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GEOCHEMISTRY OF METALS AND NUTRIENTS IN FINE-SEDIMENT PORE WATER IN BLACKTAIL AND SILVER BOW CREEKS, BUTTE, MONTANA

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by

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Abstract

Historical mining in Butte, Montana has impacted surface and groundwater in the area. Although most of the known sources of contaminants of concern have been removed or remediated, metal loading continues to occur in lower Blacktail Creek and upper Silver Bow Creek. Possible sources of metals include upwelling groundwater and interaction between the stream and metal-rich sediment in the stream bed. To assess the importance of fine sediment as a source (or sink) for metals, this investigation used sediment pore water diffusion samplers ("peepers"). Peepers are ideal for capturing cm-scale vertical gradients in pore water chemistry across the sediment-water interface. Eight peepers were deployed in Blacktail Creek, six in Silver Bow Creek, one in Grove Gulch, and two in shallow ponds south of lower Blacktail Creek. Four piezometers were also installed in the ponds. Pore-water samples extracted from the peepers and piezometers were analyzed for dissolved trace metals, major ions, alkalinity, and selected nutrients. Sediment samples collected at some peeper sites were analyzed by X-ray diffraction and handheld X-ray fluorescence. Dissolved Fe, Mn, As, PO_4^{3-}, and HCO_3^- ions generally increased with depth below the sediment-water interface. Pore-water concentrations of up to 609 mg/L Fe, 55 mg/L Mn, and 1.0 mg/L As were measured at depth. These increases in concentration were attributed to reductive dissolution of Fe- and Mn-oxides, coupled to organic matter decay, in the anoxic environment of the fine-grained sediment. Dissolved Fe^{2+} could then reprecipitate as Fe-oxides once it reached an aerobic environment and potentially reabsorb dissolved As. PO_4^{3-} and HCO_3^- concentrations could also be influenced by sulfate reducing bacteria and oxidation of organic matter. Copper, lead, and zinc behaved differently, and generally had very low concentrations in the deeper samples. Bacterial sulfate reduction was indicated by trace levels of H_2S, enough to precipitate Cu, Pb and Zn as sulfide minerals. In some cases, there was a zone where dissolved Cu and Zn concentrations increased sharply in the top 2–6 cm of the sediment column. This could indicate oxidation of fine-grained sulfide minerals in the near-surface pore water. Fick's first law was used to quantify the diffusive flux of dissolved arsenic from the sediment pore water into Silver Bow and Blacktail Creeks. The same approach was use to estimate downwards diffusion of dissolved Zn from Grove Gulch into its own sediment. The calculated fluxes are negligible for the streams due to the short residence time of water passing through Lower Area One. However, upwards diffusion of As into the shallow ponds could lead to a build-up in dissolved As over time. Although the stream sediments act as a temporary metal sink, the fine sediments are eventually dispersed back into the main stream during periods of high streamflow and bioturbation. Periodic removal of these fine-grained sediments from the stream channels would reduce the total load of metals flowing down Silver Bow Creek.

Keywords: Butte, Silver Bow Creek, Blacktail Creek, geochemistry, metal flux

Dedication

To my parents, for showing me the importance of stories and family.

Acknowledgements

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Table of Contents

List of Tables

List of Figures

Glossary of Terms

Term	Definition
µg/L	Microgram per liter
ALS	Aquatic life standard
As	Arsenic
BCC	Butte Chamber of Commerce
BP-ARCO	British Petroleum Atlantic Richfield Company
BTC	Blacktail Creek
COCs	Contaminants of concern
cfs	Cubic feet per second
Cu	Copper
Eh	Redox potential
EPA	Environmental Protection Agency
Fe	Iron
GG	Grove Gulch
IC	Ion chromatography
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LAO	Lower Area One operable unit
MBMG	Montana Bureau of Mines and Geology
DEQ	Montana Department of Environmental Quality
MTPT	Montana Pole Treatment Plant
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
Mn	Manganese
NRDP	Natural Resource Damage Program
Peeper	Pore water diffusion sampler or dialysis array
ppb	Part per billion
ppm	Part per million
SBC	Silver Bow Creek
SRP	Soluble reactive phosphate
SWI	Sediment-water interface
SRB	Sulfate reducing bacteria
XRD	X-ray diffraction
XRF	X-ray fluorescence
Zn	Zinc

1. Introduction

Metal and nutrient contamination from historical resource extraction can pose a threat to human health and the environment by creating point source and nonpoint source contamination (Moore and Luoma, 1990). In southwest Montana, the city of Butte has been impacted by porphyry-copper mining and related activities that started in the 1860s (Gammons and Madison, 2006). Remediation work has been ongoing for several decades, but metal loading is still occurring in Blacktail and Silver Bow creeks (EPA, 2018). There is controversy on the source and method of metal loading in the creeks. This study characterizes the geochemical gradients across the sediment-water interface of lower Blacktail Creek and upper Silver Bow Creek in Butte, Montana. Pore-water diffusion samplers (commonly referred to as peepers) were used to capture sharp chemical gradients on the cm-scale in the chemistry of the pore water in the fine-grained stream sediment, with the intent to identify the pathway(s) of metal loading. Specific objectives are listed after a site overview and summary of previous work in Butte related to the project.

1.1. Site description

Butte, Montana is in the Summit Valley in Silver Bow County (Fig. 1). The watershed has elevations ranging from 1642 m to 2430 m. There are three main creeks that drain the watershed and they are considered the headwaters of the Clark Fork River (LaFave, 2008). The creeks are: Basin Creek, Blacktail Creek, and upper Silver Bow Creek. Blacktail Creek and Basin Creek flow north from the Highland Mountains (3000 m). Prior to mining, upper Silver Bow Creek drained a substantial area of forested uplands north of Butte and flowed south to join Blacktail Creek in a lowland area now referred to as Lower Area One (LAO). Since the mid-1950s, most of the flow of Upper Silver Bow Creek has been captured by the Yankee Doodle tailings dam, located 2 km north of the Berkeley Pit. Upper Silver Bow Creek below the active mine operation is now a storm-water ditch (formerly known as the Metro Storm Drain) with little or no surface flow overlying a subdrain that conveys contaminated groundwater to Lower Area One for treatment. The present-day Silver Bow Creek begins at the confluence of the ditch/subdrain and Blacktail Creek (Fig. 2a and b).

Figure 1. Location map of the study area. Creeks run from south to northwest.

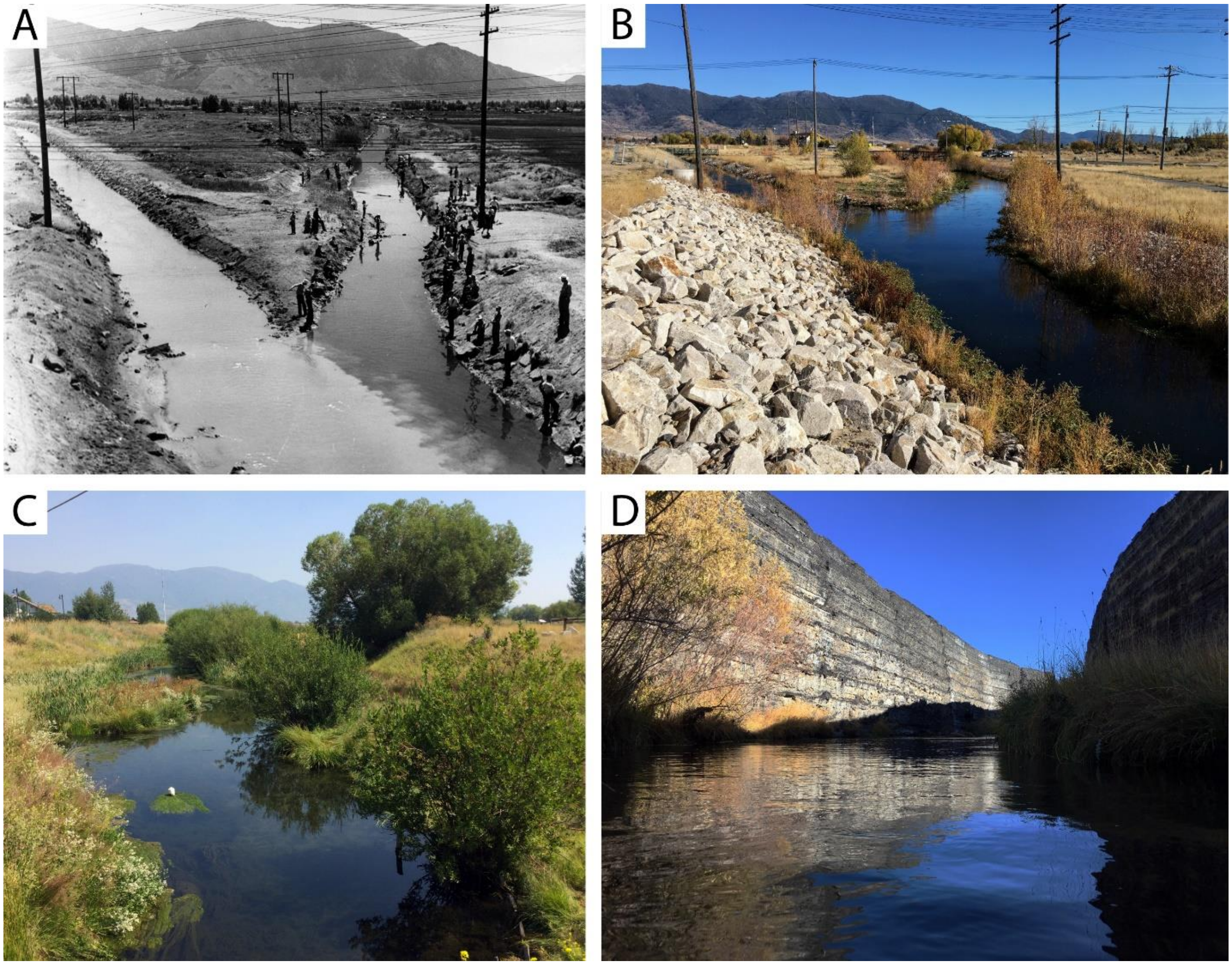


Figure 2. Important locations along Blacktail and Silver Bow Creek. (A) Fishing derby at the confluence of Silver Bow Creek and Blacktail Creek circa 1950s (108.079.07 C. Owen Smithers, Butte-Silver Bow Public Archives). (B) Confluence of Silver Bow Creek and Blacktail Creek currently, 2018. (C) Lower Blacktail Creek near the Butte Chamber of Commerce. (D) Silver Bow Creek in Slag Canyon looking upstream, 2018.

Silver Bow Creek has been ponded and rerouted to accommodate mining activities and processes since the 1860s (Weed, 1904; Gammons and Madison, 2006). As a result, Silver Bow Creek has a history of metal contamination. Mine tailings were intentionally released into Silver Bow Creek until the early 1900s (Moore and Luoma, 1990). This practice eventually led to several flood events that spread tailings over the floodplains of Silver Bow Creek creating a devegetated landscape with metal-rich salts termed slickens (Moore and Luoma, 1990; Nimick and Moore, 1994).

As a result of the metal contamination in Butte, the Silver Bow Creek/Butte Area site is one of four National Priorities List Superfund sites in the upper Clark Fork River basin. Remediation and restoration has been ongoing since the late 1990s (Gammons and Madison, 2006). The contaminants of concern (COCs) are arsenic, cadmium, copper, lead, iron, mercury, and zinc (EPA, 2018).

