right Fork	3	22% (1)	19% (2)	17% (2)	2% (5)	9% (4)	20% (2)	3% (6)	17% (3)	18% (2)
Spring	T6	8% (7)	12% (5)	11% (5)	< 1% (7)	4% (7)	13% (3)	2% (7)	11% (5)	14% (5)
Left Fork	**1**	**19% (3)**	**20% (1)**	**31% (1)**	**1% (6)**	**15% (2)**	**21% (1)**	**23% (2)**	**23% (2)**	**28% (1)**
Mn Seep	T6	9% (6)	10% (6)	9% (6)	6% (4)	6% (6)	11% (6)	6% (5)	9% (6)	6% (6)
Middle Reach	*4*	*10% (5)*	*12% (4)*	*13% (4)*	*14% (3)*	*7% (5)*	*11% (5)*	*22% (3)*	*12% (4)*	*16% (4)*
Warden Gulch Mine	**5**	**11% (4)**	**9% (7)**	**4% (7)**	**26% (2)**	**15% (3)**	**9% (7)**	**7% (4)**	**5% (7)**	**1% (7)**
Lower Reach	*2*	*21% (2)*	*18% (3)*	*15% (3)*	*51% (1)*	*44% (1)*	*15% (4)*	*37% (1)*	*23% (1)*	*17% (3)*
Non-Mining Impact	–	70%	71%	65%	73%	70%	69%	70%	73%	71%
Mining Impact	–	11%	11%	5%	26%	15%	10%	10%	6%	5%
Potential Mining Impact	–	19%	18%	30%	1%	15%	21%	20%	21%	24%
Surface Water	–	69%	70%	73%	34%	49%	74%	40%	65%	67%
Groundwater	–	31%	30%	27%	66%	51%	26%	60%	35%	33%

Percent load contributions of cumulative instream load are presented with source rank in parentheses

