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# SURFACE WATER/GROUNDWATER INTERACTIONS AND HYDROGEOCHEMICAL CHARACTERIZATION OF THE ELKHORN MINE AND MILL, BEAVERHEAD COUNTY, MONTANA

by

Tyler Kamp

A thesis submitted in partial fulfillment of the requirements for the degree of

Masters of Science Degree in Geoscience Hydrogeology Option

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### Abstract

The formation of acid mine drainage (AMD) and the contaminants associated with it have been described by some as the largest environmental problem facing the U.S. mining industry. Heavy metals associated with the drainage, such as copper, cadmium, and zinc affect the water quality of streams and can cause acute or chronic toxicity to invertebrates and fish (Martin, 1992 & Padrillah et al., 2018). Elkhorn Creek in the Pioneer Mountains of southwest Montana is one of these impacted creeks. The historic Elkhorn Mine and Mill complex has historically attributed to the creek's contamination and has undergone remediation. However, the problem has not subsided. The United State Forest service partnered with the Big Hole Watershed Committee to address the next phase of remediation efforts; as part of that effort, the goals of this project include hydrological and geochemical characterization of the stretch of the creek between the mine adit and mill area.

Three staff gages and stilling well pairs were installed in points along the creek to observe flow, establish a rating curve, and determine vertical hydraulic gradient. A transect of 13 piezometers were installed around the mill, and two peepers were put in the wetlands around the mill. The transects were meant to measure the groundwater table and draw groundwater samples. Results from the data collected over four months concluded that metals contamination was picked up below the confluence of the adit discharge and again past the mill. A shallow groundwater table of two feet or less was heavily contaminated with metals. The creek at this section was also shown to be a groundwater gaining reach, meaning contamination from the mill soils directly enters the creek. The peeper study revealed natural bioremediation through sulfatereducing bacteria was present in the soil approximately 10 centimeters below the surface.

Keywords: Elkhorn, AMD, Peeper, Hydrology, Groundwater

# Dedication

To my loving wife, without who's encouragement I wouldn't have gone back to school and who's support throughout made it manageable. And to my family and friends for always being there.

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# Glossary of Terms

Term	Definition			
μg/L	Microgram per liter			
AMD	Acid Mine Drainage			
Al	Aluminum			
As	Arsenic			
Cd	Cadmium			
Cu	Copper			
Fe	Iron			
GCL	Geosynthetic clay liner			
IC	Ion chromatography			
ICP-MS	Inductively coupled plasma – mass spectrometry			
ICP-OES	Inductively coupled plasma – optical emission spectrometry			
kg/day	Kilogram per day			
MBMG	Montana Bureau of Mines and Geology			
MTDEQ	Montana Department of Environmental Quality			
mg/L	Milligram per liter			
Mn	Manganese			
Peeper	Pore water diffusion sampler or dialysis array			
PZ	Piezometer			
USFS	United States Forest Service			
Zn	Zinc			

### 1. Introduction

The formation of acid mine drainage (AMD) and the contaminants associated with it have been described by some as the largest environmental problem facing the U.S. mining industry (U.S. Forest Service 1993; Ferguson and Erickson 1988; Lapakko, 1993). AMD is primarily a function of the mineralogy of the rock material and the availability of water and oxygen, and these sites can result in drastically low pH of soils and waters (Jacobs et al., 2014; EPA, 1994). Oxidation rates can also be significantly increased by iron-oxidizing bacteria, further promoting the dissolution of Iron Sulfides (Hargrave et al., 1998). Heavy metals associated with the drainage, such as copper, cadmium, and zinc, affect the water quality of streams and can cause acute or chronic toxicity to invertebrates and fish (Martin 1992; Padrilah et al., 2018). In the western U.S., the Forest Service estimates that between 20,000 and 50,000 mines are currently generating acid on Forest Service lands which impacts between 8,000 and 16,000 kilometers of streams (U.S. Forest Service 1993). Contaminated water can stunt terrestrial plant growth and harm wetlands, and should the groundwater get contaminated, water treatment costs drastically increase. Determining if groundwater is contaminated is not as straightforward as surface water is, and there is a need to study AMD's connection between soil, groundwater, and surface water.

This project is focused on an abandoned mine site (Elkhorn Mine) and the impacts it has on Elkhorn Creek in the Pioneer Mountains, MT. It is in conjunction with the Big Hole Watershed Committee and Winden Water LLC. The project would be part of an ongoing restoration and analysis of Elkhorn Creek and nearby sediments that have been impacted by acid mine drainage. The creek around the mine and mill site show water quality below the standards set by Montana Department of Environmental Quality (MTDEQ). Previous work by Winden Water LLC (Hurley et al. 2021) and Montana Tech Field Camp (Gammons, 2009) observed copper and lead levels almost two times the acute and chronic toxicity levels. Contamination inputs being from the adit discharge and mill seep. Further intervention is needed, and a detailed analysis of contamination spots must be determined. The objective was to i) establish groundwater and surface water interactions throughout the study reach and ii) assess contaminant levels in surface water & groundwater.

## 2. Study Area

### 2.1. Regional Setting

The Elkhorn Mine and Mill complex is part of the Coolidge historic district. Located about 50 miles southwest of Butte, Montana, on the west side of the Pioneer Mountain Range, the complex lies in a narrow north/south trending valley (Figure 1). Elkhorn Creek runs through the area and forms the upper drainage of the Wise River, which then flows to the Big Hole River (Ferguson, 2021).



Figure 1: Map depicting location of Elkhorn Mine relative to Butte, MT

Nestled between Tweedy Mountain (11,154 ft) to the east and Comet Mountain (10,212 ft) to the south, the terrain is dominated by dense forests and mountains. Due to this positioning, the area receives high snowfall. In the year of this study, the road was not accessible until late June

### 2.1.1. Geology

The Elkhorn Creek drainage is primarily underlain by granitic gneiss, amphibolite, rocks of the Missoula Group, and other shelf sequences (Zen, 1983). The Mill site and meadows are composed of talus, alluvium, colluvium, and glacial debris. The surrounding peaks are Tertiary and Cretaceous intrusive rocks from the Pioneer Batholith (Pearson et al., 1983). Bedrock is occasionally exposed throughout the study area.



Figure 2: Photo showing Elkhorn Creek to the left, a remnant structure, and Comet Mountain in the background

#### 2.1.2. Vegetation

Forests cover the study area everywhere but the mill slope, mine slope, and remnant tailings meadow. Douglas fir, lodgepole pine, and limber pine make up the forests, while whortleberry, shiny leaf spirea, rose spirea, and Utah Honeysuckle make up the shrubs. Grasses in open areas include pine reedgrass, elk sedge, and bluegrasses (Hurley & LaPorte, 2021).

#### 2.1.3. Structures

Numerous manmade structures dot the landscape from past mining activities. Several homes are still intact, while most are piles of lumber. On top of mines, roads, ditches, flumes, and foundations, the massive waste rock dumps and a remnant settling pond stand out on the terrain. The diversion ditch, where Elkhorn Creek was rerouted during mining operations, still remains and continues to take a portion of creek flows.

#### 2.1.4. Water

While only one perennial stream flows through the site (Elkhorn Creek), several springs and seeps exist. The mill slope sees intermittent seeps during high flows that converge into a drainage bog. Seeps are also seen around the waste rock pile of the adit. The restored floodplain downstream of the mill sees numerous wetlands.

#### 2.1.5. Climate

Monthly precipitation, snowpack, and temperature data were gathered from the Mule Creek SNOTEL site in the Pioneer Mountains. During the study period (June to September), an approximate total of 4.2 in of rain (Figure 32) fell on the area. Temperatures ranged from an average high of 67F to an average low of 42F (Figure 33).



Figure 3: Photo of remnant Coolidge structure



Figure 4: Photo of old cabin and debris pile

#### 2.2. Historic Context

#### 2.2.1. Mining

The Elkhorn Mining District lies at an elevation between 7000 and 8000 feet above sea level. First discovered in 1872 as a small, primarily silver, producing operation. By the twentieth century, almost all mining activity in the district was centered on the Elkhorn lode and became one of Montana's silver operations. The Montana Bureau of Mines and Geology (MBMG) stated that 1,013 ounces of gold, 180,843 ounces of silver, 370,799 pounds of copper, 4,100 pounds of zinc, and 851,725 pounds of lead were produced over its lifespan (Ferguson 2021).

In 1913, the Boston-Montana was formed and began operations at the site (Ferguson 2021). The completion of a railroad line in 1919, from Divide to Elkhorn, allowed heavy equipment and materials to be transported. It was then that the creation of the large mill was made possible. A massive flood in 1927 destroyed major portions of the railroad, the Boston-Montana company could not recover from the economic blow, and operations ended by 1930. By the end of the 1940s, most of the company's deeded properties were acquired by Beaverhead County. Some light exploration in the 1980s yielded potential, but nothing came from it. By the 1990s, timber salvage on the historic mill started, and by 1999 the historic value of the mill was lost and was considered a hazard (Ferguson 2021).



Figure 5: Photos showing the mill circa 1940s vs. just before tearing it down in 1998

#### 2.2.2. Past Restoration

Due to the large-scale mining operations of the past, several human health risks and environmental hazards are present within the site. Both the Montana Department of Environmental Quality (MTDEQ) and the United States Department of Agriculture-Forest Service (USFS) have noted acid mine drainage (AMD) and leaching of heavy metals as major problems at Elkhorn. Surveys and studies were conducted for reclamation purposes beginning in 1990. The first effort was proposed by the Montana Abandoned Mine Reclamation Bureau (now MTDEQ) and called for the removal of mine waste rock and tailings, closing of adits, and AMD treatment, but was abandoned shortly after. In 1993, USFS and MTDEQ collected additional data and contracted Schafer and Associates of Bozeman for a Site Investigation. An Engineering Evaluation and Cost Analysis was started by Schafer and amended by Pioneer Technical Services in 1998. The EE/CA called to remove the historic tailings from the abandoned Elkhorn Creek stream channel. In addition, the AMD and stormwater run-off would be diverted from the existing mine waste dump and the dump would be reshaped and covered with soil to limit water contact.

The reclamation and removal focused around three primary hazards. The first was human health risk associated with the inhalation, ingestion, and absorption of heavy metals (arsenic and lead) at various features at the site. The second was human health risk associated with inhalation of asbestos from various components associated with the milling equipment. Finally, to attempt to improve the environment (aquatic and wildlife) from arsenic, lead, copper, and zinc, the cleanup would be done in multiple phases.

#### 2.2.2.1. Phase 1 (1998)

Phase 1 addressed the primary concern of the site, which was human health and environmental impacts stemming from heavy metal contamination. The main activities conducted included excavation and removal of mill tailings from the historic stream channel and isolation of the waste rock dump from water to eliminate generation of AMD. The tailings were moved to a repository, a drainage system was installed on the bottom, and covered with a geosynthetic clay liner (GCL) to prevent infiltration. The GCL was then covered with soil. The adit rock dump was deemed culturally significant and could not be removed. So, the dump had to be treated in place and isolated from coming in contact with water. It was also reshaped, limed, and covered with soil to prevent further AMD.

#### 2.2.2.2. Phase 2 (2001)

Phase 2's primary objective was to remove environmental impacts from residual mill tailings in the stream channel, re-establishing a natural functioning stream. The tailings in the stream were placed in a second repository, covered in a GCL, and topped with soil. Three thousand three hundred twenty feet of natural stream channel were reshaped in the Elkhorn floodplain. Reshaping included armored banks, meandering bends, and the addition of culverts to allow flow to the reclaimed stream and historic diversion.