Lower Blacktail Creek meanders through willows and cottonwoods next to a walking trail (Figs. 2b and c). Downstream from the Butte Chamber of Commerce, Blacktail Creek merges with Upper Silver Bow Creek (formally Metro Storm Drain) to form Silver Bow Creek. Silver Bow Creek then passes beneath Montana Street and enters Slag Canyon. The Slag Canyon contains the remnant slag piles from the early 1900s Butte Reductions Works smelter (Fig. 2d). The slag, as well as residual mill tailings in the LAO area, could be a potential source for metal contamination in Silver Bow Creek (Kaplan, 2016). The bed sediment in the study reach are mostly a mixture of silts and gravels. Lower Blacktail Creek is a gaining stream over the entire reach of interest, whereas, Silver Bow Creek transitions from gaining to losing after it passes through the Slag Canyon. This change in hydrology is due to engineered controls including a groundwater interception channel that borders the north side of LAO.

1.2. Previous work

Over the years there has been increasing interest in the sources of metal loading occurring in Blacktail and Silver Bow creeks (Benner et al., 1995; Balistrieri et al., 2012). Many methods have been employed for data collection (e.g., drive point sampling, ceramic beads, gel diffusion samplers). However, no study has used peepers for understanding the geochemical gradients across the sediment-water interface.

Axtmann and Luoma (1991) identified high metal concentrations in the fine sediment fractions of the Clark Fork River's floodplain and bed-sediment. Benner et al. (1995) found metal accumulation in the hyporheic zone of lower Silver Bow Creek near Miles Crossing, suggesting the hyporheic zone could be both a metal sink and metal source to bed sediment of the creek. Balistrieri et al. (2012) conducted a diel study on Silver Bow Creek in Lower Area One and Miles Crossing using diffusive gradients in thin films. These films recorded changes in dissolved metal concentrations that were used to calculate time-integrated dissolved concentrations for modeling metal toxicity.

Tucci (2014) conducted a bromide tracer test in Blacktail Creek to assess the locations and the amounts of groundwater recharging the creek. The majority of lower Blacktail Creek is gaining groundwater, 2.2 cfs (22 percent of total flow) between Oregon Avenue and George Street. However, according to Tucci's data, there are two short reaches west of Kaw Avenue that are not gaining or have a net loss.

Runkel et al. (2016) conducted diel and synoptic sampling on Blacktail and Silver Bow creeks before and after a storm event. Dissolved metals were dramatically elevated (usually greater than 10-fold) during and slightly after the storm event. A previous study by Gammons et al. (2005) showed very similar results. Runkel et al. (2016) suggested resuspension of sediments from along the stream banks and/or point sources on Butte Hill caused large fluctuations in stream water metal concentrations due to rewetting and mobilization. Highest metal concentrations (Cd, Cu, and Pb) were found in Slag Canyon (Runkel et al., 2016). Slag Canyon does not have any surface inflows, so the source of the increase in metals was from contaminated groundwater, overland flow, or stream-sediment remobilization.

CDM Smith (2016) conducted a synoptic drive-point (30 and 90 cm depth) pore water and sediment sampling of Blacktail and Silver Bow creeks (Fig. 3). This report identified areas (e.g., Slag Canyon and Butte Chamber of Commerce) with elevated pore water and sediment metal contamination (As, Cd, Cu, Fe, and Zn). The north bank in Slag Canyon and the north blank along the reach of Blacktail Creek that passes by the Butte Chamber of Commerce had the highest metal concentrations. Upstream of these reaches, there were sporadic sections of elevated metals that were usually located on the north bank of Blacktail Creek.

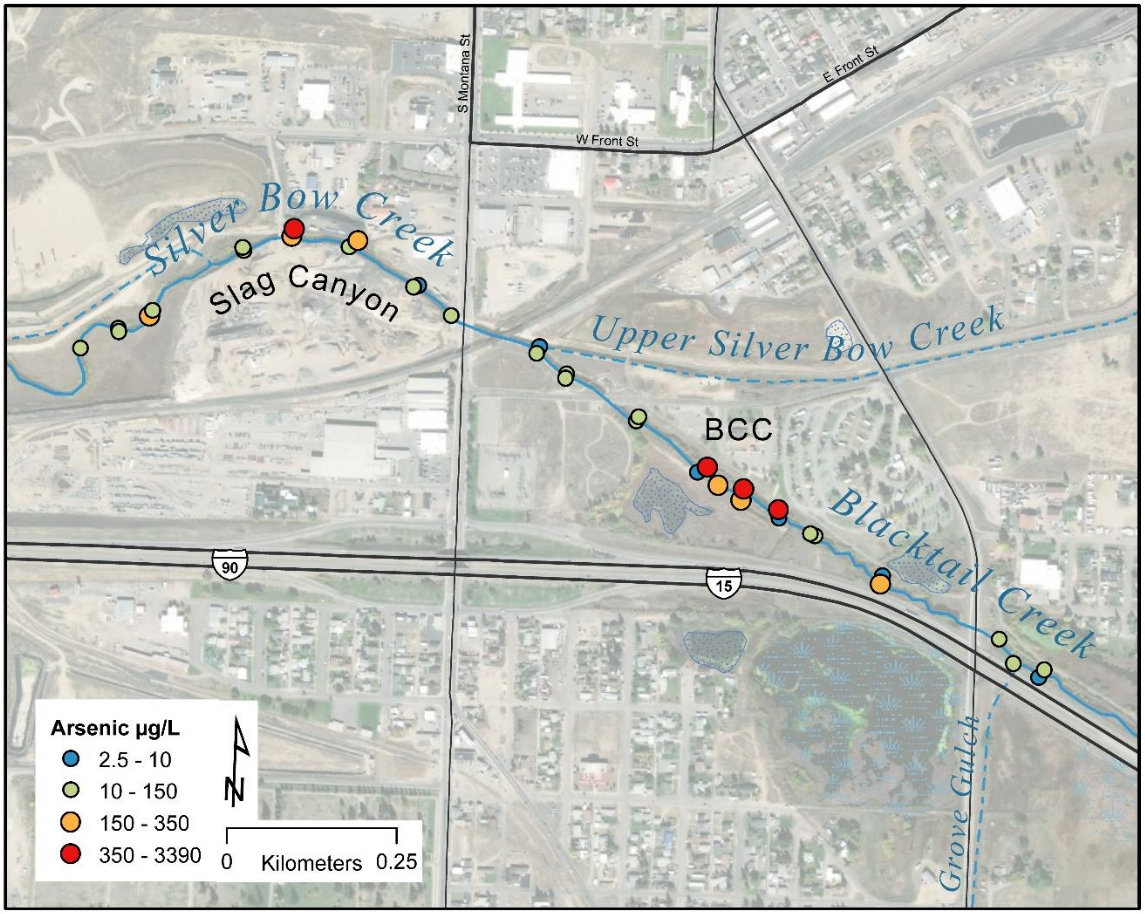


Figure 3. Pore water As concentrations from CDM Smith (2016). 150 ppb is the DEQ-7 Aquatic life standard. Elevated levels of As were identified around Slag Canyon and Butte Chamber of Commerce (BCC).

Tetra Tech (2016) conducted a similar characterization project as CDM Smith but with a focus on sampling the overbank sediment in Blacktail and Silver Bow creeks. The study identified similar areas of sediment and pore water that exceeded the Montana DEQ-7 aquatic standards (e.g., Slag Canyon).

Several studies have identified nutrient loading in Blacktail and Silver Bow creeks (Plumb, 2009; LaFave, 2008; Gammons et al., 2010). Although significant increases in dissolved phosphate and nitrate were shown to occur through the gaining reach of lower Blacktail Creek (Plumb, 2009), the single biggest source of loading was identified as the Butte Silver Bow wastewater treatment plant. Construction was completed in 2016 to upgrade the wastewater treatment plant to reduce the amount of nutrients (especially ammonium) entering Silver Bow Creek.

1.3. Research objectives

The goal of this project is to advance the understanding of metal and nutrient mobility in fine stream-sediment and pore water in a mining impacted area. Due to metal and nutrient loading occurring in Blacktail and Silver Bow creeks, it is important to identify and characterize the source(s). There are several potential sources for metals entering the creeks: contaminated groundwater, contaminated bed sediment, and/or hyporheic water that has become contaminated from interaction with stream sediment. Peepers were used because they provide cm-scale resolution of dissolved metal and nutrient concentrations in a vertical profile across the sediment-water interface. The fine resolution is helpful for 1) capturing subtle chemical shifts that would be lost with single-point sampling, 2) collection of integrated pore water concentrations over a 2–3-week period, and 3) estimating diffusive fluxes of solutes across the sediment-water interface.

Five metals and two anions (As, Cu, Fe, Mn, Zn, PO_4^{3-}, and SO_4^{2-}) are the focus of this study. The stream reach of greatest interest is from the Lexington Street overpass to above the

Montana Pole Treatment effluent. However, additional peeper samplers were deployed at other sites, including two wetland ponds on the south side of Silver Bow Creek, lower Grove Gulch, and Silver Bow Creek near Rocker. Additionally, previously unpublished results from a peeper sampling of sediment in one of the wetland ponds on the north side of Blacktail Creek that was conducted in 2011 are included in this thesis.

2. Materials and methods

2.1. Site selection

Sample sites were selected based on previous work by CDM Smith and Tetra Tech. Locations with high pore-water metal content were prioritized for the initial sampling (Table I). Sites were then selected to fill data gaps along Blacktail and Silver Bow creeks. Because it is almost impossible to install a peeper into gravel, another constraint on site selection was the availability of finer-grained sediment (sand and silt) in the streambed. The lack of suitable deployment sites explains the gap between peepers 11 and 12 (Fig. 4). Grove Gulch and two adjacent ponds were added as additional sampling sites. Grove Gulch (peeper 14) has documented contamination of Zn and other metals from a former zinc mill located near the present-day Copper Mountain recreation center (Lund, 2018). The ponds south of Blacktail Creek (peepers 6 and 7) were selected to compliment an earlier peeper study performed by Montana Tech of a wetland pond to the north of Blacktail Creek (peeper 0). The ponds are of interest because BP-ARCO plans to build more wetlands along the Upper Silver Bow Creek corridor for groundwater and storm-water capture.

2.1. Water characterization

2.1.1. Peepers

Pore and surface water sampling were conducted using dialysis arrays (commonly known as peepers; Hesslein, 1976, Fig. 5a). Peepers sample *in situ* pore water by diffusion of solutes across a membrane (Fig. 5b). Equilibration is relatively quick (e.g., weeks). This sampling method offers cm-scale resolution with depth which was used to interpret vertical trends in pore-water chemistry.

The peepers (clear acrylic, 30 cm in length, 14 10-mL cells and 28 5-mL cells) and nylon filter membranes (5 µm pore size) were purchased from Rickly Hydrological. Peepers were assembled in a cooler filled with deoxygenated deionized water. Water was deoxygenated by bubbling nitrogen gas through it for 0.5–1 hour and then a layer of heavy argon gas was placed on top of the water overnight (12 hours). Deoxygenating the water is an important step to ensure the pore water chemistry is not adversely affected by oxidizing conditions (Carignan, 1984). Peepers in the creeks were deployed in 0.3–1.0 m of water. An inflatable kayak was used for peeper deployment in the shallow ponds (~1.1 m). Peeper deployment was conducted so that two to three rows of cells were above the sediment-water-interface. This was confirmed with an underwater digital camera (GoPro® Hero 5 Session). Equilibrium between the sediment-pore water and the peeper cell was assumed to take two weeks during the summer and three weeks during the winter (Hesslein, 1976). Peepers were deployed in pairs to make prep work and sampling more efficient.