Mining/potential mining impacted stream segments are shown in bold

Groundwater inflow contributed stream segments are shown in italics

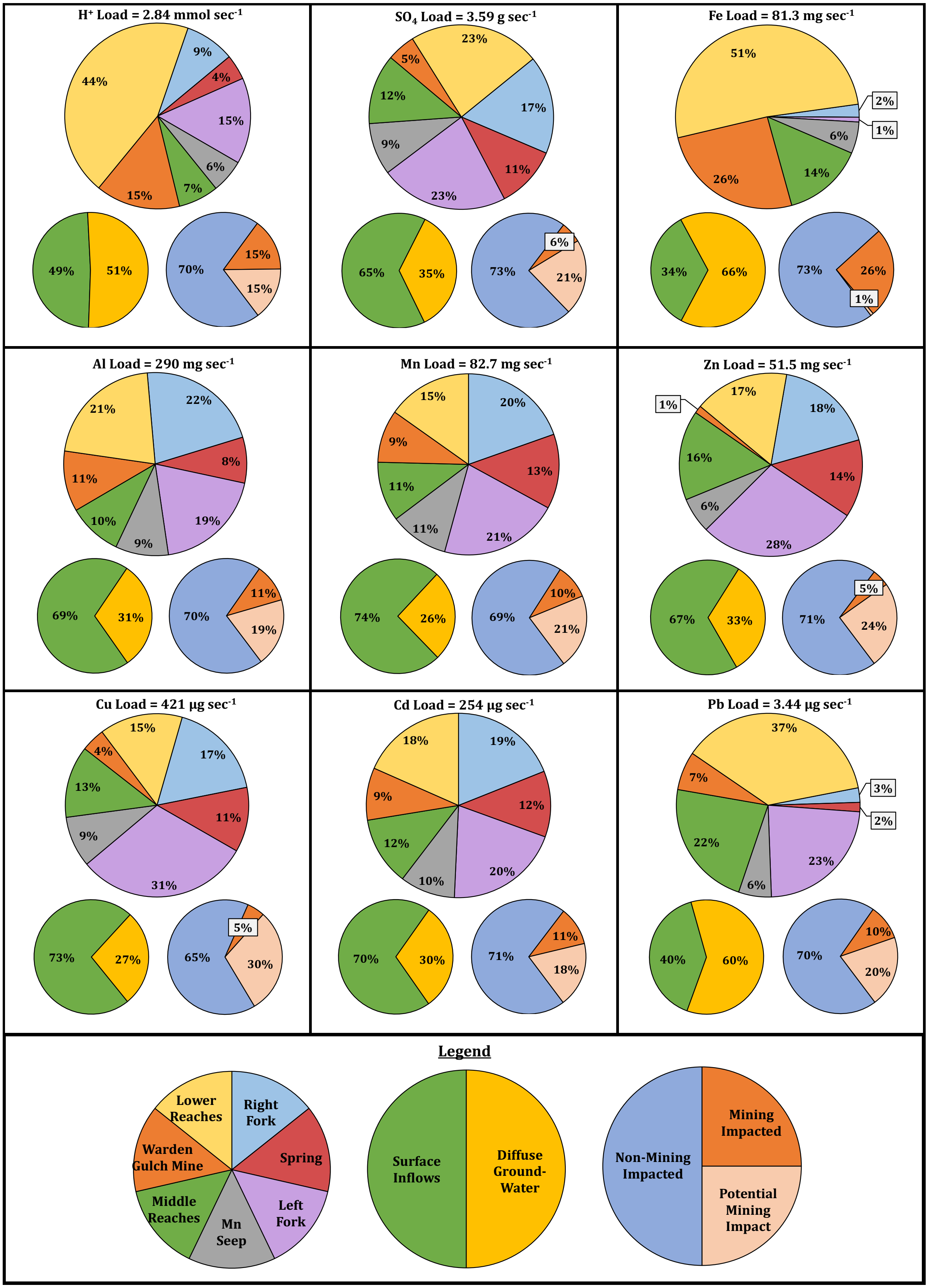

Fig. 6 Cumulative loading distributions through the 2018 Warden Gulch study reach. Plots include percent contributions by stream reach, surface or groundwater inflow percent contributions, and mining or non-mining impacted inflow percent contributions

Mn seep, characterized by a low pH (3.75) and moderate flow (9%), contributed 6% of the load. Groundwater inflow pH through the Middle Reach is unknown; however, moderate flow (≈ 10%) results in a load contribution of 7%. The Warden Gulch Mine represents the lowest flow contribution to Warden Gulch (≈ 3%); however, the low pH (≈ 3.6) results in a load contribution of 15%. The Lower Reach has the largest H^+ load contribution (44%), despite having the second lowest flow contribution (≈ 7%) (Fig. 6). Most of the H^+ is contributed to the last two segments of the Lower Reach (Fig. 5), where acidic groundwater similar to WG-620 (which had the lowest pH of all of the samples, ≈ 2.9, Fig. 4) may be entering Warden Gulch.

Constituent loads ranged in magnitude from g sec^{-1} (SO_4) to mg sec^{-1} (Al, Fe, Mn, Zn) to µg sec^{-1} (Cd, Cu, Pb). Loading profiles for most constituents (Al, Cd, Cu, Mn, SO_4, Zn) were similar, with loading well distributed through all stream segments in Warden Gulch (Fig. 6), ranging as follows: Right Fork (17–22%), Spring (8–14%), Left Fork (19–31%), Mn Seep (6–11%), Middle Reach (10–16%), Warden Gulch Mine (4–11%), and Lower Reach (15–23%) (Table 2). One exception to this trend for the referenced constituents was observed for Zn with a load contribution from the Warden Gulch Mine of only 1%.

Fe loading within Warden Gulch was characterized by low loading contributions from the Right Fork (2%), the Spring (< 1%), Left Fork (1%), and Mn Seep (6%). Moderate loading occurred through the Middle Reach, contributing 14% of the total load. Despite low flows from the Warden Gulch Mine, it contributed 26% of the total Fe load. Diffuse groundwater inputs through the Lower Reach resulted in the largest Fe loading contribution to Warden Gulch (51%) (Fig. 6). Precipitation of Fe below the Warden Gulch Mine (WG-365) results in the loss of dissolved Fe, and the instream load profile diverges from the cumulative instream load along the entire length of the Lower Reach (Fig. 5).