#### 2.2.2.3. Phase 3 (2005)

The primary objective of phase 3 was to remove the remaining human health risks from tailings around the mill. This was not done earlier due to timber salvage operations of the building. With the mill also being of cultural historical significance, preserving as much of the original integrity was required. Ultimately, the main activity was piling and burning woody debris followed by excavation of the tailings. The removal of mill tailings and contaminated building materials was complicated by the requirement to preserve as much of the site's integrity as possible. Therefore, not all contaminants were removed.

#### 2.2.2.4. Phase 4 (2005)

This phase addressed safety concerns associated with the 1000-level adit by stabilizing the portal. However, discharge from the adit continues to pose a surface and groundwater contamination threat to the area.

#### 2.2.3. Next Phases of Restoration

In 2021, the Big Hole Watershed Committee (acting as project sponsor) and the US Forest Service (as landowner) entered a cooperation in coordination with Montana's Department of Environmental Quality (DEQ) and State Historic Preservation Office. The goal is to identify the extent of contamination to best remediate the site. Based on the presence, concentration, and extent of contamination, a Best Management Practice plan can be made.

### 3. Methods

### 3.1. Monitoring

#### 3.1.1. Surface Water Monitoring

Three staff gages and stilling wells were implemented along Elkhorn Creek (Figures 6 and 7). Stilling well/staff gage number one (EC1) was placed in Elkhorn Creek above the mine to capture all incoming flows to the system. EC2 was placed below the diversion culvert on the Elkhorn Creek side to capture water entering the creek and, by interpolation, how much the diversion is taking. Finally, EC3 was placed in Elkhorn Creek below the mill to capture influxes coming from the mill. The Elkhorn Creek diversion, referred to as the "diversion", was measured twice in June and not at all in July. By August 2<sup>nd</sup>, zero flow was observed in the diversion and water was stagnant.



Figure 6: Map of stilling well locations at the Elkhorn site



Figure 7: Photos of staff gages and stilling wells in place at EC1 (A), EC2 (B), and EC3 (C)

Staff gages were created by hand based on the Montana Bureau of Mines and Geology's (MBMG) standard operating procedure on staff gage creation (figure 8). A treated 2x4 wood plank was used as the support for the staff gage and stilling well. Inset holes were drilled in the plank to allow the carriage bolts to be flush with the board. A seam was cut on the back of the board to allow easier attachment to the tee-post. A 2-inch, schedule 40, PVC pipe was used as the stilling well. Holes were drilled in the pipe from the bottom to about a foot up. The pipe was attached using metal pipe straps screwed into the board. The type C staff gage was then screwed into the board, covering the carriage bolts and strapping.



Figure 8: Assembling the staff gage, inset for carriage bolt (A), seam for T-post alignment (B) and all together (C)

Site selection for the staff gage/stilling well is based on stream morphology and in-stream structures. Consideration must be taken for potential blowouts, wash-outs, or debris accumulation. In the case of Elkhorn Creek, these in-stream structures were natural. The staff gages must be placed in a pool (Figures 9 and 10) upstream of a control structure (riffles). The site must also be compatible with flow data collection.



Figure 9: Diagram of staff gage placement structures taken from the National Park Service



Figure 10: Photo of staff gage/stilling well and piezometer placement at EC3

Stream stage readings were taken every week from June 20<sup>th</sup> to August 8th, preceding streamflow measurements. When baseflow conditions appeared to have been reached, measurements were collected every two weeks. A total of 12 measurements were collected from June 8<sup>th</sup> to October 7<sup>th</sup>. A YSI 30 Conductivity probe was used to measure specific conductivity (SC) and temp at each staff gage in conjunction with stage measurements.

On July 2<sup>nd</sup>, 2021, three Solinst data loggers were placed in the three stilling wells. To obtain an accurate barometric pressure correction, a Solinst Baro Logger was air mounted at EC1. The level loggers recorded temperature and pressure every hour until they were pulled on September 15<sup>th</sup>.

Flow measurements were taken every visit, when possible, using a FlowTracker. Finding the proper place for flow measurements should coincide with staff gage placement. An ideal section should have a reasonably uniform flow, streambed free of structures, and a straight channel. The FlowTracker can only read water depths from 0.25 feet to 3.5 feet. Using a tape measure, stake the tape across the channel, perpendicular to the flow. Using the length of the channel, break the stream into 20 sections for which the FlowTracker to measure. This creates a more detailed velocity profile of the entire stream channel. A rating curve can be established by coupling the velocity data with the staff gage heights.

#### 3.1.2. Groundwater Monitoring

On June 28<sup>th</sup>, 2021, 13 nested Piezometers (PZ) were implemented surrounding the mill area (Figure 11). The PZs were created by hand and manually installed. The chosen material was one-inch, schedule 40 PVC pipe cut into 5-foot sections. 7/64-inch holes were drilled every inch from the bottom for a total screen length of 1 foot, and then the bottom was capped (Figure 12). A 6-foot iron spud bar was used as a pilot and pounded in with a post pounder until the proper depth was reached or could no longer move. When hand pulling was not possible, a chain and lift jack was used to break the suction. The PZ was placed in the hole and pounded in with the back of an axe. Depths of PZs ranged from 0.59 meters to 0.96 meters below the surface (Table I).



Figure 11: Map of transect piezometers and peeper locations

	Lat	Long	Staff Stick Up (m)	Well Length below Ground (m)
P1	45°29'38.51"N	113° 2'24.53"W	0.89	-0.64
P2	45°29'39.08"N	113° 2'25.01"W	0.65	-0.88
P3	45°29'38.76"N	113° 2'25.62"W	0.83	-0.70
P4	45°29'39.96"N	113° 2'25.24"W	0.64	-0.88
P5	45°29'39.93"N	113° 2'25.76"W	0.92	-0.61
P6	45°29'39.57"N	113° 2'26.57"W	0.74	-0.78
P7	45°29'40.92"N	113° 2'25.86"W	0.77	-0.76
P8	45°29'41.88"N	113° 2'25.96"W	0.59	-0.94
Р9	45°29'40.56"N	113° 2'27.17"W	0.92	-0.61
P10	45°29'41.52"N	113° 2'27.75"W	0.96	-0.56
P11	45°29'42.55"N	113° 2'27.68"W	0.85	-0.67
P12	45°29'43.46"N	113° 2'27.05"W	0.62	-0.91
P13	45°29'41.15"N	113° 2'26.47"W	0.83	-0.70

### Table I: Piezometer well locations, stick-up heights, and depth below ground

Sites were chosen based on coverage of contaminated areas and ease of implementation. These PZs were backfilled with native sediment and finished with a bentonite seal on top to prevent surface contamination. Near the end of the season, the tops of the transect PZs were surveyed in using a theodolite and 13 foot graduated rod. The well tops were surveyed relative to P10, where P10 equals 0 and wells are either above P10 or below.

One PZ was also installed next to each of the three staff gages (Figure 10). The PZ at EC3 was installed on 6-28-2021, while those at EC2 and EC1 were installed on 8-9-2021. EC2 and EC1 PZs broke on the initial try in June. A new tool was fabricated for their installation in August to prevent breaking.



Figure 12: Picture of capped piezometer base

A Keck Water Level E-tape was used every site visit to determine the static water level (SWL) of the groundwater in the wells. The E-tape probe will beep when it comes in contact with water. The reading on the tape is the distance from the top of the PZ to the water. The height of the PZ above the ground must be measured to determine the depth of water underground. SWL was measured seven times from July 2<sup>nd</sup> to October 7<sup>th</sup>. Using the YSI 30 Conductivity probe, SC and temp measurements were also taken.
## 3.1.3. Peepers

Soil pore-water chemistry down gradient of the old mill was monitored using dialysis arrays, also known as peepers. The peepers allow in-situ pore-water sampling by diffusion of solutes across a membrane (Hesslein, 1976) (Figure 13). The instrument is made of acrylic, 30 cm long, with 14 x 10-ml cells and 28 x 5-ml cells. A nylon membrane (5  $\mu$ m pore size) is laid in between the acrylic layers. The peeper is assembled in a cooler filled with deoxygenated, deionized water. The deoxygenation of water was done by bubbling nitrogen gas through it for approximately 1 hour. This step is crucial to ensure pore water does not become oxidized in the field (Carignan, 1984). Deoxygenation was done again, in the field, on the day of installation. Argon gas was bubbled through water in the cooler, and the peeper was then placed in the water to fill the cells. The top was attached in the cooler as well.



Figure 13: Picture of a peeper (A), and illustration of pore water diffusion (B)

The peepers were deployed in the bog between PZ 11 and 12 (Figure 11) and left for two weeks. Peeper 1 encountered rocks and therefore had ten rows of cells sticking up. Peeper 2 was able to be fully submerged. Upon site visit the next week, most of the standing water in the pool had drained. Peeper 1 was now exposed to row 12 (Figure 14), and peeper 2 was exposed to row 8 (Figure 15).

On September 24<sup>th</sup>, the peepers were extracted. Each peeper was placed in a glove bag filled with argon to minimize oxidation of the pore waters. Acid-washed sample bottles were prefilled in the lab to ensure swift field sampling. For trace metal samples, 20 mL of DI water was put in each bottle, topped with 0.3 mL Trace Metal grade nitric acid to obtain approximately 1% acid in solution. For dissolved sulfide and sulfate samples, acid-washed bottles were filled with 20mL DI water but no acid was added. For alkalinity sampling, 40 mL DI water was added to acid-washed bottles. All bottles were weighed before and after the field sampling event, thereby allowing dilution factors to be precisely determined.

When sampling the peepers, samples for ICP-MS trace-metal analysis were collected first. This was done by drawing up the water in each sample cell into a needle-tipped, 60 mL syringe. The collected sample was then pushed through a  $0.2 \mu m$ , PES (polyethersulfone) syringe filter into the pre-massed and pre-acidified sample bottles. For each sample, a different filter was used. This filtration step was also done for the anion (sulfate) samples but not for the dissolved sulfide and alkalinity samples.

Once analytical results were in from the lab, concentrations had to be adjusted by a dilution factor. The factor was dependent on the ending mass of the sample minus the initial mass of the sample, then divided by final mass again. The dilution factor for H2S was around 4, while the

factor for Sulfates was around 6. ICP-MS dilution factor was around 6x and a 10x dilution factor for alkalinity.



Figure 14: Peeper 1 on September 5<sup>th</sup> (left) and on September 14<sup>th</sup> (right)



Figure 15: Peeper 2 on September 5<sup>th</sup> (left) and on September 14<sup>th</sup> (right)

# 3.2. Sample Collection

## 3.2.1. Surface Water

Water quality samples were taken periodically throughout the field season. Twenty-two surface water samples were taken from the stream using a 60mL syringe between June 6<sup>th</sup> and August 29<sup>th</sup> (Table II). In addition to sampling the stilling well sites, one round of sampling was done at the following sites (Figure 16): the mouth of the adit ("Elkhorn Discharge"), Elkhorn Creek above adit confluence with Elkhorn Creek ("Elkhorn Creek above Adit"), a groundwater seep below transect wells ("Mill Seep") and above EC3, and in the restored meadow below EC3 ("Elkhorn Creek Below Meadow") (Table XIV). A Hydrolab MS5 was used for the above samples only. Water collected was sampled for anions, cations, trace metals, and water isotopes. Anion and cation samples were filtered, using a Corning 0.2 micron PES filter, into a 30mL bottle and stored at 4° C. Full-suite analysis samples were filtered into a 250mL bottle and preserved with 1% nitric acid and stored at 4° C. Part of the full-suite analysis also included a "raw" sample (unfiltered and unacidified), which the lab uses to perform pH and alkalinity measurements. Sulfur and Oxygen isotopes ( $\delta^{34}$ S and  $\delta^{18}$ O) were also collected from several sites to analyze the sulfate molecule.