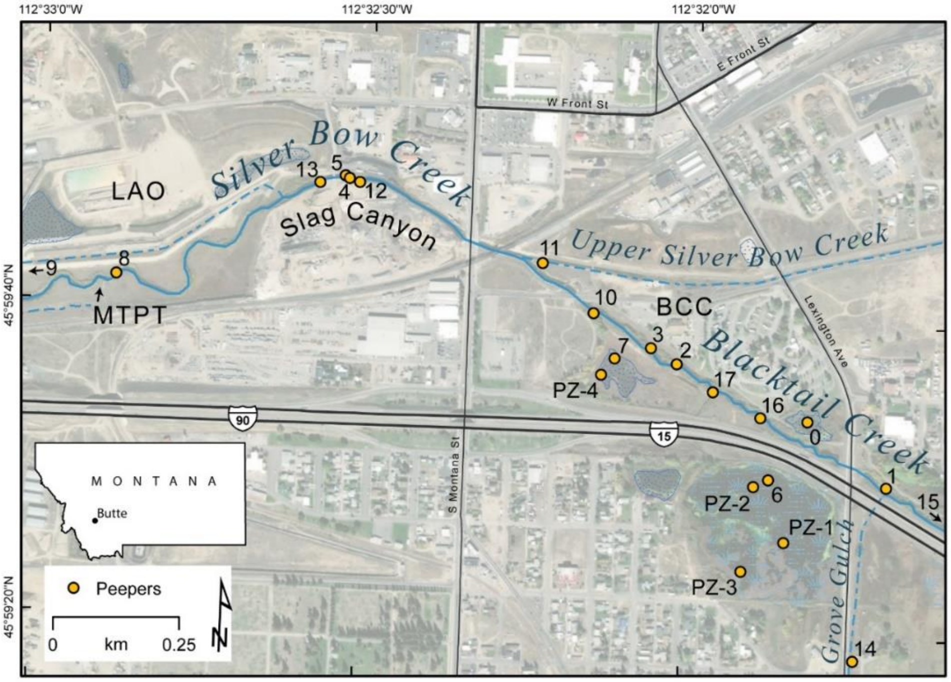


Figure 4. Sample site locations. Butte Chamber of Commerce (BCC), Lower Area One (LAO), Montana Pole Treatment Plant effluent (MTPT). Peepers 9 and 15 were located outside of the core study area.

Table I. Peeper and piezometer locations, deployment dates, and sampling dates. Creek bank side is denoted as right (R), left (L), or middle (M), facing downstream. Butte Chamber of Commerce (BCC), MT Pole Treatment Discharge (MTP), Upper Silver Bow Creek (USBC), piezometers (PZ).

Peeper	Location	Deployed	Sampled	Bank Side	Comments
0	45.992670, -112.530102	2 Feb. 2011	18 April 2011	—	KOA small pond
1	45.991598, -112.528194	26 July 2017	25 Aug. 2017	R	Mouth of Grove Gulch
2	45.993669, -112.533671	21 Jan. 2018	11 Feb. 2018	R	BCC
3	45.993942, -112.534335	21 Jan. 2018	6 March 2018	R	BCC
4	45.996761, -112.542193	29 March 2018	20 April 2018	R	Slag Canyon
5	45.996803, -112.542309	29 March 2018	20 April 2018	R	Slag Canyon
6	45.991807, -112.530976	2 May 2018	24 May 2018	—	North Pond
7	45.993766, -112.535354	2 May 2018	24 May 2018	—	South Pond
8	45.994494, -112.551867	13 July 2018	29 July 2018	R	MTP
9	46.001403, -112.602706	13 July 2018	29 July 2018	R	Santa Claus Bridge
10	45.994505, -112.535841	9 August 2018	5 Sept. 2018	L	BCC
11	45.995400, -112.537215	9 August 2018	5 Sept. 2018	M	USBC
12	45.996705, -112.541932	16 Sept. 2018	6 Oct.2018	L	Slag Canyon
13	45.996671, -112.542936	16 Sept. 2018	6 Oct. 2018	L	Slag Canyon
14	45.987728, -112.529001	21 Oct. 2018	21 Nov. 2018	M	Grove Gulch
15	45.905351, -112.465827	21 Oct. 2018	Frozen in place	R	Nine Mile
16	45.992713, -112.531234	1 Dec. 2018	17 Dec. 2018	R	KOA
17	45.993208, -112.532688	1 Dec. 2018	17 Dec. 2018	L	KOA
PZ-1	45.990095, -112.530503	24 May 2018	24 May 2018	—	South Pond
PZ-2	45.991532, -112.531613	24 May 2018	24 May 2018	—	South Pond
PZ-3	45.989948, -112.531825	24 May 2018	24 May 2018	—	South Pond
PZ-4	45.993320, -112.535813	24 May 2018	24 May 2018	—	North Pond

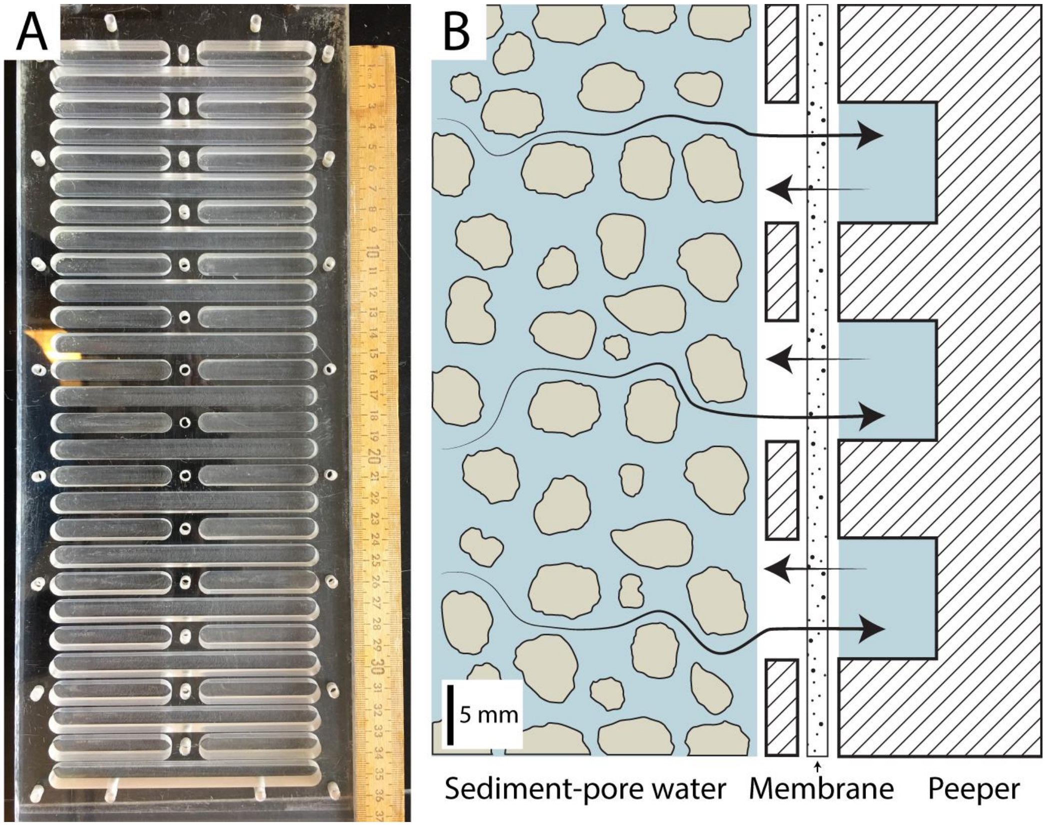
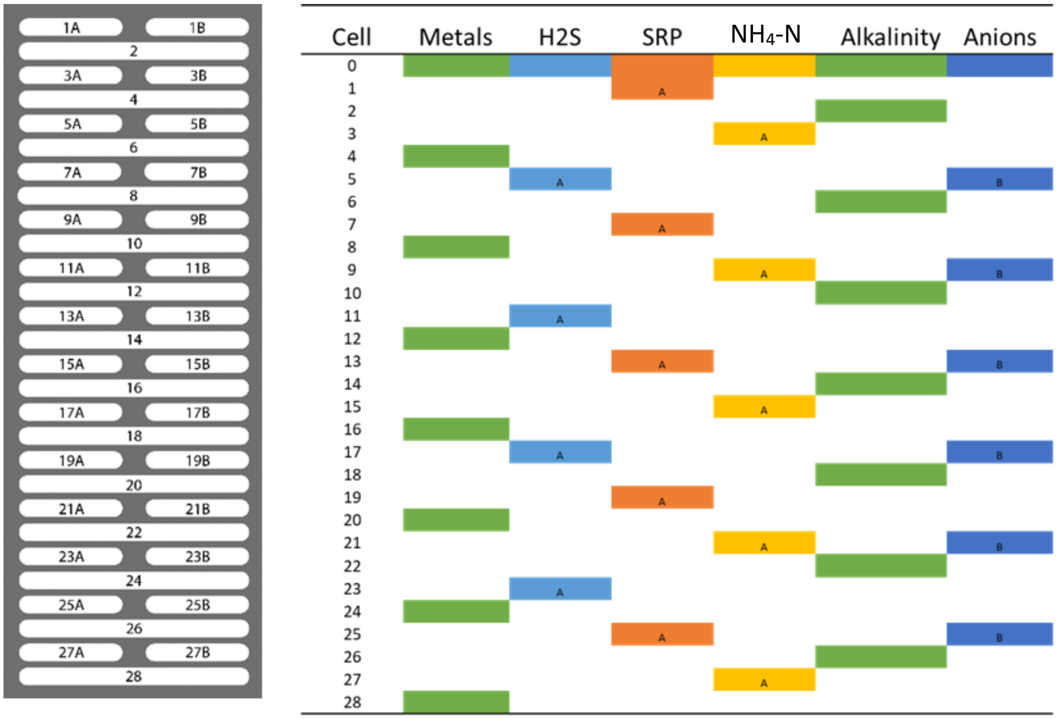


Figure 5. Illustration of peeper design and function. (A) Peeper cells before membrane is placed on top. (B) Solutes in sediment-pore water diffuse across the membrane to equilibrate with water in the peeper cell.

Immediately after the peepers were removed from the sediment, they were placed in a glove bag filled with argon gas to avoid oxidation. Extraction of water in the peeper cells was conducted immediately, on site, with a needle-tipped 60 mL syringe following the sampling plan (Fig. 6). Water in the syringe was filtered with a Nalgene Rapid-Flow 0.2 µm PES polyether sulfone filter into a 60 mL high density polyethylene (HDPE) bottle. Bottles for H_2S, NH_4-N, and anions were pre-filled with 20 mL of deionized water and massed. Bottles for alkalinity were pre-filled with 40 mL of deionized water and massed. Bottles for metals were pre-filled with 20 mL of deionized water and 0.3 mL of trace metal grade nitric acid and massed. With the exception of peeper 0, all of the peepers in this study were installed from August 2017 to December 2018. Peeper 15 was installed in November 2018 and could not be recovered due to being frozen in place. Peeper 0 was installed on 3 February 2011 and sampled on 18 April 2011. The period of deployment was unusually long because the peeper was installed through ice which later became unsafe when it was time to recover the sampler. Once the ice left, the peeper was located with a boat and was sampled following the methods outlined above.



Cell	Metals	H2S	SRP	NH_4-N	Alkalinity	Anions
0	🟩	🟦	🟧	🟨	🟩	🟦
1			🟧 A			
2					🟩	
3				🟨 A		
4	🟩					
5		🟦 A				🟦 B
6					🟩	
7			🟧 A			
8	🟩					
9				🟨 A		🟦 B
10					🟩	
11		🟦 A				
12	🟩					
13			🟧 A			🟦 B
14					🟩	
15				🟨 A		
16	🟩					
17		🟦 A				🟦 B
18					🟩	
19			🟧 A			
20	🟩					
21				🟨 A		🟦 B
22					🟩	
23		🟦 A				
24	🟩					
25			🟧 A			🟦 B
26					🟩	
27				🟨 A		
28	🟩					

Figure 6. Peeper sampling plan for peepers 1-13.