Pb loading in Warden Gulch was primarily dominated by contributions from the Left Fork (23%), Middle Reach (22%), and Lower Reach (37%). Minor contributions from the Right Fork, Spring, Mn Seep, and Warden Gulch Mine are observed, ranging from 2 to 7% of the total load (Fig. 6). Similar to the Fe loading profile, spatial profiles of instream load diverge from the cumulative load in the last two segments of the Lower Reach (Fig. 5), reflecting the loss of dissolved Pb due to sorption onto Fe precipitates.

Discussion

Stream Geochemistry

Loading of constituents to Peru Creek and the Snake River occurs continuously, dominating the instream geochemistry, degrading water quality, and impacting aquatic organisms within the Snake River watershed (Runkel et al 2013; Sullivan and Drever 2001). Due to the elevated concentrations of Fe in the AMD/ARD impacted streams, Fe precipitation reactions occur as anoxic inflows from the subsurface enter oxidized surface waters. The Fe precipitates further drive stream geochemistry through sorption reactions with dissolved trace metals. Due to the highly acidic surface waters in Warden Gulch, most constituents remained in soluble form and were conservatively transported downstream into Peru Creek. As circumneutral inflows (Chihuahua Gulch) mix with the acidic waters of Peru Creek, the pH increases and the conservatively transported trace metals from Warden Gulch and other sources to Peru Creek are deposited in the stream sediments by Fe and Al precipitation and trace metal sorption reactions, which are more favorable at higher pH.

Constituent Sources

Stream segments were ranked based on the percent contribution of constituent loading to Warden Gulch, with the highest average rank denoted as the top overall ranked source to Warden Gulch (Table 2). The Left Fork was the largest source of Cd, Cu, Mn, and Zn, and the second largest source of H^+, Pb, and SO_4, making it the largest overall source. The Lower Reach was the largest source of Fe, H^+, Pb, and SO_4, and the second largest source of Al, making it the second largest overall source. The Right Fork was the largest source of Al and the second largest source of Cd, Cu, Mn, and Zn, making it the third largest overall source.

Further analysis was conducted to determine the impacts of mining to Warden Gulch, and to determine source contributions from both surface water inflows and groundwater inflows (Table 2 and Fig. 6). Field reconnaissance conducted in 2019 confirmed a lack of surface flow from the Allen Emory and Orphan Boy Mines high in the watershed, and topographic features suggest that any subsurface contributions would likely flow towards WP-117 and the Left Fork (Fig. 2). Mining-impacted totals were therefore calculated as the sum of loading from the Warden Gulch Mine and WP-117 and loading from the Left Fork (with WP-117 loading removed) was conservatively categorized as potentially mining-impacted. The remaining loading sources (Right Fork, Spring, Mn Seep, Middle Reach, Lower Reach) were classified as non-mining impacted. For all constituents, loading to Warden Gulch was dominated by non-mining impacted sources, ranging from 65 to 73% of the total load. For most constituents, minimal loading was attributed to mining, with load contributions ranging from 5 to 15% (Fig. 6). The remaining loading attributed to potential mining impacts ranged from 15 to 30%. One exception is noted where mining-impacted and potentially mining-impacted loads of Fe contributed 26% and 1% of the load, respectively.

This is primarily attributed to substantial loading from the Warden Gulch Mine (Table 2).

It is important to note that in general, loading percentages attributed to mining likely include contributions from both ARD and AMD. Mining activities are generally performed in mineralized areas that likely produced ARD prior to the advent of mining. No attempt has been made herein to subdivide these percentages into their ARD and AMD components, or to estimate pre-mining conditions, as was done by Runkel et al. (2007, 2018). Nonetheless, it can be concluded that most of the loading within Warden Gulch is attributable to natural ARD sources (Fig. 6).

To determine loading contributions by source water type, stream segments were classified as surface inflows (Right Fork, Spring, Left Fork, Mn Seep, Warden Gulch Mine) and groundwater inflows (Middle Reach, Lower Reach) (Table 1). For most constituents (Al, Cd, Cu, Mn, SO_4, Zn), loading was dominated by surface inflows with percent contributions ranging from 65 to 74% of the total load (Table 2). Three exceptions to this were noted (Fe, H^+, Pb) where percent loading contributions were dominated by groundwater inflows ranging from 51 to 66% of the total load (Fig. 6).