Figure 16: Map of additional sample run locations

### 3.2.2. Groundwater

Groundwater samples were collected once, in the late season. A different method was used because the PZs could not be pumped continuously. On August 9<sup>th</sup>, the static water levels were measured, and each well was pumped to dryness. A "slug" of argon gas was then injected into the wells so that the air space in the pipe was filled with argon (a heavy gas), preventing oxidation of water as the wells slowly recovered. On August 11<sup>th</sup>, the static water levels were again measured to gage the percent recovery. Some of the wells recovered nearly to their initial water levels, although many did not. The wells that recovered (PZs 3, 6, 8, 11, and 12 (Table III)) were sampled with peristaltic tubing, a peristaltic pump, and a Hydrolab MS5 datasonde hooked up to a low-volume flow cell. Samples were collected and preserved using the same methods as for surface water. Filtration was particularly difficult owing to the high turbidity of the groundwater but was essential to get accurate laboratory data.

Sample			
Number	Sample Name	Date	Test
001	Adit Discharge	7/11/2021	ICP-MS/Sulfates
002	Elkhorn Ck above Mine	7/11/2021	ICP-MS/Sulfates
003	Mill Seep	7/11/2021	ICP-MS/Sulfates
004	Elkhorn Ck below Meadow	7/11/2021	ICP-MS/Sulfates
005	EC1	6/6/2021	Isotopes
006	EC1	6/20/2021	lsotopes
007	EC1	7/2/2021	Full Suite/Isotopes
008	EC1	8/9/2021	Full Suite/Isotopes
009	EC1	8/29/2021	Isotopes
010	EC2	6/20/2021	Isotopes
011	EC2	6/28/2021	Isotopes
012	EC2	7/2/2021	Full Suite/Isotopes
013	EC2	8/9/2021	Full Suite/Isotopes
014	EC2	8/29/2021	Isotopes
015	EC3	6/6/2021	Isotopes
016	EC3	6/20/2021	Isotopes
017	EC3	6/28/2021	Isotopes
018	EC3	7/2/2021	Full Suite/Isotopes
019	EC3	8/9/2021	Full Suite/Isotopes
020	EC3	8/29/2021	Isotopes
021	DC3	6/6/2021	Isotopes
022	DC3	6/20/2021	Isotopes

Table II: Surface water samples and analysis type

# Table III: Groundwater samples and analysis type

Sample Number	Sample Name	Date	Test
001	Р3	8/11/2021	ICP-MS/Sulfates
002	P6	8/11/2021	ICP-MS/Sulfates
003	P8	8/11/2021	ICP-MS/Sulfates
004	P11	8/11/2021	ICP-MS
005	P12	8/11/2021	ICP-MS/Sulfates

### 3.3. Analytical Methods

## 3.3.1. Alkalinity

Alkalinity of the peeper water samples (Table XXI) was tested using a digital titrator with bromocresol green-methyl red indicator and 0.1600 N  $H_2SO_4$  cartridge (HACH method 8203). 14 cells were sampled between the two peepers deployed, three from peeper 1 and ten from peeper 2. Titrations were performed back in the lab, within hours of field extracting.

#### 3.3.2. Dissolved Sulfide

The methylene blue method (HACH method 8131) was used to quantify dissolved sulfide  $(H_2S)$  in peeper (pore-water) samples only (Table XIX). In the field, ten cells were sampled (four from peeper 1 and six from peeper 2) and approximately 5mL of peeper water was added to each bottle using a syringe, with no filtration (The filtration step was skipped to avoid possible oxidation of  $H_2S$ ). Sulfide 1 reagent was immediately added and stirred, followed by sulfide 2 reagent. The presence of sulfide would turn the water a hint of blue. At the lab, the concentration was measured using a HACH DR/2010 portable spectrophotometer at wavelength 610µm. All results were corrected for dilution.

#### 3.3.3. Major lons and Trace Metals

All samples collected for trace metals (As, Cu, Fe, Mn, Zn) were filtered in the field and acidified to 1% v/v Trace Metal Grade HNO<sub>3</sub> (TableXVI). The samples were then submitted and analyzed at the Montana Bureau of Mines and Geology (MBMG) Analytical Laboratory, Butte, MT, using inductively coupled plasma mass spectrometry (ICP-MS) on a Thermo Scientific iCAP Q ICP-MS, following EPA method 200.8. Any sample collected for analysis of major cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) was also submitted to the MBMG lab and analyzed using an iCAP 6000 Series ICP-OES for ICP optical emission spectrometry (ICP-OES) following EPA method 200.7. Anions

(Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3</sup>, SO<sub>4</sub><sup>2-</sup>) were analyzed using ion chromatography (IC) at the MBMG lab for quantification using a Metrohm Compact IC Plus, following EPA 300.1. Due to budget constraints, most anion analyses were limited to sulfate only ( $SO_4^{2-}$ ).

#### 3.3.4. Sulfate Isotopes

Samples collected for S- and O- isotope analysis of dissolved sulfate (Table XX) were precipitated as barite following the procedures of Carmody et al. (1998). The precipitates were then filtered, rinsed with DI water, and dried overnight at 50°C. Once dried, they were shipped to the University of Nevada-Reno for analysis using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer (IRMS). Analysis followed the methods of Giesemann et al. (1994) for  $\delta^{34}$ S and Kornexl et al. (1999) for  $\delta^{18}$ O. Based on replicate laboratory analyses, analytical uncertainties are  $\pm 0.2\%$  for  $\delta^{34}$ S-sulfate and  $\pm 0.4\%$  for  $\delta^{18}$ Osulfate. The results are reported in  $\delta$  notation in units of ‰ vs. Vienna Canon Diablo Troilite (VCDT) for  $\delta^{34}$ S and VSMOW for  $\delta^{18}$ O.

# 3.4. Data Analysis

## 3.4.1. Surface Water Balance

To Determine the flow of groundwater  $(Q_{gw})$  into the creek at two distinct reaches during different times of the season, the following equation was used:

$$Q_{us} + Q_{gw} + Q_{trib} = Q_{ds} \tag{1}$$

where  $Q_{us}$  is the measured discharge at the upstream point of the reach (either EC1 for reach 1, or EC2 for reach 2), and  $Q_{ds}$  is the measured discharge at the second point in the reach (EC2 for reach 1, or EC3 for reach 2).  $Q_{trib}$  only applied when the diversion ditch was flowing, otherwise it was 0.

Equation 1 can be rewritten the following way:

$$Q_{gw} = Q_{ds} - Q_{us} - Q_{trib}$$

## 3.4.2. Load Balance

To determine the change in groundwater load within each reach  $(M_{gw})$ , the following equation was used:

$$M_{us} + M_{gw} = M_{ds} \tag{2}$$

Where M is the discharge multiplied by the concentration.  $M_{us}$  is the measured discharge from the upstream station multiplied by the concentration of the same section.  $M_{gw}$  is the measured flow of the downstream section multiplied by the concentration of the same section.

Equation 2 can be rewritten as the following:

$$(M_{gw}) = M_{ds} - M_{us}$$
$$M_{us} + M_{gw} = M_{ds}$$
(2)

### 3.4.3. Two Component Mixing

To determine the fraction of acid mine drainage (AMD)  $(f_{AMD})$  and fraction of regional groundwater  $(f_{regional})$  for the entire drainage basin the following equations were used:

$$f_{regional} + f_{AMD} = 1 \tag{3}$$

$$c_{regional}f_{regional} + c_{AMD}f_{AMD} = c_{riv}$$
(4)

where concentration of regional groundwater ( $c_{regional}$ ) is the SC of EC1 At the driest date, which is 49.2 µS/cm. The concentration of AMD ( $c_{AMD}$ ) is taken from the maximum value of measured SC of the transect wells (see Table IX), and the concentration of the river (Elkhorn Creek) ( $C_{riv}$ ) is the measured SC at each staff gage.

$$f_{of} = (1 - f_{AMD})$$

$$f_{gw} = \frac{(c_{riv} - c_{regional})}{(c_{AMD} - c_{regional})}$$

# 4. Results

### 4.1. Surface Water

The following results were compiled from the staff gage/stilling wells and the corresponding Solinst data logger. Manual FlowTracker discharge measurements were plotted against manual stream stage readings on a log/log scale to produce a rating curve at each of the monitoring sites (Figure 17). The power curve of the plots yielded an equation for which discharge was calculated. The "X" in the equation is the stream stage measured from the pressure transducer (Figure 18) and the "Y" values of stream discharge were calculated using the power curve. Hydrographs show that high flows occurred during snowmelt in June and July, but flows decreased during baseflow in August and September (Figure 19). Flows ranged from 1809.6 L/s during snowmelt and decreased to 34.10 L/s during baseflow. The highest average flows occurred at EC1, and the lowest average flows occurred at EC2. Recall that the diversion's flow was only measured twice in June and not at all in July. By August, the diversion had stopped flowing. This could explain some of the differences in flow between sites at EC2 and EC3. Periodic jumps in stage data, as seen near July 23<sup>rd</sup>, August 2<sup>nd</sup>, and August 22<sup>nd</sup>, correspond with large rain events.



Figure 17: Rating Curve of EC1 (A), EC2 (B), and EC3 (C) on a log/log scale showing stage vs discharge



Figure 18: Hourly stage data for EC1(A), EC2(B), and EC3(C) from Solinst data logger showing stream stage over time



Figure 19: Hydrographs in Liters per second, created from rating curve equation and stage data

# 4.2. Groundwater

To create a groundwater contour map, survey elevations relative to P10 (Table IV A) are added to an arbitrary contour level of 15 ft (4.57m). Once relative well top elevations are calculated, they are added to the SWL for each well at each date. The resulting adjusted water elevation table (Table IV B) was used for water table contour maps. Two contour maps were drawn, one for July and one for August (Figure 20 and Figure 21). These maps show relatively little change, and a non-uniform layout. Groundwater elevation maps for July and August show that the gradient generally follows topography with flows from SE to NW towards Elkhorn creek There appears to be a slight groundwater valley centered around wells P10, P9 and P13.

Water table elevations, throughout the season, ranged from 0.96 meters at P8, to 5 meters at P6. Generally, water levels dropped at each well from snowmelt to baseflow (Table IV B) as the system got dryer. Groundwater relative elevations range from around 1m to above 5m (Table IV B). There was very little change between July and August but it generally gets lower as the season progresses.

Specific conductivity values ranged from 233  $\mu$ S/cm at P6 to 1269  $\mu$ S/cm at P5 (Table IX). Groundwater temperatures ranged from 10.7 °C to 19.11 °C, with the warmest at well P6 and coldest at P9. A general warming trend is observed as the season progresses (Table X). Groundwater averaged 0.27 m below the ground surface, ranging from 0.6 m below the surface at P7 to above the surface at P11.