Seventeen peepers were deployed and sampled. Peeper location and dates of deployment and sampling are listed in Table 1. pH and Eh microelectrodes (Microelectrodes Inc., Bedford, New Hampshire) were used for both pH and Eh measurements. pH was calibrated using 7 and 10 pH buffers. Zobell's solution was used to calibrate Eh. Measurements were taken directly after the samples were extracted into the syringe from the peeper cell by inserting the microelectrode into the water sample through the syringe tip. Results from early experiments cast doubt as to whether the microelectrodes were working due to slow equilibration time. Because of this, they were only used for a few peeper sampling events. Surface water pH and Eh measurements were taken with a Hydrolab MS5 Data Sonde.

2.1.2. Piezometers

Piezometers were used in the ponds to measure hydraulic head and to obtain water quality samples. One-inch PVC was used to construct the piezometers with a screen made by cutting slots into the lower 30 cm of pipe, capping, and filled the well with coarse sand to act as a filter pack. While Peepers 6 and 7 were installed, 4 small piezometers were driven by hand (0.9–1.2 m) into various locations in the pond sediment using an inflatable kayak (Fig. 4 and Table 1). Piezometers 1 to 3 (PZ1–3) were driven into sediment in the same pond as peeper 6, whereas PZ4 was installed in the same pond as peeper 7.

After installation, a peristaltic pump was used to pump dry the piezometers, and the wells were purged with argon gas to minimize contact with oxygen. The wells were then allowed to recover, and static water level was measured. The piezometers were then pumped again, and the water was collected in 60-mL Nalgene bottles. The rest of the analyses followed the methods from the peepers.

2.1.3. Temperature logging

Onset® TidbiT® v2 temperature data loggers were deployed with four peepers (4, 8, 10, and 12). The temperature of pore water was needed to estimate diffusion rates and inform groundwater gradient direction. The loggers were set up so that one sensor was just above the sediment-water interface and the other was in the sediment at 25–30 cm depth. This was accomplished by taping the data loggers to a 91 cm stainless-steel rod. One logger was placed about 46 cm below the sediment-water interface, while the other was just above the sediment-water interface. The loggers collected temperature every hour for the duration of the peeper installation.

2.1.4. Alkalinity

Alkalinity as $CaCO_3$ was quantified by using a digital titrator with bromcresol green-methyl red indicator and 0.1600 N H_2SO_4 cartridge (HACH method 8203). Unfiltered 10 mL samples from the peeper cells were diluted with 40 mL of de-ionized water in a 60 mL bottle. Samples were massed to determine the amount of dilution and titrated within two hours after extraction from the peeper. The measured alkalinity was then corrected for dilution.

2.1.5. Soluble reactive phosphate (SRP)

Soluble reactive phosphorus was determined by the PhosVer® 3 Ascorbic Acid Test 'N Tube™ method (HACH method 8048). Molybdate reacts with orthophosphate to make a complex that is then reduced by ascorbic acid to produce a blue color which is quantified at a wavelength of 880 nm. Samples (roughly 5 mL) were filtered into pre-massed Test 'N Tube containers. A PhosVer 3 powder packet was then added and vigorously shaken for 15 seconds. In the lab, the samples were re-massed to determine the dilution factor and analyzed with a HACH DR/2010 portable spectrophotometer. The quantified amount was then adjusted for dilution and converted to mg/L as P. The linear range of the test is 0.06–5.00 mg/L with a practical quantification limit of 0.01 mg/L as PO_4^{3-}. Analyses were done with no calibration standards. Arsenate can interfere with the test at all concentrations due to the similar chemistry of AsO_4^{3-} and PO_4^{3-}. This was a concern in this study because some peeper cells had high concentrations of total dissolved arsenic. Other interferences of potential concern can come from Cu (> 10 mg/L), Fe (> 100 mg/L), S^{2-} (> 6 mg/L), and Zn (> 80 mg/L).

2.1.6. Ammonia

Dissolved total ammonia (NH_4^+ and NH_3) was quantified using the Nessler Method (HACH method 8038). Samples of approximately 5 mL of pore water were extracted from the peeper cells, filtered, and discharged into pre-massed 60 mL bottles with 20 mL of deionized water. In the laboratory, samples were re-massed, and reagents were added (3 drops mineral stabilizer, 3 drops polyvinyl alcohol dispersing agent, and 1.0 mL Nessler Reagent). Nessler Reagent reacts with ammonia giving the solution a yellow cast that is quantified at a wavelength of 425 nm. This method has a linear range of 0.02 to 2.50 mg/L NH_3-N and a practical quantification limit of 0.02 mg/L. Used reagents were stored as hazardous waste (mercuric iodide). Only peepers 1–6 were analyzed for ammonium. Because of an interference with dissolved Fe^{2+} (Lee, 2012), the ammonium results (in the appendix) should be treated with caution. Analyses were done with no calibration standards.

2.1.7. Dissolved Sulfide

Total dissolved sulfide (H_2S and HS^-) was quantified using the methylene blue method (HACH method 8131). Samples (roughly 5 mL) were extracted from the peeper cells, filtered, and added to a pre-massed bottle containing 20 mL deionized water. Sulfide 1 and 2 reagents were immediately added and agitated. If sulfide was present, the solution turned a deep blue color. The concentration of sulfide was determined using a HACH DR/2010 portable spectrophotometer within three hours of sampling at a wavelength of 610 nm. The linear range is from 0.01 to 0.70 mg/L as S^{2-} with a detection limit of 0.01 mg/L as S^{2-}. The results were corrected for dilution. The complete results are included in the appendix. Analyses were done with no calibration standards, due the difficulty of preserving dissolved sulfide standards.

2.1.8. Major ions and trace metals

Filtered samples (roughly 10 mL) for trace metal analysis were added to acid washed 60 mL HDPE bottles containing 20 mL of deionized water with 0.3 mL of trace metal HNO_3. The samples were analyzed at the Montana Bureau of Mines and Geology (MBMG) Analytical

Laboratory, Butte, MT. Water samples for trace metals (As, Cu, Fe, Mn, Zn) were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) on a Thermo Scientific iCAP Q ICP-MS, following EPA method 200.8. The same samples were also used for analysis of major cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) via ICP optical emission spectrometry (ICP-OES) at the MBMG lab using a Thermo Scientific iCAP 6000 Series ICP-OES following EPA method 200.7.

A different set of non-acid preserved samples was collected for quantification of anions (Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}). These samples (roughly 5 mL) were filtered and added to 20 mL of deionized water. Ion chromatography (IC) was used by the MBMG lab for quantification of anions on a Metrohm Compact IC Plus (EPA 300.1). Due to cost constraints, analysis of the full suite of anions was discontinued early in the project and only sulfate was quantified and reported for most of the peeper samples.

2.2. Sediment characterization

Sediment samples were collected using grab samples and 2 cm diameter, transparent plastic pipe. The sediment-core samples were extruded and cut into 4-cm sections. All of the samples were dried for 24 hours at 60°C. The samples were then screened to remove coarse organic matter. Selected sediment samples near peepers 2, 3, 4, and 12 were analyzed using X-ray diffraction (XRD), and a detailed XRD depth-profile was conducted for Peeper 12 (Fig. 7).

2.2.1. X-ray diffraction

The major mineralogy of the sediment samples was identified by using an Olympus TERRA Portable X-ray diffractometer (XRD). The X-ray source was cobalt. Fifteen-minute scans were conducted on sieved (200 mesh, 74 μm) samples. XPowder Ver. 2010.01.35 PRO was used for peak matching with the AMCS database (Martin-Ramos, 2010).

Figure 7. Peeper 12 sediment core.

2.2.2. X-ray fluorescence

The elemental composition of the sediment samples was determined by a Thermo Scientific Niton XL3t GOLDD+ X-ray fluorescence (XRF) Analyzer (scan time 20 sec majors, 10 sec high, 10 sec low, 10 sec light). The accuracy of the instrument was assessed by using three standards TILL 4, NIST 2709a, and NIST 2780 (Fig. 8). All the metals of interest (As, Cu, Fe, Pb, Zn) showed excellent agreement between the measured and true concentrations for each certified standard. Three sediment samples were analyzed raw and sieved (200 mesh, 74 µm) to determine if there was a difference in XRF data for the coarse vs. finer fractions. The fine-grained samples consistently had greater metal concentrations compared to the unsieved samples. All subsequent sediment samples were sieved before XRF analysis to provide an upper limit on the metal concentrations. This is considered more realistic in the field setting, since it is the fine fraction of the sediment that is most reactive with the sediment pore-water (Jobson and Carey, 1989; Acosta et al., 2011). The metal values were then compared with the maximum reported values for undisturbed background soils in Silver Bow County (Hydrometrics, 2013). The two locations (45.73663, -112.64711 and 45.98556, -112.77536) used were in areas that have had very little anthropogenic disturbances (e.g., away from mines and roads; Hydrometrics, 2013). This study used the information to provide a rough comparison between metal concentrations in the creek sediment compared to soil reference locations in greater Silver Bow County.

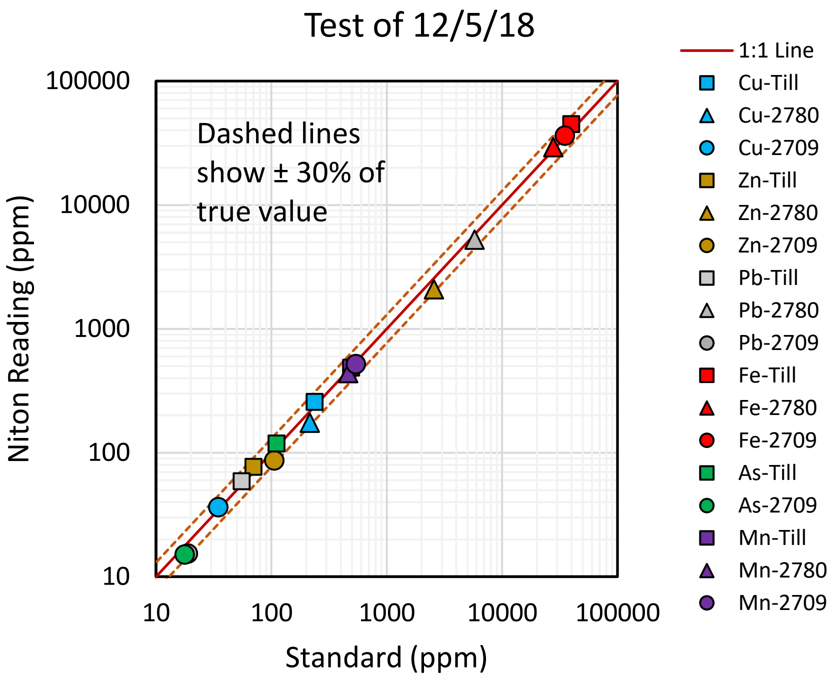


Figure 8. Test of Niton XRF vs standards. Dashed lines show ± 30% tolerance.

3. Results

The following results are divided into three sections, with the first presenting data sequentially for each pair of peepers. This is followed by a summary of the results organized by solute, and the results from the sediment analyses. The horizontal lines in the graphs which follow (Figs. 8 to 24) indicate the approximate location of the sediment-water interface (SWI). All depth measurements were computed relative to the SWI. Open symbols were used to indicate when an analyte was below detection. As a reference, the Montana DEQ-7 (DEQ-7) chronic aquatic life standard was added as a dotted line when appropriate (Montana DEQ, 2012). Several dissolved metals (Cu and Zn) have hardness dependent water standards. When this was the case, a value of 125 mg/L as $CaCO_3$ (an average value for all of the peeper cells) was used to calculate the DEQ-7 standard. A complete compilation of data can be found in Appendices A and B.

3.1. Peeper results by pair

Peeper 1 was deployed on July 26, 2017 and sampled on August 25, 2017 (Fig. 9). This peeper was used to see whether the peeper approach previously used by Montana Tech and other research groups in lacustrine environments could be adapted to a fluvial environment. The peeper was pushed into a thick pile of fine sediment in slack water across from and slightly downstream of the mouth of Grove Gulch. This peeper had very low metal concentrations for As, Fe, and Mn, and somewhat elevated concentrations of Zn and PO_4^{3-} (SRP).