Comparisons to Previous Work

Given that there have been no major landscape changes in the vicinity of Warden Gulch since the time of the previous synoptic study (O'Shea 2007), changes in water quality from 2006 to 2018 are potentially attributable to climate change, as documented by previous studies (Crouch et al. 2013; Nordstrom 2009; Rue and McKnight 2021; Todd et al. 2012). Although synoptic studies are not designed to address the effects of climate change, inferences may be made by comparing the 2006 and 2018 datasets. These comparisons should take into account the year-to-year variability in snowpack and the strength of the monsoon season, two factors that can have large impacts on both streamflow and concentrations in alpine catchments (concentrations typically decrease in wetter years due to the effects of dilution). Although both studies were conducted at base flow conditions, streamflow varied substantially. Streamflow at the nearest gaging station exceeded median values in October 2006, but was less than the median in September 2018 (Fig. S-1.1). In addition, Warden Gulch received fresh snow in the days prior to the October 2006 study, and snowmelt was occurring during sample collection (O'Shea 2007). As a result, September 2018 concentrations generally exceed concentrations observed in October 2006 (Fig. S-1.2), and this is attributable to hydrologic variability. The confounding effects of this hydrologic variability can be addressed by a comparison of instream loads based on constituent mass, as described below.

Comparison of instream loads from the 2006 and 2018 studies yields mixed results, with four constituents exhibiting an increase (Cd, Cu, Mn, Zn), four exhibiting a decrease (H^+, SO_4, Al, Pb), and one (Fe) essentially unchanged (Fig. 7). Despite these mixed results, some support for a climate change hypothesis may be found by considering the reactivity of the individual constituents. Given the low pH observed in Warden Gulch (<4.1, Fig. 4), Al, Cd, Cu, Mn, SO_4, and Zn would be expected to behave conservatively, such that increased loading from the catchment would lead to higher concentrations and loads. Fe and Pb, in contrast, would be expected to undergo precipitation and sorption reactions, and these solubility controls would limit the response to increased catchment loading. The results partially bear this out, with four of the six conservative constituents exhibiting increased loads and both of the reactive constituents showing no change or a decrease. Conservative constituents Al and SO_4 decreased in load and represent exceptions to this argument. These exceptions, and the dynamic snowmelt conditions reported by O'Shea (2007), prevent the formulation of any definitive conclusions.

Implications for Remediation

Through the synoptic mass balance approach, accurate characterization of source loads to Warden Gulch provides valuable insight into the effects of ARD/AMD within the watershed. By separating the relative contributions of the various sources, we are able to quantify these impacts, which may inform remedial decisions within Warden Gulch. Furthermore, through comparisons between previous studies, we were able to gain insight as to how these impacts are changing over time. Based on the results of prior and current studies, it is clear that constituent loading to Warden Gulch is well distributed, with substantial contributions from diffuse ARD sources and non-AMD impacted surface water sources. This characterization of source loads within Warden Gulch and other AMD-impacted streams allows for targeted allocation of resources for the remediation of abandoned mines.

The largest overall source of constituent loading to Warden Gulch was determined to be the Left Fork. Although there is the potential for AMD impacts to the Left Fork, these are more likely due to diffuse subsurface flow from the Allen Emory and Orphan Boy Mines in the upper watershed, making AMD discharges difficult to isolate for remediation. Furthermore, the second largest overall source to Warden Gulch was determined to be the Lower Reach. Source contributions throughout this stream reach are dominated by non-mining ARD inflows that enter the stream through diffuse groundwater inflows, likely resulting in costly and impractical remediation strategies. Lastly, the third largest overall source was determined to be the Right Fork. Although this inflow is a point source surface water inflow, constituent