	Survey Elevation	Well Top Elevation
Well ID	(m)	(m)
1	-0.93	3.65
2	-1.00	3.57
3	1.08	5.65
4	-1.25	3.32
5	-0.39	4.18
6	1.28	5.86
7	-1.44	3.13
8	-2.59	1.98
9	0.43	5.00
10	0.00	4.57
11	-0.52	4.05
12	-1.95	2.62
13	-0.95	3.62

Table IV: Tables showing the survey elevation for each well relative to P10 and the resulting arbitrary well top elevations relative to 4.57 meters (A); and adjusted water tables for each well throughout the season (B)

Adjusted Water Elevation (m)							
Wall ID	Date						
weirid	7/2/2021	7/11/2021	7/18/2021	7/25/2021	8/1/2021	8/9/2021	
1	2.40	2.36	2.34	2.33	2.33	2.32	
2	2.47	2.36	2.29	2.27	2.27	2.26	
3	4.83	4.82	4.70	4.64	4.70	4.67	
4	2.57	2.54	2.50	2.47	2.44	2.41	
5	3.25	3.23	3.11	3.13	3.06	3.16	
6	4.97	5.00	4.98	4.96	4.89	4.76	
7	2.04	1.80	1.73	1.73	1.73	1.73	
8	1.03	1.06	0.96	0.97	0.97	0.97	
9	4.05	4.03	4.01	3.97	3.93	3.86	
10	3.57	3.58	3.37	3.34	3.29	3.23	
11	3.23	3.04	3.20	3.20	3.20	3.19	
12	1.74	1.80	1.68	1.63	1.64	1.63	
13	2.71	2.72	2.63	2.60	2.57	2.46	

B



Figure 20: Hand drawn groundwater contour map for July 2<sup>nd</sup>, where P10 is '0'



Figure 21: Hand drawn groundwater contour map for August 9th where P10 is '0'

## 4.3. Surface water/Groundwater Interaction

## 4.3.1. Surface Water Balance

Results from the surface water balance show that Reach 1 was apparently losing until August when it changes to a slight gain (figure 22). However, these results are confused by the absence of flow measurements at the diversion just above EC2 (Figure 6), so the total losses are a combination of groundwater and surface water gains/losses. It was not until August when the diversion went completely dry (dashed line on Figure 22) and the surface water balance between EC1 and EC2 could be attributed entirely to groundwater gains or losses. For the two measurements with a flowing diversion (orange bars in Figure 22), the water balance was calculated treating the entire stretch between EC1 and EC3 as one reach. During this time gains from groundwater were observed at first, then a loss to groundwater.

Reach 2, however, was observed to be a gaining reach throughout the whole study. Gains in the dry season (after August) were approximately twice as much as gains in Reach 1.



Figure 22: Chart of surface water balances for reach 1 (EC1 to EC2) and reach2 (EC2 to EC3) throughout the season, calculated using equation 1, The orange bars represent balances between EC1 to EC3, where the diversion had flow measurements. The dashed line represents the time at which the diversion had no more flows.

# 4.3.2. Load Balance

Groundwater load balance results (Figure 23) show that there is positive loading into the dry season. The change in load in June represent the entire reach (EC1 to EC3) and show generally a loss of loading. During high flow, there are several tributaries and overland flow that could be diluting the SC values with distance. In general, during July, loads increased from Reach 1 to 2 by approximately 45  $\mu$ S/cm. Then, in August, Reach 1 has higher loads.



Figure 23: Chart showing load balances for each reach throughout the field season, calculated using equation 2, dashed line represents time at which diversion has no flows

# 4.3.3. Two Component Mixing

The two components of regional specific conductivity and heavy metal contaminated groundwater (AMD) specific conductivity yielded a general trend of an increasing proportion of AMD affected groundwater as the season progresses (Figure 24). The lower percent of AMD water in July can be attributed to the higher flows of snowmelt diluting the concentrations. During the latter part of the season, AMD contributions result in an increase of approximately 2% to 5%, with percent increase from decreasing total stream flow.



Figure 24: Chart showing the fraction of acid mine affected groundwater entering the system

# 4.4. Water Chemistry

#### 4.4.1. Surface water and Groundwater

Generally, concentrations of trace metals increase with distance downstream through the study area. However, of note, dramatic increases are seen just below the adit discharge (EC2). Minor increases are observed again below the mill (EC3) (Figure 25). Figure 26 shows the trace metal concentrations of the surface water sites and the other sampling event, depicted in order of upstream to downstream. Concentrations from the adit are the highest (e.g. over 1000  $\mu$ g/L for Mn), then drop by several orders of magnitude (to 2  $\mu$ g/L for Mn) by EC1. An important note, in the restored reach, concentrations continued the trend seen from EC1 to EC3, which continues to increase. This sampling run observed two water quality exceedances in both chronic and acute standards for protection of aquatic life (Table XII)). Hardness had to be calculated before exact exceedance levels could be known. Zinc was in exceedance at EC2 only in August, and EC3 was in exceedance in July and August.

Figure 27 shows the metal loads from each surface water site. A similar pattern to the metal concentrations is seen. Loads decrease in August, most likely to decreasing flows. Table IV shows the change in loads between reaches. In almost all instances, the load was increasing between the reaches. Reach 1 has greater increases than Reach 2. The change in loads during July are too small due to the diversion taking flows. It is important to note that while Reach 1 (EC1 to EC2) has a greater increase in load, Reach 2 (EC2 to EC3) has overall higher loads (kg/day).

Two patterns emerge in groundwater metals concentrations (Figure 28 A-G). For Al, Cd, Cu, and Zn, the highest concentrations were centered around P11 and mainly originated in the bare tailings sediment. P11 being the PZ just south of the wetland/bog, while the PZs with lower concentration for those same metals are located in more grassy areas. The differences in concentration from P11 to P12 was important. P12, being the bottom (north) of the bog, shows

concentrations much lower, sometimes several orders of magnitude. Aluminum at P11 was 705  $\mu$ g/L, and by P12 drops to below 75  $\mu$ g/L not 20 meters away. Copper has concentrations above 2000  $\mu$ g/L at P11 and dropped to below 200  $\mu$ g/L at P12. The peeper results in the following section touches more on possible reasons for this concentration gradient.



Figure 25: Trace metal concentrations from surface water sites taken in July (A) and August (B)



Figure 26: Trace metal concentrations for additional July sample run



Figure 27: Metal loading from surface water sites on 7/2/2021 (A) and 8/9/2021 (B).

	Metals Load (kg/day)					
	EC1		EC2		EC3	
Analyte	7/2/2021	8/9/2021	7/2/2021	8/9/2021	7/2/2021	8/9/2021
Al	0.210	0.015	0.322	0.109	0.395	0.134
Mn	0.082	0.011	0.251	0.122	0.315	0.166
Cu	0.041	0.005	0.101	0.045	0.188	0.063
Zn	0.041	0.005	0.543	0.342	0.713	0.414
Cd	0.008	0.001	0.004	0.001	0.004	0.002
As	0.008	0.001	0.004	0.001	0.004	0.001
Fe	0.206	0.027	0.088	0.079	0.208	0.184

Table V: Table of metal loads per surface water site

Table VI: Change in loads by reach

	Change in loads by reach (kg/dy)				
	R	each 1	Reach 2		
Analyte	7/2/2021	8/9/2021	7/2/2021	8/9/2021	
Al	0.112*	0.094	0.073	0.025	
Mn	0.169*	0.111	0.064	0.044	
Cu	0.060*	0.039	0.086	0.018	
Zn	0.502*	0.336	0.171	0.072	
Cd	(-)0.005*	0.000	0.000	0.000	
As	(-)0.005*	0.000	0.000	0.000	
Fe	(-)0.117*	0.051	0.120	0.105	

\*Change in loads are too small due to diversion taking flows between EC1 and EC2














Figure 28: Groundwater trace metal heat maps for Al (A), As (B), Cd (C), Cu (D), Fe (E), Mn (F), Zn (G)

### 4.4.2. Peepers

The figures are displayed to represent concentrations with depth (depth being negative from the surface). Trace metal results were best displayed on a log x-axis scale. To best show correlations,  $H_2S$  and sulfate were plotted on the same graph (Figures 29). Overall, as  $H_2S$  increased with depth (0mg/L to 0.106 mg/L), sulfate decreased with depth (from 353mg/L to 55mg/L). This was true in both peepers. Only one alkalinity dataset (Peeper 2) was plotted, as Peeper 1 resulted in no change in alkalinity (Figure 30). Alkalinity was undetectable from 0 cm to 21 cm below surface, then increased to 8.6 mg/L at 21 cm below the surface.

Trace metals (Figure 31) also showed an overall decreasing trend with depth below the surface, often by several orders of magnitude (e.g., Cu with 4391 $\mu$ g/L at 2 cm below the surface to 22.3  $\mu$ g/L at 16 cm below the surface). Iron, however, increased with depth. In Peeper 1, Fe started with 111  $\mu$ g/L at 2 cm below the surface and ended with 3160  $\mu$ g/L 16 cm below the surface. In peeper 2, Fe started with 444  $\mu$ g/L at 2 cm below the surface and ended at 26,902  $\mu$ g/L at 20 cm below the surface.



Figure 29: Graph of H<sub>2</sub>S and Sulfate for Peeper 1 (A) and Peeper 2 (B) plotted against depth.



Figure 30: Alkalinity results for Peeper 2 against depth



Figure 31: Concentrations of contaminants of interest in Peeper 1 (A) and Peeper 2 (B) vs. depth

### 4.4.3. Sulfate Isotopes

Results for the isotopic composition of dissolved sulfate for the Elkhorn Adit discharge and the main seep below the Elkhorn Mill are summarized in Table VII. Although it was planned to get isotope data for sulfate from Elkhorn Creek above and below the mine site, the concentrations of dissolved sulfate were too low to process the samples. The results for the two AMD sources show very similar values of  $\delta^{34}$ S and  $\delta^{18}$ O. In other words, there is no apparent difference in the isotopic composition of sulfate coming from the adit discharge vs. sulfate coming from acidic groundwater springs in the vicinity of the mill. The implication is that sulfate isotopes cannot be used to discriminate the source of sulfate, a potential tracer of AMD, in Elkhorn Creek.

Location	Date of sampling	Sulfate concentration* mg/L SO <sub>4</sub>	δ <sup>34</sup> S, ‰ VSMOW	$\delta^{18}$ O, ‰ VSMOW
Adit discharge	7/11/2021	89	5	-13.1
Mill Seep	7/11/2021	184	5.4	-12.7
Elkhorn Creek above adit discharge	7/11/2021	2.5	n.a.	n.a.
Elkhorn Creek near EC3	7/11/2021	8.3	n.a.	n.a.

Table VII: S and O isotope composition of dissolved sulfate

\*Sulfate concentration determined by ion chromatography.

## 5. Discussion

## 5.1. Hydrology

### 5.1.1. Surface Water

The beginning of field data (end of June) caught the very end of the snowmelt runoff, as seen in Figure 19 and supported by Figure 35. Snowmelt had the greatest effect at EC1, where higher flows and greater fluctuations were evident (Figure 19). On July 6<sup>th</sup>, 2021, for example, flow was at 390 L/s and 12 hours later at 250L/s, then after another 12 hours was at 315 L/s. EC2 and EC3 flows up to August should be higher, but flow is split between the diversion and the creek. In August, however, EC3 is observed to have higher flows than the other sites. This can be interpreted as either continued groundwater inputs or groundwater being released from storage in the meadow.