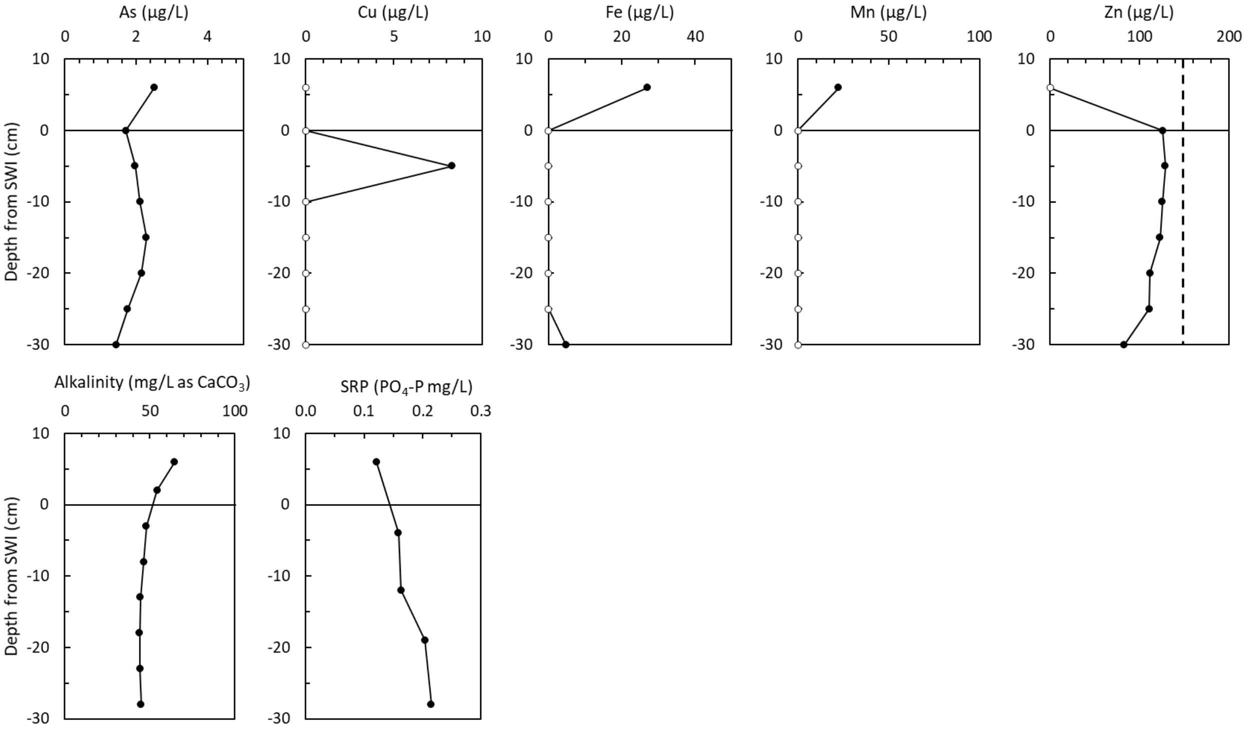


Figure 9. Peeper 1 results. The solid line is the sediment water interface (SWI) and the dotted line is the Montana Department of Environmental Quality chronic aquatic life standard (DEQ, 2017).

3.1.1. Peepers 2 and 3

Peepers 2 and 3 were deployed on January 21, 2018 and sampled on February 11, 2018 (Figs. 10 and 11). These peepers were placed in a previously identified high metal area in lower Blacktail Creek near the Butte Visitor's Center. For both peepers, metal concentrations increased with depth for As, Fe, and Mn. There was a sharp increase in As and Fe at 10 cm in the sediment. In peeper 2, Cu and Zn increased in the first 5 cm of sediment and then decreased below 10 cm. pH, Eh values stayed relatively constant with depth in peeper 3. The constancy of values could be an artifact of slow equilibration of the microelectrodes with the sample water. Overall, the microelectrode data suggest the sediment-pore waters had a pH slightly above neutral and a transitional (moderately reducing) Eh. Alkalinity and SRP concentrations increased with depth for both peepers and sulfate concentrations did not vary dramatically with depth.

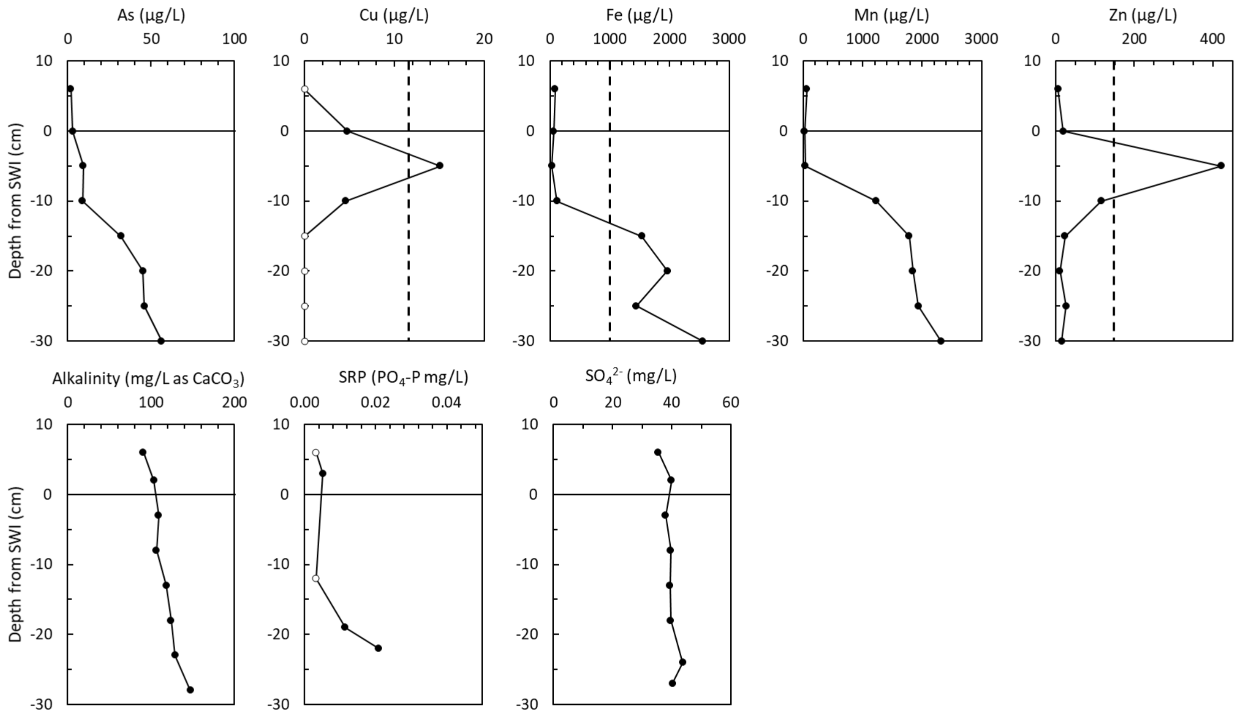


Figure 10. Peeper 2 results.

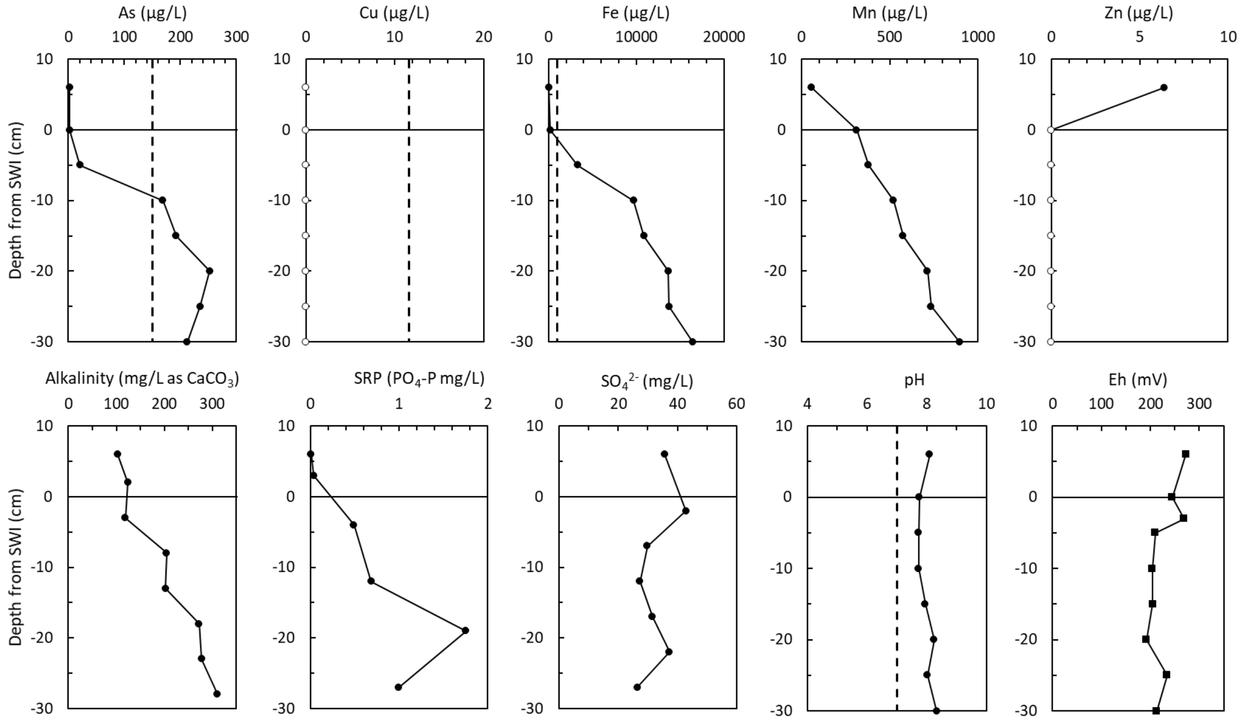


Figure 11. Peeper 3 results.

3.1.2. Peepers 4 and 5

Peepers 4 and 5 were installed on March 29, 2018 and sampled on April 20, 2018 (Figs. 12 and 13). The locations were selected based on previous reconnaissance in Slag Canyon at low streamflow that identified an area of Fe-oxide stained sediment. The metal concentrations from peepers 4 and 5 were some of the highest sampled for As, Fe, Mn, and Zn in this study (up to 2.53 mg/L, 609 mg/L, 57.4 mg/L, and 27.8 mg/L respectively). Temperature of the creek ranged from 2.0–7.6°C with an average of 4.5°C, whereas the pore water ranged from 5.7–6.9°C with an average of 6.2°C. The pH for peeper 4 was near neutral, and Eh was transitional (moderately reducing), with lower values deeper in the sediment.