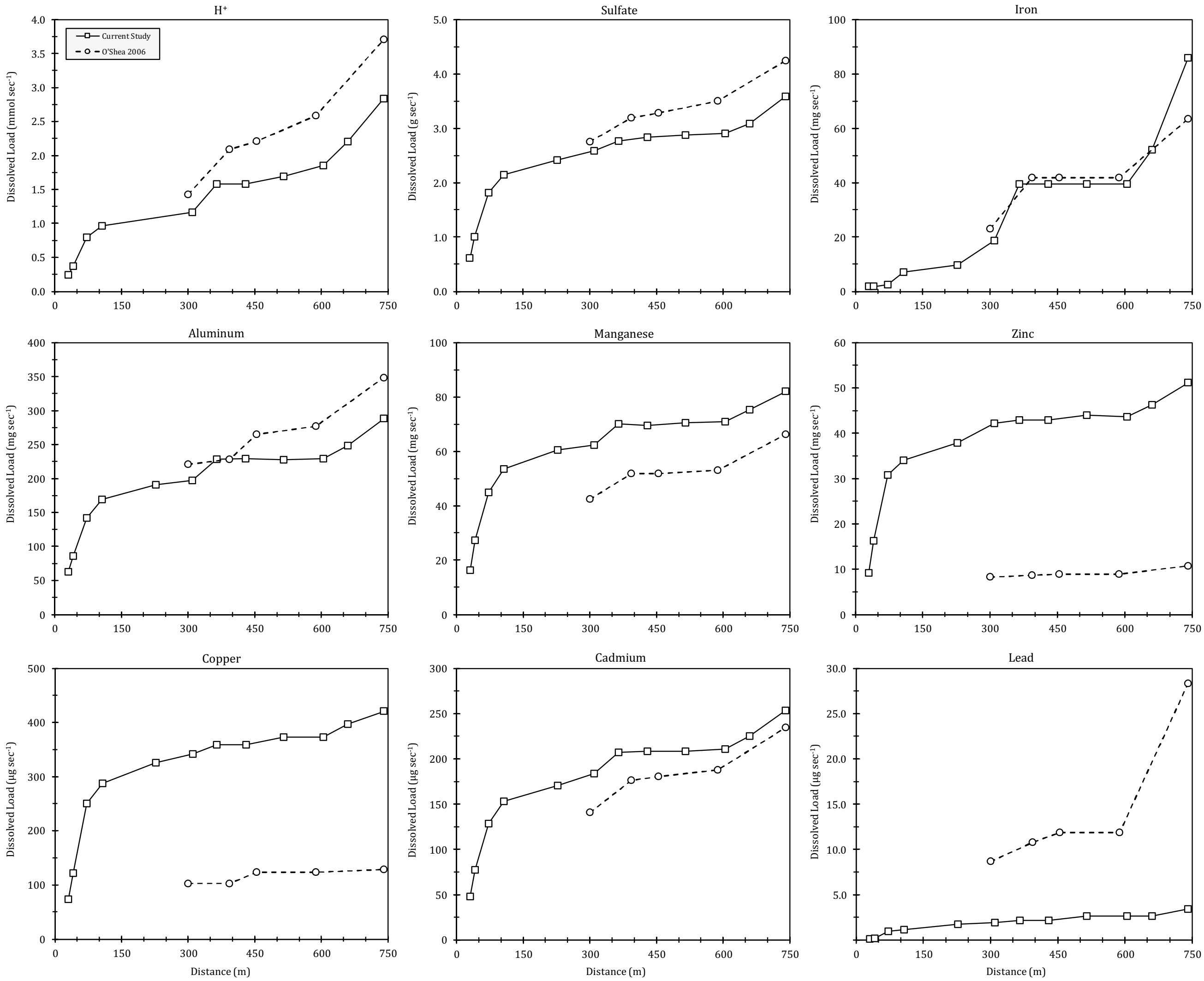

Fig. 7 Cumulative instream loading plots from Warden Gulch within the current synoptic sampling study and the O'Shea 2006 Study. 2018 instream samples are represented by squares while the 2006 instream samples are represented by circles

loading is due to natural ARD and thus not subject to remedial efforts. Based on these characteristics of the top sources to Warden Gulch, there may be limited potential for cost effective remediation to reduce constituent loading to Warden Gulch.

The Warden Gulch Mine is the only actively discharging mine adit in the Warden Gulch watershed. Despite elevated concentrations discharging from the mine, its low flow results in minimal impacts to the overall water quality degradation to Warden Gulch. This low loading contribution limits the potential benefits of remediation efforts. While cost effective remedial strategies are available to address the Warden Gulch Mine (e.g. installation of bulkheads), reducing flows from the mine would only address ≈ 10% or less of the total loading to Warden Gulch, with the exception of Fe and H^+. Remedial measures directed at this source are thus unlikely to substantially improve the water quality of Peru Creek and the larger Snake River watershed.

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