It should be noted that in both Figures 18 and 19, a substantial drop in EC3 stage and flow occurs on August 2<sup>nd</sup>, 2021. Manual measurements, of both stage and flow, also confirm the drop at the same time. While the diversion flows were not measured in July, it is known that by August 2<sup>nd</sup>, the diversion was not flowing. The lack of flow in the diversion is unlikely to be the reason for the sudden drop. It is more likely to either be a small blowout of the log dam downstream or the staff gage was moved through human or animal interference.

Elkhorn Creek at and before EC1 runs through steep, loose rock, hillsides, while EC3 enters a flatter valley bottom with wide meadows. Compared to gentle slopes, steep slope runoff has a shorter yield time, meaning the time between rainfall and flow increases, and flows are more turbulent (Li et al., 2020). Similarly, runoff decreases in meadows due to their intercepting quality (Jeffery et al., 2014). Exemplified in the flashier flow peaks (Figure 19) in EC1 and, to a lesser degree, EC2 during storm events compared to EC3.

### 5.1.2. Surface Water/Groundwater Interaction

Surface water balances from Figure 22 and the groundwater table maps from Figures 20 and 21 support that the mill area, in general, is a groundwater fed reach. Reach 2 saw positive groundwater flows throughout the entire study except for August 29<sup>th</sup>, 2021. The groundwater table map also shows flows directly into the creek instead of following the creek's flow. Referencing Figure 19, the higher flows seen in EC3 may be attributed to the addition of groundwater flows to the creek. It may also be possible that the diversion, which sits at a higher elevation than EC3, could be contributing to groundwater. Reach 1 may not entirely reflect balances due to a lack of diversion flow measurements. However, a positive balance was observed when diversion flow was measured (June 8<sup>th</sup> and June 20<sup>th</sup>, 2021).

From Figure 23, load balances in Reach 1 are mostly inconclusive due to the lack of diversion flows. Losses seen while the diversion is flowing could be a combination of groundwater and lost diversion flows. However, once the diversion dries up in August, the reach is observed to have positive influx of groundwater loads. Reach 1 is not as easily explained, again, due to a lack of diversion flow measurements. The negative loads indicated are not necessarily a loss of groundwater load, the difference could have been found in the diversion. Groundwater loads were positive when diversion measurements were made (June 8<sup>th</sup> and June 20<sup>th</sup>, 2021). Surface water balances also support a groundwater-fed reach. In August, Reach 1 surface water losses are a quarter of what they were previously. Then, by mid-August, Reach 1 changed to a gaining system. One interpretation may be that losses before August could be attributed to the diversion and indicate a losing system.

## 5.2. Water Chemistry

### 5.2.1. Surface Water

Surface water trace metal results show a clear indication that contamination picked up after the confluence of the adit discharge (between EC1 and EC2 in Figure 25), and again picked up below the mill (EC3 in Figure 25). Figure 4-26, which includes the additional sampling results, indicates that the adit added a great deal of contamination. However, by the time water reached Elkhorn Creek (EC2), concentrations are less. This may indicate that the settling ponds are working, to a degree, but contamination above standards are still observed. Note that, while other metals are very high, there is almost no iron found in the adit sample (Figure 4-26), there were, however, ferricrete lining the adit stream bed. It could be reasoned that the ferricretes are taking the iron up (Church et al., 2007), evident from EC1 results taken above the confluence, showing very low Iron concentrations. Seasonal differences of the chemistry of the adit discharge is also possible. The "Mill Seep" portion, considered a groundwater spring, adds its contamination, which shows up at EC3. Elkhorn Meadow and EC3 results show that contamination continued to pick up through the restored section, at least. Further support was found in the 2-Component mixing model (Figure 24), which suggests that by late season approximately, 4.5% of flows is AMD affected water. Surface water balances, load balances, and water tables maps indicate groundwater inputs through the system. Given that the mill area was a short portion of the reach but sees significant contamination inputs to the creek, it suggests the area is highly contaminated.

Trace metal loading (Figure 27) depicts an increasing gap between surface water sites, particularly between Zinc in EC2 and EC3. Of the sampled analytes, Cu and Zn were above MTDEQ water quality standards in July and August for both EC2 and EC3. The increasing SC in surface water sites as distance increases (Table XV), may suggest the incoming metal loads can

(at least partially) be responsible. The exceedances at both EC2 and EC3 indicate that just cleaning the mill seep will not clean the system. Contamination is still coming from the adit discharge.

Nimick et al. (2003) discussed diel (24-h) cycles of dissolved metal concentrations in streams. In many streams with near-neutral or alkaline pH, concentrations of dissolved Zn and Cd tend to increase at night and decrease during the day, reaching a minimum in the afternoon. These changes are linked to diel variation in water temperature and pH. Because all of the stream samples in this study were collected in the afternoon, this means that the concentrations reported in this thesis for Zn and Cd in Elkhorn Creek may be less than the 24-h average concentrations of these trace metals on the same sampling days. Future studies of metal concentrations and loads in Elkhorn Creek may want to employ automated samplers to collect a full 24-h set of samples to test the magnitude of any diel variations.

#### 5.2.2. Groundwater

Trace metal results from the mill PZ transects (Figure 28 A-G) indicate a clear concentration of metal contamination around the bare mill soils. The greatest concentration of contamination was observed around P11, which was primarily the bare tailings by the mill. P11 was right before the wetlands and directly below a toe seep at the base of the mill. The seep ditch and wetlands may funnel some of the contaminated groundwater. Contaminated soils around the mill and a shallow groundwater table running through the soils indicate that Elkhorn Creek at that portion picks up contamination. The mill seep contamination was most likely seen at EC3 (Figure 25). Removal of the surface tailings would have some impact on cleaning the water in the area. While groundwater would not be immediately clean, the major metal source may be removed.

Concentrations of dissolved Mn, Fe, and As showed concentrations more centered around P6. P6 was chosen as a PZ location for its proximity to the old assay house directly uphill of it. These metals concentrations may have something to do with the remnant assay sediments. Arsenic far exceeds human health standards (10 ppb), while concentrations of zinc and iron are also very high. Microbial decay of organic matter turns groundwater anoxic (Drever, 1997), and when the dissolved oxygen (DO) is gone, bacteria begin to dissolve the Mn-oxide and Fe-oxide minerals (Langmuir, 1997). This process of dissolving Mn- and Fe-oxides causes the concentrations of both dissolved Mn<sup>2+</sup>and Fe<sup>2+</sup>to increase. Also, because arsenic tends to adsorb onto Fe-oxides (Langmuir, 1997), dissolution of Fe-oxides often results in a coupled increase in dissolved As. Previous work using peepers in the Warm Springs settling ponds near the tail end of Silver Bow Creek showed sharp increases in the concentrations of Fe, Mn, and As in the shallow sediment (Lee, 2012; Boese, 2015).

Peeper results in the wetlands below the mill suggest that sulfate-reducing bacteria (SRB) are present and working. In anaerobic conditions, dissolved sulfate is reduced to hydrogen sulfide by SRB.  $H_2S$  concentrations never get greater than 1 ppm (mg/L) because  $H_2S$  reacts with Fe and other metals to form metal sulfides. Formation of sulfide minerals is the best explanation for the sharp decreases in concentrations of Cd, Cu, and Zn with depth in the peeper profiles (Figure 4-14). In contrast, sulfides of Fe, Mn, and As are more soluble (Langmuir, 1997), allowing these metals to have higher concentrations at the low levels of  $H_2S$  present.

## 6. Conclusions and Future Work

### 6.1. Conclusions

Elkhorn Creek around Coolidge continues to receive metals contamination from both adit discharge and groundwater through contaminated mill sediments. However, most of the metal contamination is still coming from the adit discharge and just cleaning the mill sediments will not be enough. The creek section flowing through the mill area is a groundwater gaining section, and piezometers in the soils show high levels of metal concentrations. Thus, it is reasonable to conclude that groundwater entering the creek is also highly contaminated. In fact, arsenic is the groundwater is well above water quality standards for human health. Signs could be placed around the area of the mill wetland and seep, discouraging drinking the water, from humans or pets.

The top of groundwater table around the mill ranges from .27 m below surface to at surface. By late season (August/September) groundwater was below the reach of piezometers.

The peeper study showed that natural bio-remediation for heavy metals is occurring on a small scale. Allowing these microbial reactions to continue undisturbed would be recommended. Building a fence around the mill seep area is recommended to prevent disturbance of the wetland from wildlife and pets. It may also be concluded that, with extra remediation, the wetlands could be able to expand.

## 6.2. Future Work

A more in-depth hydrologic study of the diversion would help understand the system better. Without knowing how much is being diverted, loads and balances for Reach 1 was not conclusive. Additional peeper studies could be performed around the southern portion of the mill transect, particularly around P6. The groundwater metal concentrations indicated possible anaerobic environments which may promote more SRB. Removing approximately 2 feet of soils around the mill would greatly reduce the metals impact coming into the creek, but not all contamination. Further investigation into the ferricretes around the adit, as well as the effectiveness of the current discharge treatments is needed as well.

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## 8. Appendix A: Supplemental SW/GW Parameters

	EC1		EC	2	EC	3
	SC (µS/cm)	Temp ( C )	SC (µS/cm)	Temp ( C )	SC (µS/cm)	Temp ( C )
6/20/21 1:30 PM	25	7.5			33	9.2
6/28/21 4:00 PM	30	12.8	37	12.9	38	13.6
7/2/21 2:00 PM						
7/11/21 2:30 PM	37	12.4	49	11.7	50	11.7
7/18/21 1:00 PM	42	12.4	55	11.7	57	12.4
7/25/21 2:00 PM	44	13.1	58	12.1	59	11.8
8/1/21 2:20 PM	46	13.8	61	13.1	63	13.2
8/9/21 1:30 PM	46	10.2	64	8.9	64	8.7
8/29/21 12:45 PM	50	7.4	68	6.9	70	7.1
9/5/21 3:50 PM	51	9.5	74	10.2	75	11.4
10/7/2021 12:15	53	4.7	79	4.6	80	6.5

## Table VIII: Specific conductivity and temp for surface water sites

#### Table IX: Specific conductivity for piezometers by date

	SC of Transect Wells (μS/cm)								
Well	7/2/2021	7/11/2021	7/18/2021	7/25/2021	8/1/2021	8/9/2021	9/5/2021		
1		550	260	413	369		333		
2		465	430	437	518		496		
3		411	560	672	495	483.6			
4		379	367	353	356		358		
5		737	994	1269	965				
6		233	236	235	237	242			
7		445	501	601	653				
8		491	406	401	379	301	435		
9		267	293	354	371				
10		418	316	297	256				
11		352	356	362	371	297	345		
12		339	336	330	322	295	285		
13		251	358	374	354				

	Temp ( C )							
Well	7/2/2021	7/11/2021	7/18/2021	7/25/2021	8/1/2021	8/9/2021	9/5/2021	
1		12.3	12.5	13.3	13.3		12.2	
2		11.1	12.7	11.9	12.2		12.7	
3		14.1	14.9	14.6	15	18.94		
4		13.8	13.5	13.5	13.3		11.5	
5		14.1	14.6	14.2	15.1			
6		13.2	14	14	14.2	19.11		
7		12.8	13.2	13.5	13.8			
8		14.7	15.1	15	15.6	18.1	13.4	
9		10.7	12.3	12.9	13.5			
10		13.9	14.8	14.4	15.1			
11		11.7	12.7	12.9	13.8	16.78	11.1	
12		12.8	13	12.3	13.3	16.04	11.1	
13		14.2	14.7	15	15.3			