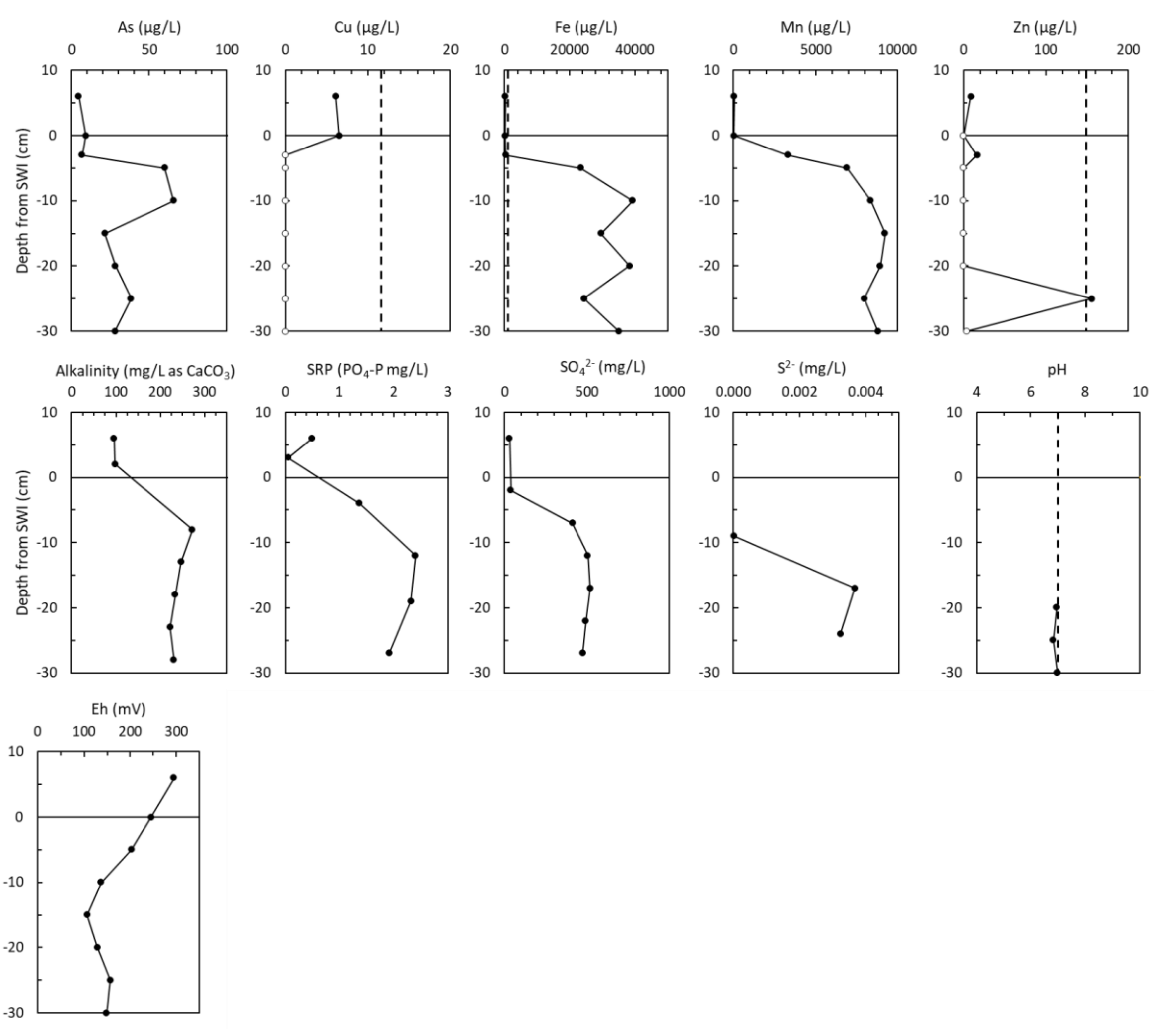


Figure 12. Peeper 4 results. pH is incomplete due to batteries running out.

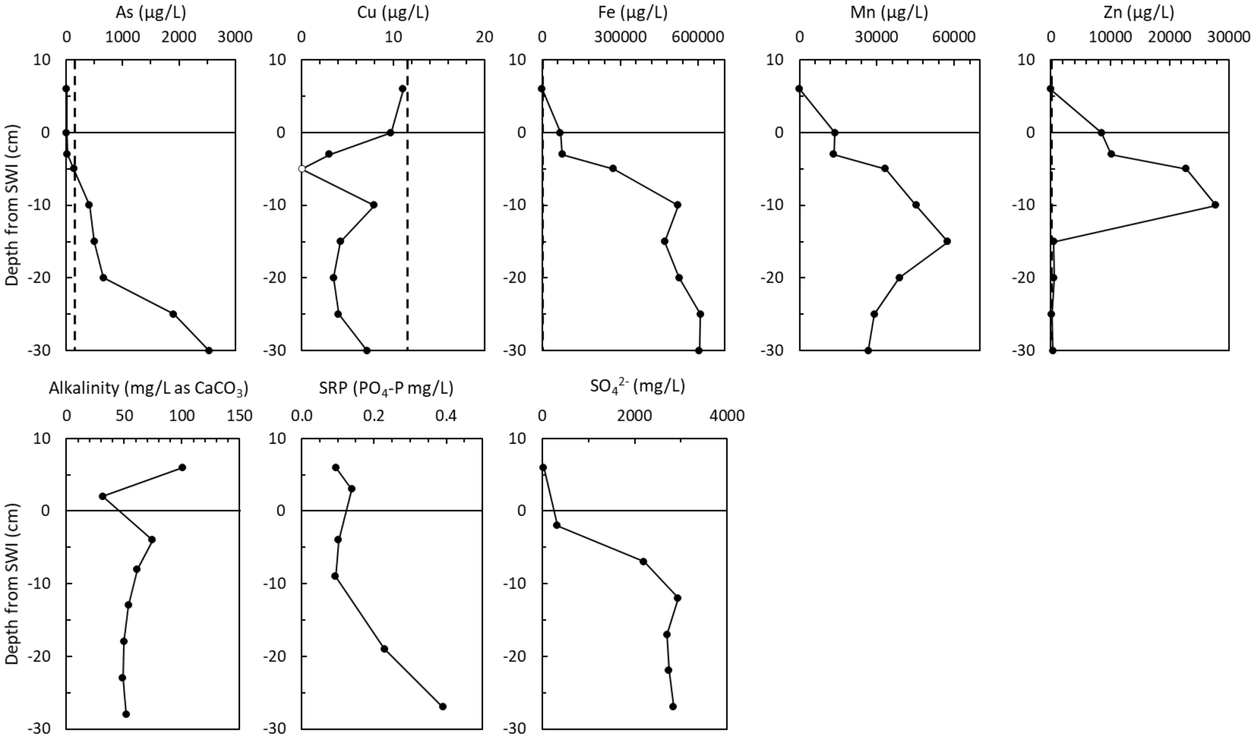


Figure 13. Peeper 5 results.

3.1.3. Peepers 6 and 7 and nearby piezometers

Peepers 6 and 7 were installed in May 2, 2018 and sampled on May 24, 2018 (Figs. 14 and 15). Two wetland ponds immediately south of Blacktail Creek were selected for peeper installation because Blacktail and Silver Bow creeks had very high flows that were deemed impractical for peeper installation. Surface water temperatures ranged from 12.4–16.3°C and pore water ranged from 9.8–15.8°C on the day of sampling. As, Fe, and Mn concentrations generally increased with depth below 5 cm. Sulfate (SO_4^{2-}) decreased with depth which coincided with the detection of sulfide (S^{2-}).

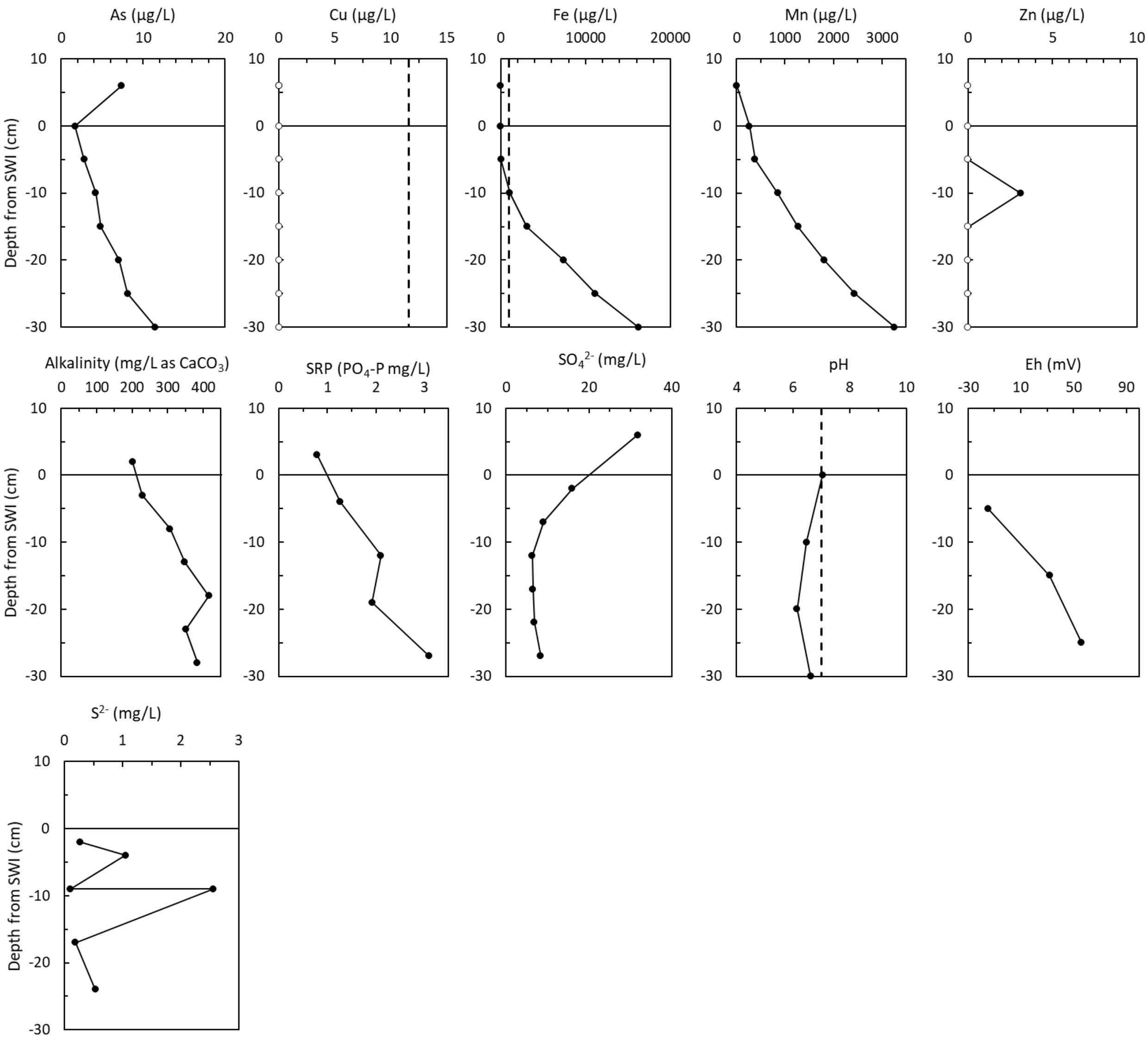


Figure 14. Peeper 6 results. A duplicate for S^{2-} was run at 10 cm depth.

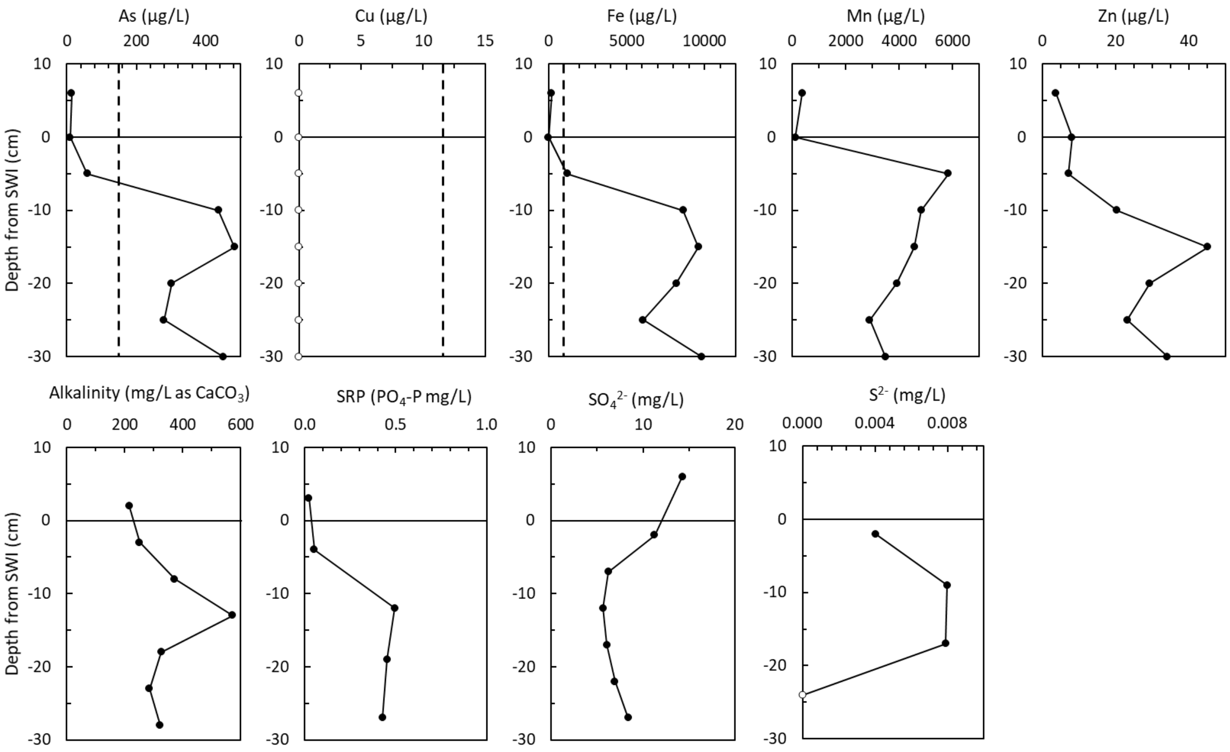


Figure 15. Peeper 7 results.

On the date of sampling of peeper 6, the static water level in PZ-3 was lower than that of the pond itself, indicating a downward vertical gradient consistent with the idea that the pond slowly drains into Blacktail Creek. PZ-4 was installed into sediment with cattails at the south (upgradient) side of the smaller pond where peeper 7 was located. This piezometer indicated groundwater up flow and could be pumped continuously at a slow but steady rate. PZ-2 and PZ-4 had the highest concentrations of Fe and Mn in the piezometers (21.3 and 3.15 mg/L respectively). These values were like those identified in peepers 6 and 7. Peeper 7 and PZ-2 had the highest As concentrations (449 and 39.6 µg/L respectively). The Zn concentrations at PZ-2 were significantly higher than those at peeper 6 (36.9 and 3.1 µg/L respectively); however, PZ-4 and peeper 7 have a similar average (~20 µg/L). PZ-2 and PZ-3 also have significant decreases in SO_4^{2-} from surface water to pore water (this will be discussed later). Please refer to Appendix C for a complete tabulation of the piezometer data.

3.1.4. Peepers 8 and 9

Peepers 8 and 9 were installed on July 13, 2018 and sampled on July 29, 2018 (Figs. 16 and 17). Peeper 8 was installed into Silver Bow Creek below the Slag Canyon and upstream of the effluent from the Montana Pole treatment plant. This site was selected because this portion of Silver Bow Creek was engineered during remediation activities at LAO to be a losing stream. Thus, the site provides an interesting contrast to the gaining reaches further upstream. The peeper 9 location was chosen to investigate pore-water chemistry in the former “dead zone” reach of Silver Bow Creek (Gammons et al., 2010) in the first few km downstream of the effluent from the municipal wastewater treatment plant. Data for Peeper 8 show elevated Cu and Zn concentrations near the top of the sediment which decrease rapidly with depth. The opposite trend is shown for Fe, Mn, As and P. Sulfate concentrations decreased with depth, consistent with the detection of sulfide. Peeper 8 surface water temperature ranged from 11.9–20.3°C with an average of 15.8°C and pore water ranged from 13.5–14.8°C with an average of 14.0°C.

Sediment pore water in peeper 9 showed relatively few changes with depth (Fig. 17). Unlike all other peeper profiles in this study, there was no increase in dissolved Fe with depth, although there was a slight increase in Mn in the lowermost cells. It should be noted that the sediment that peeper 9 was driven into had a coarse-grained, sandy consistency (Fig. 56E, Appendix) compared to the finer sediment used for the upstream peeper sites. The peeper 9 sediment probably had higher porosity and permeability, allowing oxygenated water in the creek to penetrate to deeper levels in the sediment column.

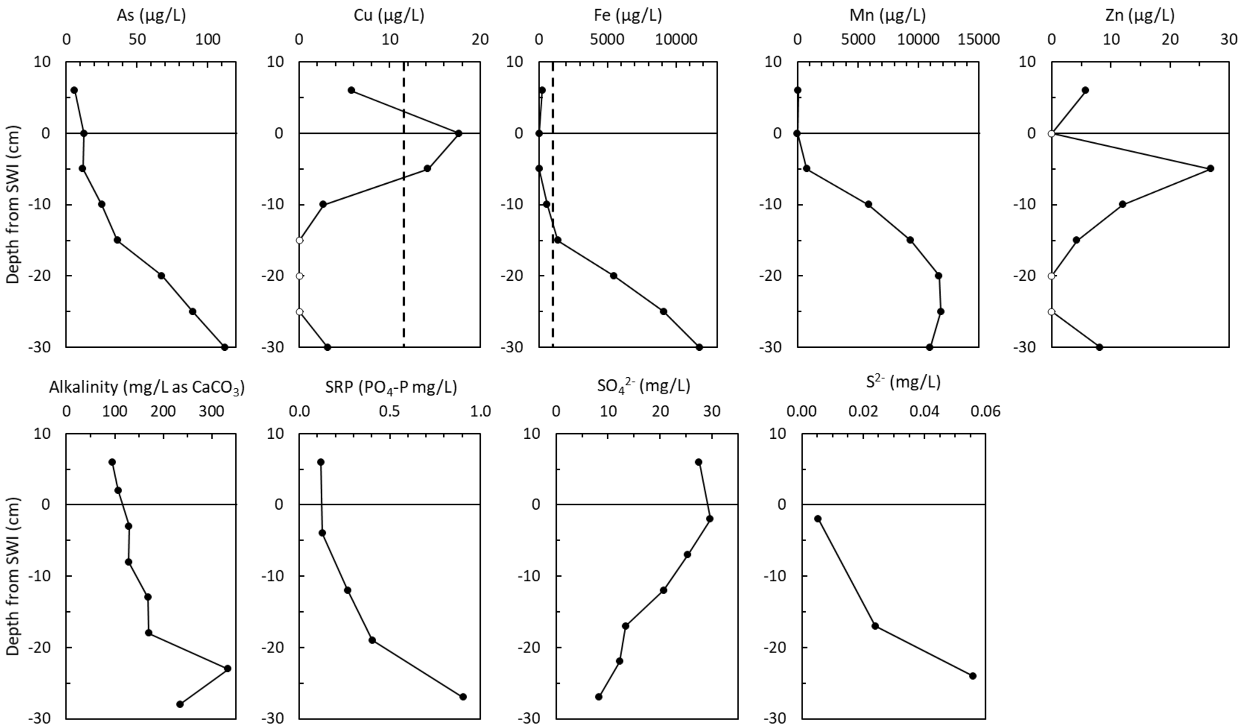


Figure 16. Peeper 8 results.

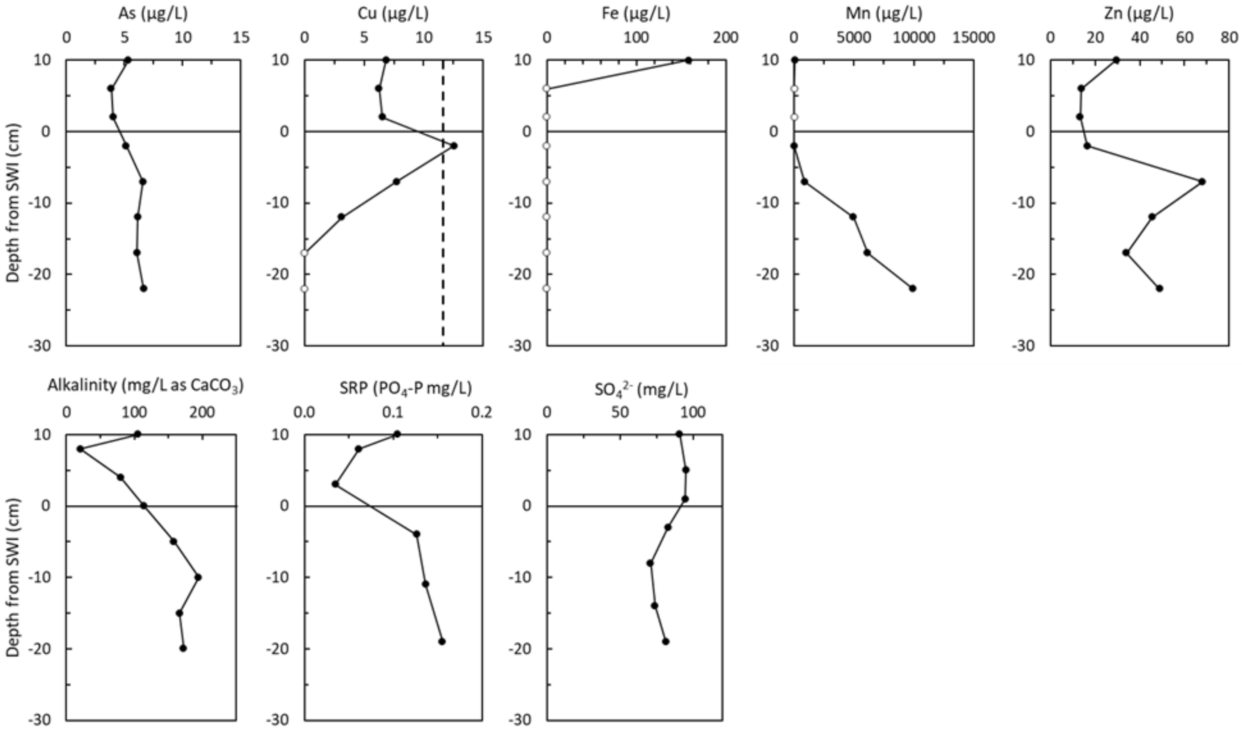


Figure 17. Peeper 9 results.

3.1.5. Peepers 10 and 11

Peepers 10 and 11 were deployed on August 9, 2018 and sampled on September 5, 2018. Peeper 10 was installed at the mouth of Blacktail Creek immediately upstream of USGS gauging station 12323240. The sediment at this location was thick with green algae and had unusual patches of white turbidity just above the sediment-water interface (Fig. 18). The origin of this turbidity is unknown, but may be elemental sulfur formed by oxidation of H_2S diffusing up from the sediment (C. Gammons, pers. commun., 2018). The data for peeper 10 (Fig. 19) shows a sharp drop in sulfate concentration and increase in alkalinity with depth, consistent with bacterial sulfate reduction (see next chapter). Concentrations of As, Fe, and Mn increased to values as high as 530 µg/L, 116 mg/L, and 7.0 mg/L, respectively, at a depth of 10 cm and remained elevated to the bottom-most cells. Concentrations of Cu and Zn quickly dropped to below-detect levels. Surface water temperatures at peeper 10 ranged from 9.0–19.3°C with an average of 13.2°C and pore water ranged from 12.2–14.0°C with an average of 13.1°C.

Figure 18. White turbidity above sediment water interface at peeper 10.