Table X: Temperature for piezometers by date

Table XI: Measured SWL for each transect well on a given date

		SWL (m)							
Well	7/2/2021	7/11/2021	7/18/2021	7/25/2021	8/1/2021	8/9/2021	9/5/2021		
1	1.25	1.28	1.30	1.31	1.32	1.32	1.35		
2	1.11	1.22	1.29	1.30	1.30	1.31	1.37		
3	0.81	0.83	0.94	1.01	0.95	0.98	DRY		
4	0.75	0.79	0.83	0.86	0.88	0.91	0.97		
5	0.94	0.95	1.08	1.05	1.12	1.02	DRY		
6	0.88	0.85	0.88	0.90	0.96	1.10	DRY		
7	1.09	1.33	1.40	1.40	1.41	1.41	DRY		
8	0.95	0.92	1.02	1.01	1.01	1.01	1.05		
9	0.94	0.97	0.99	1.02	1.07	1.14	DRY		
10	1.01	1.00	1.20	1.23	1.28	1.34	DRY		
11	0.82	1.01	0.85	0.85	0.85	0.86	0.92		
12	0.88	0.83	0.94	0.99	0.98	0.99	1.14		
13	0.91	0.91	0.99	1.02	1.06	1.16	DRY		

	Trace metal concentrations that exceed MTDEQ standards (in red)									
	27AI	55Mn	63Cu	66Zn	111Cd	75As	56Fe			
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L			
ECI 7/2/21	5.11	2	1	1	0.20	0.20	5			
EC2 7/2/21	18.2	14.2	5.74	30.7	0.20	0.20	5			
EC3 7/2/21	20.7	16.5	9.84	37.4	0.20	0.20	10.9			
EC1 8/9/21	2.70	2	1	1	0.20	0.20	5			
EC2 8/9/21	17.9	20.1	7.40	56.3	0.230	0.20	13.0			
EC3 8/9/21	17.9	22.2	8.45	55.3	0.218	0.20	24.6			

Table XII: Raw trace metal surface water data that exceed MTDEQ standards for aquatic life

Calculating hardness and aquatic life standards for EKC samples using ICP-OES data									
		Ca (ppm)	Mg (ppm)	hardness (mg/L)					
EC1	7/2/2021	4.36	0.394	12.51					
EC2	7/2/2021	5.38	0.478	15.41					
EC3	7/2/2021	5.52	0.502	15.86					
EC1	8/9/2021	6.44	0.584	18.49					
EC2	8/9/2021	8.3	0.778	23.94					
EC3	8/9/2021	8.64	0.798	24.87					

eqn for hardness: (ppm Ca x 2.5) + (ppm Mg x 4.1) = hardness

Table of % Exceedances								
	C	u		Zn				
	Acute	Chronic	Acute	Chronic				
EC2 7/2/21	151.4%	201.4%						
EC3 7/2/21	259.7%	345.4%	101.1%	101.1%				
EC2 8/9/21	195.4%	259.8%	152.1%	152.1%				
EC3 8/9/21	222.9%	296.5%	149.6%	149.6%				

Since hardness for all samples was <25 mg/L. the values for aquatic standards were taken directly from MTDEQ-7

# 9. Appendix B: Raw ICP-MS Results

		Lab ID	2022W0507	2022W0508	2022W0509	2022W0510	2022W0511	2022W0512
		Field	ECI	EC2	EC3	EC1	EC2	EC3
Apolyt	Conc	ID Dilutio	//2/21	//2/21	//2/21	8/9/21	8/9/921	8/9/21
e		n	1	1	1	1	1	1
7Li	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
9Be	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
11B	µg/L	0.2	0.415	< 0.2	0.402	< 0.2	0.442	0.455
27AI	µg/L	0.5	5.11	18.2	20.7	2.70	17.9	17.9
31P	µg/L	5	< 5	< 5	< 5	< 5	< 5	< 5
31P	mg/L	0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
39K	µg/L	5	25.7	27.9	29.9	33.1	40.1	41.3
39K	mg/L	0.005	0.0257	0.0279	0.0299	0.0331	0.0401	0.0413
43Ca	µg/L	5	1860					
43Ca	mg/L	0.005	1.86					
49Ti	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
51V	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
52Cr	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
55Mn	µg/L	2	< 2	14.2	16.5	< 2	20.1	22.2
55Mn	mg/L	0.002	< 0.002	0.0142	0.0165	< 0.002	0.0201	0.0222
56Fe	µg/L	5	< 5	< 5	10.9	< 5	13.0	24.6
56Fe	mg/L	0.005	< 0.005	< 0.005	0.0109	< 0.005	0.0130	0.0246
59Co	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
60Ni	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
63Cu	µg/L	1	< 1	5.74	9.84	< 1	7.40	8.45
66Zn	µg/L	1	< 1	30.7	37.4	< 1	56.3	55.3
71Ga	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
75As	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
82Se	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
85Rb	µg/L	0.5	0.612	0.704	0.727	0.806	1.00	0.989
88Sr	µg/L	1	25.8	38.7	40.0	41.2	68.2	70.0
90Zr	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
93Nb	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
98Mo	µg/L	0.5	2.76	2.96	2.85	4.28	4.38	4.68
105Pd	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
107Ag	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
111Cd	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.230	0.218

#### Table XIII: ICP-MS lab results for surface water sites

118Sn	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
121Sb	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
133Cs	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
137Ba	µg/L	1	8.04	8.52	8.75	10.2	11.4	11.3
139La	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
140Ce	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
141Pr	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
146Nd	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
182W	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
205TI	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
207Pb	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
208Pb	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
232Th	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
238U	µg/L	0.2	0.641	0.677	0.676	0.83	0.822	0.82

		Lab ID	2022W0513	2022W0514	2022W0515	2022W0516
		Field ID	Elkhorn Discharge	Elkhorn Creek above mine	Mill Seep	Elkhorn Creek below Meadow
	Field	SC	218	37	300	47
Analyte	Conc	Dilution	1	1	1 / 10	1
7Li	µg/L	0.5	3.37	< 0.5	24.7	< 0.5
9Be	µg/L	0.2	< 0.2	< 0.2	1.01	< 0.2
11B	µg/L	0.2	1.03	1.16	5.96	1.37
27AI	µg/L	0.5	73.0	6.50	2080	21.6
31P	µg/L	5	< 5	< 5	< 5	< 5
31P	mg/L	0.005	< 0.005	< 0.005	< 0.005	< 0.005
39K	µg/L	5	123	32.0	287	39.0
39K	mg/L	0.005	0.123	0.0320	0.287	0.0390
43Ca	µg/L	5			14500	
43Ca	mg/L	0.005	12.3	2.39	14.5	3.07
49Ti	µg/L	0.5	0.785	< 0.5	1.21	< 0.5
51V	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5
52Cr	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2
55Mn	µg/L	2	1550	< 2	1100	21.6
55Mn	mg/L	0.002	1.55	< 0.002	1.10	0.0216
56Fe	µg/L	5	379	< 5	77.8	56.6
56Fe	mg/L	0.005	0.379	< 0.005	0.0778	0.0566
59Co	µg/L	0.5	2.02	< 0.5	3.39	< 0.5
60Ni	µg/L	0.5	< 0.5	< 0.5	3.31	< 0.5
63Cu	µg/L	1	56.2	< 1	2340	9.13
66Zn	µg/L	1	1323	1.57	2950	45.8
71Ga	µg/L	0.5	< 0.5	< 0.5	1.64	0.530
75As	µg/L	0.2	5.84	< 0.2	0.466	< 0.2
82Se	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2
85Rb	µg/L	0.5	3.22	0.766	10.5	0.933
88Sr	µg/L	1	456	34.8	276	55.4
90Zr	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5
93Nb	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5
98Mo	µg/L	0.5	10.7	3.97	< 0.5	3.91
105Pd	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5
107Ag	µg/L	0.2	< 0.2	1.40	0.790	1.13
111Cd	µg/L	0.2	6.12	< 0.2	19.0	< 0.2
118Sn	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5
121Sb	µg/L	0.2	0.337	< 0.2	0.654	< 0.2
133Cs	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5

## Table XIV: ICP-MS for additional sample run

137Ba	µg/L	1	7.83	10.3	37.5	11.2
139La	µg/L	0.2	1.18	< 0.2	15.1	< 0.2
140Ce	µg/L	0.2	2.14	< 0.2	13.7	< 0.2
141Pr	µg/L	0.2	0.242	< 0.2	2.33	< 0.2
146Nd	µg/L	0.2	0.979	< 0.2	7.89	< 0.2
182W	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2
205TI	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	0.2	1.79	< 0.2	128	< 0.2
207Pb	µg/L	0.2	1.93	< 0.2	137	< 0.2
208Pb	µg/L	0.2	1.90	< 0.2	136	< 0.2
232Th	µg/L	0.2	< 0.2	< 0.2	0.212	0.213
238U	µg/L	0.2	1.17	0.823	12.1	0.786

		Lab ID	2022W0517	2022W0518	2022W0519	2022W0520	2022W0521
		Field ID	Elk 3	Elk 6	Elk 8	Elk 11	Elk 12
	Field	SC		291	335	331	178
Analyte	Conc.	Dilution	1 / 10	1 / 10	1 / 10	1 / 10	1 / 10
7Li	µg/L	0.5	< 0.5	< 0.5	4.03	28.8	< 0.5
9Be	µg/L	0.2	< 0.2	< 0.2	< 0.2	1.10	< 0.2
11B	µg/L	0.2	123	10.8	14.9	9.03	17.3
27AI	µg/L	0.5	7.20	70.1	3.79	705	14.8
31P	µg/L	5	29.8	84.8	< 5	< 5	5.67
31P	mg/L	0.005	0.0298	0.0848	< 0.005	< 0.005	0.00567
39K	µg/L	5	1386	302	619	578	120
39K	mg/L	0.005	1.39	0.302	0.619	0.578	0.120
43Ca	µg/L	5	15260	12100	16200	16100	16200
43Ca	mg/L	0.005	15.3	12.1	16.2	16.1	16.2
49Ti	µg/L	0.5	1.34	3.86	1.09	1.49	0.690
51V	µg/L	0.5	0.767	3.95	0.868	1.12	0.508
52Cr	µg/L	0.2	0.517	0.549	< 0.2	< 0.2	< 0.2
55Mn	µg/L	2	732	1862	1800	1410	804
55Mn	mg/L	0.002	0.732	1.86	1.80	1.41	0.804
56Fe	µg/L	5	< 5	35000	6520	2120	4320
56Fe	mg/L	0.005	< 0.005	35.0	6.52	2.12	4.32
59Co	µg/L	0.5	< 0.5	2.37	< 0.5	4.44	< 0.5
60Ni	µg/L	0.5	0.554	1.52	< 0.5	8.92	< 0.5
63Cu	µg/L	1	14.7	18.1	< 1	2078	2.64
66Zn	µg/L	1	46.8	28.4	7.06	5457	18.0
71Ga	µg/L	0.5	7.99	5.95	5.38	2.98	36.3
75As	µg/L	0.2	1.25	45.5	129	3.48	28.0
82Se	µg/L	0.2	< 0.2	0.440	< 0.2	< 0.2	< 0.2
85Rb	µg/L	0.5	6.54	4.29	5.58	7.90	4.66
88Sr	µg/L	1	1143	524	932	728	680
90Zr	µg/L	0.5	1.47	2.48	1.06	0.627	0.707
93Nb	µg/L	0.5	1.30	0.547	< 0.5	< 0.5	< 0.5
98Mo	µg/L	0.5	8.02	27.7	105	2.93	19.7
105Pd	µg/L	0.5	1.20	< 0.5	0.609	0.551	< 0.5
107Ag	µg/L	0.2	< 0.2	0.852	0.709	0.719	0.738
111Cd	µg/L	0.2	< 0.2	< 0.2	< 0.2	42.4	< 0.2
118Sn	µg/L	0.5	< 0.5	0.502	< 0.5	< 0.5	< 0.5
121Sb	µg/L	0.2	2.84	6.62	7.25	0.787	1.82
133Cs	µg/L	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
137Ba	µg/L	1	193	144	136	70.5	547

Table XV: ICP-MS lab results for groundwater wells

139La	µg/L	0.2	< 0.2	1.27	< 0.2	1.62	< 0.2
140Ce	µg/L	0.2	< 0.2	1.80	0.270	1.75	< 0.2
141Pr	µg/L	0.2	< 0.2	0.307	< 0.2	< 0.2	< 0.2
146Nd	µg/L	0.2	< 0.2	1.30	< 0.2	0.655	0.230
182W	µg/L	0.2	0.283	0.350	1.06	< 0.2	0.349
205TI	µg/L	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	0.2	< 0.2	8.50	0.251	5.39	0.460
207Pb	µg/L	0.2	< 0.2	8.89	0.274	5.82	0.493
208Pb	µg/L	0.2	< 0.2	8.92	0.267	5.70	0.489
232Th	µg/L	0.2	< 0.2	0.449	0.292	< 0.2	< 0.2
238U	µg/L	0.2	0.545	1.83	2.53	0.899	6.06

	Lab ID	2022W0555	2022W0556	2022W0557	2022W0558	2022W0559
	Field ID	1-0	1-14	1-16	1-18	1-20
		1	1	1 / 10	1 / 10	1 / 10
7Li	µg/L	< 0.5	19.9	13.0	11.3	8.60
9Be	µg/L	< 0.2	0.337	< 0.2	< 0.2	< 0.2
11B	µg/L	4.08	6.88	5.27	4.96	4.49
27AI	µg/L	< 0.5	147	49.2	38.1	69.5
31P	µg/L	< 5	< 5	< 5	< 5	< 5
31P	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
39K	µg/L	< 5	226	165	146	132
39K	mg/L	< 0.005	0.226	0.165	0.146	0.132
43Ca	µg/L	6.86		7910	6060	4430
43Ca	mg/L	0.00686	8.19	7.91	6.06	4.43
49Ti	µg/L	< 0.5	0.899	0.680	0.529	0.525
51V	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
52Cr	µg/L	4.23	< 0.2	< 0.2	< 0.2	< 0.2
55Mn	µg/L	< 2		866	725	600
55Mn	mg/L	< 0.002	1.15	0.866	0.725	0.600
56Fe	µg/L	3.64	39.0	13.3	78.8	1274
56Fe	mg/L	0.00364	0.0390	0.0133	0.0788	1.27
59Co	µg/L	< 0.5	6.92	5.14	2.51	0.698
60Ni	µg/L	< 0.5	5.80	3.84	1.61	< 0.5
63Cu	µg/L	1.47		225	16.8	4.35
66Zn	µg/L	2.39		3800	1875	221
71Ga	µg/L	< 0.5	1.32	1.27	1.02	0.594
75As	µg/L	< 0.2	1.02	0.846	1.22	3.02
82Se	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
85Rb	µg/L	< 0.5	2.04	1.34	0.916	0.857
88Sr	µg/L	< 1	196	161	128	103
90Zr	µg/L	< 0.5	0.602	< 0.5	< 0.5	< 0.5
93Nb	µg/L	< 0.5	0.514	< 0.5	< 0.5	< 0.5
98Mo	µg/L	< 0.5	6.99	10.6	13.1	12.8
105Pd	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
107Ag	µg/L	0.558	0.835	0.646	0.497	0.477
111Cd	µg/L	< 0.2	49.4	27.9	10.7	0.461
118Sn	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
121Sb	µg/L	< 0.2	8.27	7.37	7.95	1.11
133Cs	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
137Ba	µg/L	< 1	29.2	28.4	22.6	13.2
139La	µg/L	< 0.2	0.460	< 0.2	< 0.2	< 0.2

Table XVI: ICP-MS lab results for peeper samples

140Ce	µg/L	< 0.2	0.433	< 0.2	< 0.2	< 0.2
141Pr	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
146Nd	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
182W	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
205TI	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	< 0.2	47.8	10.0	3.80	1.63
207Pb	µg/L	0.204	51.4	10.7	4.08	1.71
208Pb	µg/L	0.205	50.9	10.7	4.01	1.69
232Th	µg/L	< 0.2	0.452	< 0.2	< 0.2	< 0.2
238U	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	0.227

		2022W0560	2022W0561	2022W0562	2022W0563	2022W0564
	Lab ID	1-22	1-24	1-26	1-28	2-8
	Field ID	1 / 10	1 / 10	1 / 10	1 / 10	1 / 10
7Li	µg/L	5.98	5.01	3.76	2.46	73.2
9Be	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	1.92
11B	µg/L	4.28	4.17	4.19	4.23	20.2
27AI	µg/L	57.2	72.0	49.6	38.5	2497
31P	µg/L	6.04	12.0	5.78	< 5	< 5
31P	mg/L	0.00604	0.0120	0.00578	< 0.005	< 0.005
39K	µg/L	113	103	87.1	59.8	1250
39K	mg/L	0.113	0.103	0.087	0.060	1.25
43Ca	µg/L	3420	2120	1630	1160	20100
43Ca	mg/L	3.42	2.12	1.63	1.16	20.1
49Ti	µg/L	0.632	0.772	0.577	0.348	3.17
51V	µg/L	< 0.5	0.575	0.579	< 0.5	< 0.5
52Cr	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	0.703
55Mn	µg/L	489	530	377	241	5950
55Mn	mg/L	0.489	0.530	0.377	0.241	5.95
56Fe	µg/L	1805	3190	2069	538	666
56Fe	mg/L	1.80	3.19	2.07	0.538	0.666
59Co	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	17.8
60Ni	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	19.2
63Cu	µg/L	4.30	5.00	3.81	3.80	11019
66Zn	µg/L	31.6	13.9	5.72	146	25475
71Ga	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
75As	µg/L	2.19	1.58	1.59	2.54	6.07
82Se	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	0.593
85Rb	µg/L	0.671	0.593	0.482	< 0.5	22.2
88Sr	µg/L	74.2	66.0	53.1	33.6	531
90Zr	µg/L	0.545	0.708	0.651	< 0.5	0.789

93Nb	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
98Mo	µg/L	14.0	15.6	10.9	8.43	< 0.5
105Pd	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	0.812
107Ag	µg/L	0.498	0.452	0.495	0.426	0.286
111Cd	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	168
118Sn	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
121Sb	µg/L	0.578	0.413	0.463	0.207	5.29
133Cs	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
137Ba	µg/L	10.0	9.18	8.15	5.39	3.48
139La	µg/L	< 0.2	0.247	< 0.2	< 0.2	18.1
140Ce	µg/L	0.239	0.353	0.250	< 0.2	17.9
141Pr	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	2.77
146Nd	µg/L	< 0.2	0.206	< 0.2	< 0.2	9.62
182W	µg/L	0.203	0.311	< 0.2	< 0.2	< 0.2
205TI	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	2.41	2.10	1.31	1.44	1291
207Pb	µg/L	2.60	2.23	1.42	1.51	1341
208Pb	µg/L	2.56	2.24	1.40	1.52	1346
232Th	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
238U	µg/L	0.295	0.427	0.289	0.210	12.8

		2022W0565	2022W0566	2022W0567	2022W0568	2022W0569
	Lab ID	2-10	2-12	2-14	2-16	2-18
	Field ID	1 / 10	1	1 / 10	1 / 10	1 / 10
7Li	µg/L	35.2	11.0	3.51	3.38	3.65
9Be	µg/L	0.970	0.570	< 0.2	< 0.2	< 0.2
11B	µg/L	9.81	5.26	3.95	3.86	3.59
27AI	µg/L	1018	331	19.1	21.6	14.9
31P	µg/L	< 5	< 5	< 5	< 5	< 5
31P	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
39K	µg/L	466	178	121	105	119
39K	mg/L	0.466	0.178	0.121	0.105	0.119
43Ca	µg/L	10900		4590	3350	3870
43Ca	mg/L	10.9	7.88	4.59	3.35	3.87
49Ti	µg/L	1.52	0.790	0.621	0.602	0.574
51V	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
52Cr	µg/L	< 0.2	< 0.2	< 0.2	0.323	< 0.2
55Mn	µg/L	2850		505	389	460
55Mn	mg/L	2.85	0.893	0.505	0.389	0.460
56Fe	µg/L	154	152	8798	7420	8992
56Fe	mg/L	0.154	0.152	8.80	7.42	8.99

59Co	µg/L	9.86	4.40	< 0.5	< 0.5	< 0.5
60Ni	µg/L	11.3	5.83	< 0.5	< 0.5	< 0.5
63Cu	µg/L	4167		1.07	2.89	1.03
66Zn	µg/L	16975		28.4	10.8	7.07
71Ga	µg/L	< 0.5	< 0.5	0.972	0.800	0.915
75As	µg/L	2.49	4.79	3.38	2.37	3.10
82Se	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
85Rb	µg/L	7.54	3.04	2.19	1.87	2.15
88Sr	µg/L	216	138	88.1	68.9	83.8
90Zr	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
93Nb	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
98Mo	µg/L	< 0.5	< 0.5	0.884	0.730	1.10
105Pd	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
107Ag	µg/L	0.298	0.751	0.826	0.704	0.557
111Cd	µg/L	92.2	24.8	< 0.2	< 0.2	< 0.2
118Sn	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
121Sb	µg/L	2.87	0.827	0.434	0.461	0.376
133Cs	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
137Ba	µg/L	3.01	10.1	21.9	17.8	20.5
139La	µg/L	9.03	3.25	0.227	0.340	< 0.2
140Ce	µg/L	8.72	3.09	0.263	0.420	0.233
141Pr	µg/L	1.32	0.439	< 0.2	< 0.2	< 0.2
146Nd	µg/L	4.46	1.48	< 0.2	0.300	< 0.2
182W	µg/L	< 0.2	< 0.2	0.233	0.410	0.279
205TI	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	2315		1.73	2.29	1.25
207Pb	µg/L	2460		1.88	2.46	1.31
208Pb	µg/L	2441		1.83	2.67	1.30
232Th	µg/L	< 0.2	0.344	0.384	< 0.2	< 0.2
238U	µg/L	5.18	2.29	0.445	0.774	0.462

		2022W0570	2022W0571	2022W0572	2022W0573	2022W0574
	Lab ID	2-20	2-22	2-24	2-26	2-28
	Field ID	1 / 10	1 / 10	1 / 10	1 / 10	1 / 10
7Li	µg/L	3.76	3.66	3.83	3.70	3.68
9Be	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
11B	µg/L	3.15	3.10	3.64	3.71	3.72
27AI	µg/L	11.8	14.7	16.0	21.5	20.0
31P	µg/L	< 5	< 5	< 5	5.75	5.88
31P	mg/L	< 0.005	< 0.005	< 0.005	0.00575	0.00588
39K	µg/L	123	116	111	106	108

39K	mg/L	0.123	0.116	0.111	0.106	0.108
43Ca	µg/L	4140	4460	3980	3760	4420
43Ca	mg/L	4.14	4.46	3.98	3.76	4.42
49Ti	µg/L	0.557	0.561	< 0.5	0.511	< 0.5
51V	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
52Cr	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
55Mn	µg/L	477	527	522	509	567
55Mn	mg/L	0.477	0.527	0.522	0.509	0.567
56Fe	µg/L	9357	8650	6497	6353	8786
56Fe	mg/L	9.36	8.65	6.50	6.35	8.79
59Co	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
60Ni	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
63Cu	µg/L	0.814	1.15	1.44	1.34	1.52
66Zn	µg/L	5.77	2.29	4.77	1.09	2.26
71Ga	µg/L	0.821	0.832	0.865	0.882	1.01
75As	µg/L	2.70	2.19	2.54	1.52	1.70
82Se	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
85Rb	µg/L	2.04	1.73	1.44	1.30	1.31
88Sr	µg/L	86.6	91.2	89.0	86.0	89.9
90Zr	µg/L	< 0.5	< 0.5	< 0.5	0.530	< 0.5
93Nb	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
98Mo	µg/L	1.27	1.46	1.25	1.39	1.49
105Pd	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
107Ag	µg/L	0.451	0.414	0.36299993	0.720	0.489
111Cd	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
118Sn	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
121Sb	µg/L	0.449	0.272	0.270	0.532	0.379
133Cs	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
137Ba	µg/L	19.1	18.5	19.2	19.6	22.3
139La	µg/L	< 0.2	< 0.2	< 0.2	0.248	0.212
140Ce	µg/L	< 0.2	< 0.2	< 0.2	0.281	0.228
141Pr	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
146Nd	µg/L	< 0.2	< 0.2	< 0.2	0.211	< 0.2
182W	µg/L	< 0.2	< 0.2	< 0.2	0.296	0.335
205TI	µg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
206Pb	µg/L	0.774	1.43	1.52	1.55	1.61
207Pb	µg/L	0.814	1.51	1.64	1.63	1.77
208Pb	µg/L	0.817	1.52	1.63	1.65	1.73
232Th	µg/L	< 0.2	< 0.2	< 0.2	0.462	0.210
238U	µg/L	0.415	0.434	0.486	0.622	0.615

		2022W0575	2022W0576
	Lab ID	SW-1	SW-2
	Field ID	1 / 10	1 / 10
7Li	µg/L	9.99	10.6
9Be	µg/L	0.203	0.243
11B	µg/L	4.11	5.10
27Al	µg/L	43.0	336
31P	µg/L	< 5	< 5
31P	mg/L	< 0.005	< 0.005
39K	µg/L	127	179
39K	mg/L	0.127	0.179
43Ca	µg/L	4860	7050
43Ca	mg/L	4.86	7.05
49Ti	µg/L	< 0.5	0.671
51V	µg/L	< 0.5	< 0.5
52Cr	µg/L	< 0.2	< 0.2
55Mn	µg/L	474	679
55Mn	mg/L	0.474	0.679
56Fe	µg/L	48.7	69.1
56Fe	mg/L	0.0487	0.0691
59Co	µg/L	0.891	1.63
60Ni	µg/L	1.03	1.70
63Cu	µg/L	210	591
66Zn	µg/L	805	2212
71Ga	µg/L	0.551	1.20
75As	µg/L	0.770	0.640
82Se	µg/L	< 0.2	< 0.2
85Rb	µg/L	1.62	3.21
88Sr	µg/L	102	132
90Zr	µg/L	< 0.5	< 0.5
93Nb	µg/L	< 0.5	< 0.5
98Mo	µg/L	5.70	0.586
105Pd	µg/L	< 0.5	< 0.5
107Ag	µg/L	0.344	0.319
111Cd	µg/L	7.57	14.9
118Sn	µg/L	< 0.5	< 0.5
121Sb	µg/L	1.06	0.542
133Cs	µg/L	< 0.5	< 0.5
137Ba	µg/L	12.0	26.8
139La	µg/L	< 0.2	2.43
140Ce	µg/L	< 0.2	2.18

141Pr	µg/L	< 0.2	0.357
146Nd	µg/L	< 0.2	1.22
182W	µg/L	< 0.2	< 0.2
205TI	µg/L	< 0.2	< 0.2
206Pb	µg/L	1.64	55.9
207Pb	µg/L	1.75	60.0
208Pb	µg/L	1.71	58.4
232Th	µg/L	< 0.2	< 0.2
238U	µg/L	< 0.2	1.32

# 10. Appendix C: Raw ICP-OES Lab Results

	Sample	2022W0507	2022W0508	2022W0509	2022W0510	2022W0511	2022W0512
	Field ID	EC1 7/2/21	EC2 7/2/21	EC3 7/2/21	EC1 8/9/21	EC2 8/9/21	EC3 8/9/21
Conc.	Analyte						
mg/L	AI	<0.0129	0.0218	0.0243	<0.0129	0.0208	0.0199
mg/L	As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
mg/L	В	<0.0101	<0.0101	<0.0101	<0.0101	<0.0101	<0.0101
mg/L	Ва	<0.0108	<0.0108	<0.0108	0.0118	0.0131	0.0133
mg/L	Ве	<0.0082	<0.0082	<0.0082	<0.0082	<0.0082	<0.0082
mg/L	Ca	4.36	5.38	5.52	6.44	8.3	8.64
mg/L	Cd	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066
mg/L	Со	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062
mg/L	Cr	<0.0157	<0.0157	<0.0157	<0.0157	<0.0157	<0.0157
mg/L	Cu						
mg/L	Fe						
mg/L	К	0.295	0.345	0.342	0.408	0.491	0.497
mg/L	Li	<0.0333	<0.0333	<0.0333	<0.0333	<0.0333	<0.0333
mg/L	Mg	0.394	0.478	0.502	0.584	0.778	0.798
mg/L	Mn						
mg/L	Мо	<0.0073	<0.0073	<0.0073	<0.0073	<0.0073	<0.0073
mg/L	Na	1.3	1.57	1.46	1.79	2.24	2.18
mg/L	Ni	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009
mg/L	Р	<0.0171	<0.0171	<0.0171	<0.0171	<0.0171	<0.0171
mg/L	Pb	<0.0124	<0.0124	<0.0124	<0.0124	<0.0124	<0.0124
mg/L	Sb	<0.0141	<0.0141	<0.0141	<0.0141	<0.0141	<0.0141
mg/L	Se	<0.0223	<0.0223	<0.0223	<0.0223	<0.0223	<0.0223
mg/L	Si	2.66	2.96	3.03	3.23	3.91	3.99
mg/L	Sr	0.029	0.0426	0.0442	0.0442	0.0733	0.077
mg/L	Ti	<0.0097	<0.0097	<0.0097	<0.0097	<0.0097	<0.0097
mg/L	TI	<0.0234	<0.0234	<0.0234	<0.0234	<0.0234	<0.0234
mg/L	v	<0.0121	<0.0121	<0.0121	<0.0121	<0.0121	<0.0121
mg/L	Zn						

## Table XVII: ICP-OES lab results

# 11. Appendix D: Raw IC Lab Results

		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Sample	Field ID	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
2022W0510	EC1 8/9/21	0.104	0.375	<0.01	<0.01	0.0610	0.0510	3.30
2022W0511	EC2 8/9/21	0.123	0.397	<0.01	<0.01	0.0590	0.0290	10.6
2022W0512	EC3 8/9/21	0.127	0.394	<0.01	<0.01	<0.01	<0.02	11.2
2022W0513	Elkhorn Discharge							88.9
2022W0514	Elkhorn Creek Above							2.45
2022W0515	Mill Seep							184
2022W0516	Elkhorn Creek below meadow							8.31
2022W0517	Elk3							123
2022W0518	Elk6							1.82
2022W0519	Elk8							71.2
2022W0521	Elk12							2.90
NOTE: Nitrite and Nitrate are reported as N. Phosphate is reported as P.								

## Table XVIII: IC lab results

## 12. Appendix E: Hydrogen Sulfide, Sulfate, and Alkalinity Results

H <sub>2</sub> S Results							
	Mass Sample*			H2S corrected	Depth from SWL		
Sample #	(g)	Dilution	H <sub>2</sub> S (mg/L)	(mg/L)	(cm)		
1-15	6.2	4.226	0.000	0.000	-3		
1-19	6.4	4.125	0.000	0.000	-7		
1-23	6.3	4.175	0.060	0.250	-11		
1-27	6.3	4.175	0.106	0.443	-15		
2-7	1.5	14.333	0.000	0.000	1		
2-11	6	4.333	0.000	0.000	-3		
2-15	5.9	4.390	0.019	0.083	-7		
2-19	5.9	4.390	0.032	0.140	-11		
2-23	6.5	4.077	0.027	0.110	-15		
2-27	6	4.333	0.020	0.087	-19		
*Mass sample - after field weight - pro field weight							

Table XIX:	H <sub>2</sub> S results for	both peepers

\*Mass sample = after field weight - pre field weight

#### Table XX: Sulfate results for both peepers

IC-Sulfates							
				Sulfate corr.	depth below SWL		
Sample #	Mass Sample* (g)	Dilution	Sulfate (mg/L)	(mg/L)	(cm)		
1-13	3.8	6.263	56.3	352.616	-1		
1-15	3.8	6.263	40.4	253.032	-3		
1-17	4.1	5.878	34.8	204.556	-5		
1-19	3.5	6.714	35.4	237.686	-7		
1-21	3.2	7.250	11.5	83.375	-9		
1-23	3.5	6.714	10.7	71.843	-11		
1-25	2.9	7.897	6.52	51.486	-13		
1-27	1.5	14.333	3.85	55.183	-15		
2-9	3.9	6.128	244	1495.282	-1		
2-13	3.6	6.556	56	367.111	-5		
2-17	3.7	6.405	33.2	212.659	-9		
2-21	3.7	6.405	37.9	242.765	-13		
2-25	3.6	6.556	38.4	251.733	-17		
*Mass sample = after field weight - pre field weight							

Alkalinities							
Peeper 2				Corrected alkalinity	Depth from SWL		
Cell Row	mass sample (g)	alk	blank	(mg/L CaCO3)	(cm)		
9	3.9	0.5	1.8	b.d.	-1		
11	4.1	0.7	1.8	b.d.	-3		
13	3.9	0.7	1.8	b.d.	-5		
15	2.3	1.5	1.8	b.d.	-7		
17	4	1.8	1.8	b.d.	-9		
19	3.7	1.4	1.8	b.d.	-11		
21	3.5	2.1	1.8	8.6	-13		
23	3.78	2.1	1.8	7.9	-15		
25	3.8	2	1.8	5.3	-17		
27	2.7	2.3	1.8	18.5	-19		
Peeper 1							
Cell Row							
13	4	1.1	1.8	b.d.			
17	4.3	0.9	1.8	b.d.			
21	no sample						
25	3.7	4.3	1.8	67.6			
Note: detection lim	nit is roughly 5 mg/L						

## Table XXI: Alkalinity results for both peepers
## 13. Appendix F: Weather Data



Figure 32: Chart of monthly precipitation totals for the study year



Figure 33: Chart of monthly average high and low temperatures for the study year



Figure 34: Daily precipitation increments for the study year



Figure 35: Snow water equivalent (snow pack) for the study year