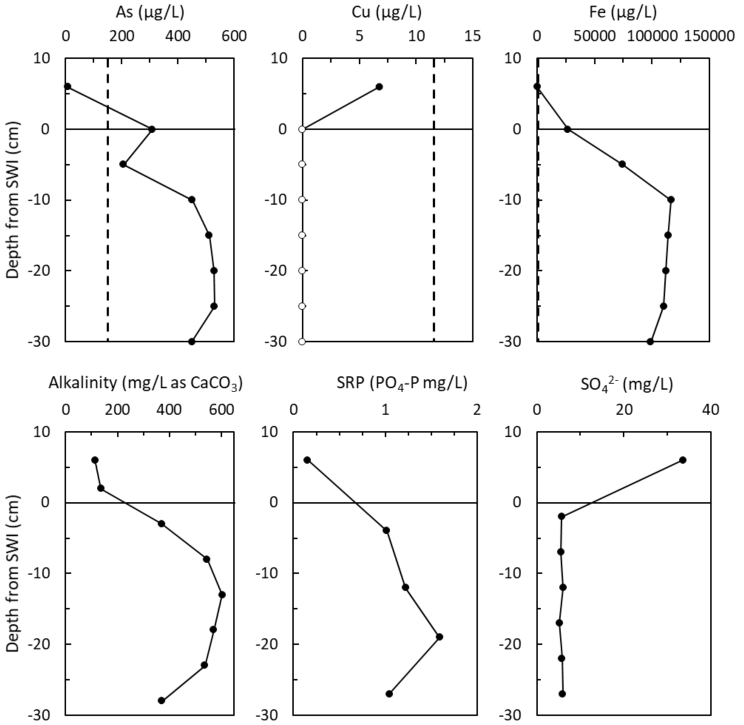


Figure 19. Peeper 10 results.

Peeper 11 was placed into muddy sediment in slack water backed up into Upper Silver Bow Creek (formerly known as the Metro Storm Drain) above its confluence with Blacktail Creek. Trends in metal and sulfate concentration with depth (Fig. 20) are very similar to those for Peeper 10, although maximum metal concentrations are a bit lower.

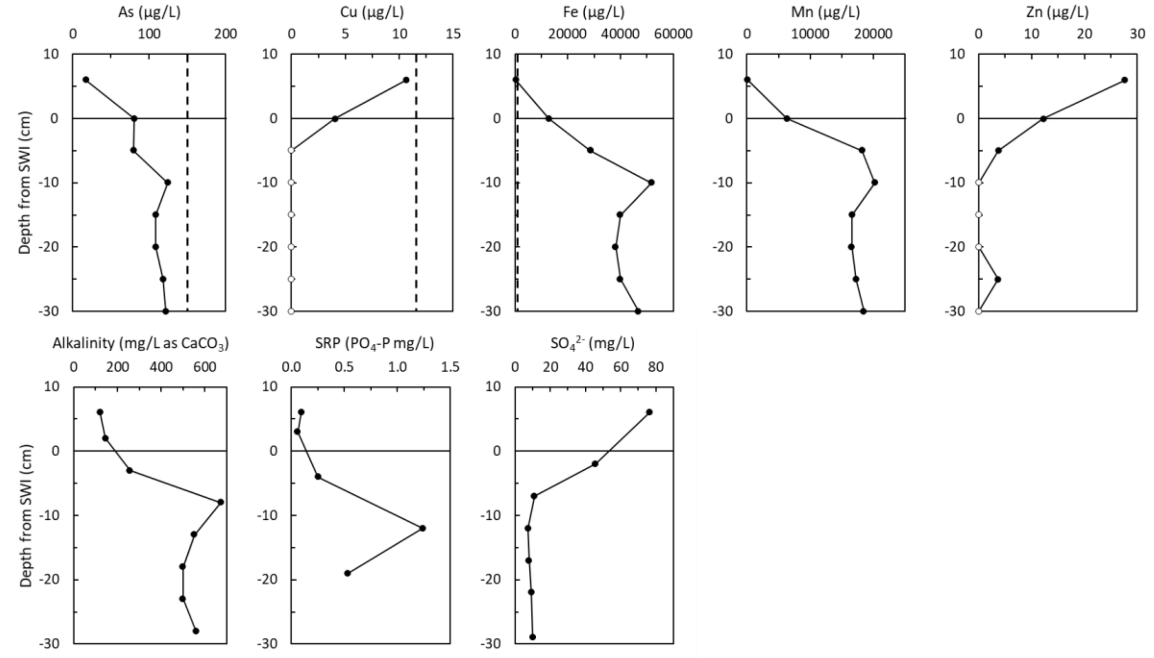


Figure 20. Peeper 11 results.

3.1.6. Peepers 12 and 13

Peepers 12 and 13 were installed into Slag Canyon on September 16, 2018 and sampled on October 6, 2018 (Figs. 21 and 22). Peeper 12 was placed on the left river bank, 20 m upstream from peeper 4, and peeper 13 was installed 80 m downstream from peeper 12 on the left river bank. The intention of these peepers was to sample the south bank of Silver Bow Creek in Slag Canyon. Peeper 12 was installed at the tail of a point bar in organic rich sediment that graded into fine sand around 15 cm below the sediment-water interface. Peeper 13 was installed along the creek bank in a predominantly sandy substrate except for the top 5 cm that were organic rich. The metal concentrations for As, Fe, Mn, and Zn increased with depth in peeper 12. The distinct increase in concentrations of these metals below 15 cm could be due to buried mill tailings (discussed in later sections). The peeper 13 metal concentrations stayed constant with depth, except for As which decreased in concentration with depth. The surface water temperature ranged from 5.2–12.9°C with an average of 8.5°C and pore water ranged from 7.3–10.8°C with an average of 9.1°C at peeper 12.

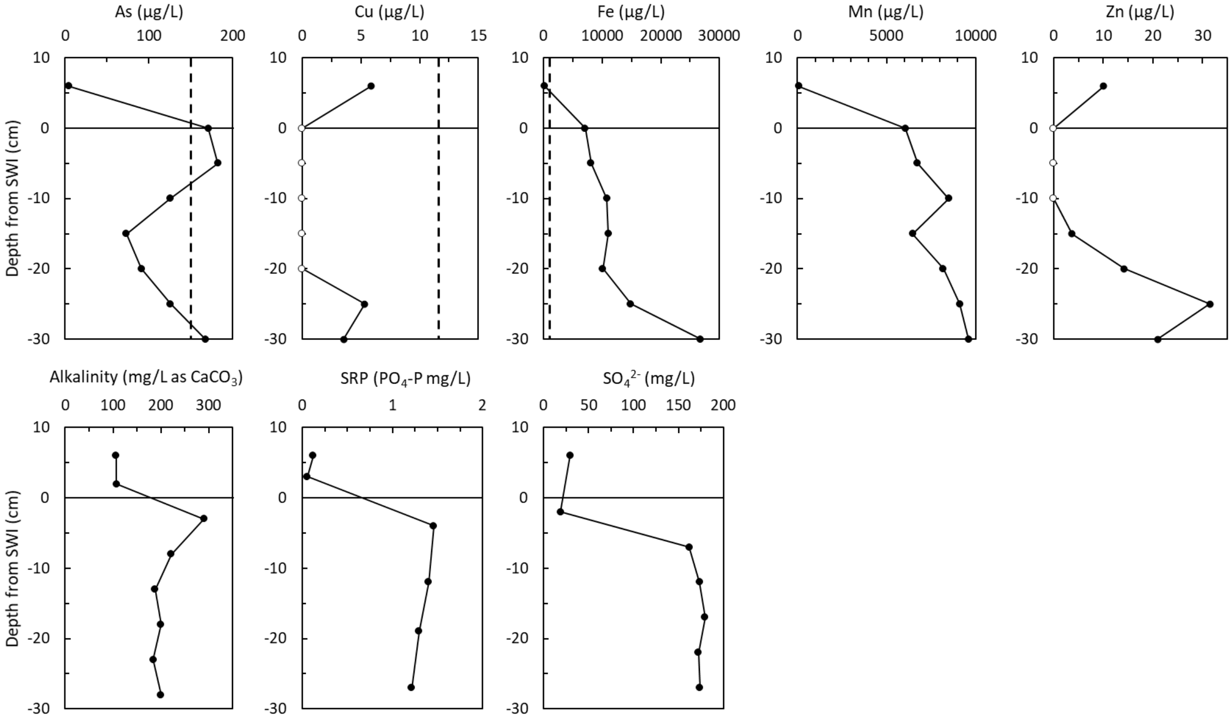


Figure 21. Peeper 12 results.

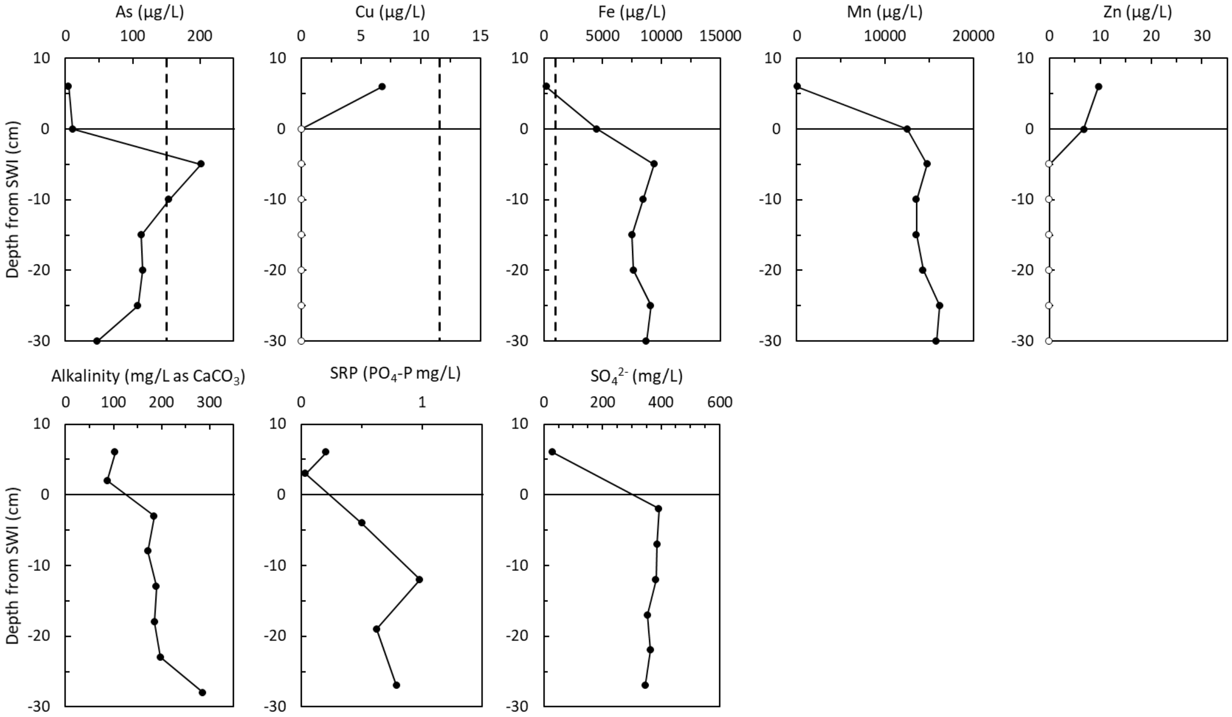


Figure 22. Peeper 13 results.

3.1.7. Peepers 14 and 15

Peepers 14 and 15 were installed on October 21, 2018 and peeper 14 was sampled on November 21, 2018 (Fig. 23). Peeper 15 was frozen in place and could not be sampled. Peeper 14 was placed into sediment near the mouth of Grove Gulch Creek after discussing with Dr. Raja Nagisetty and his students about their surface water findings in the area. A new sampling method was employed to collect more samples for ICP-MS at the expense of ammonia samples. Data for Peeper 14 show the typical increases in Fe and Mn with depth, with comparatively little change in As. Dissolved Zn concentrations were very high in the surface water (as is typical of Grove Gulch), but decreased to near-detect values immediately below the sediment-water interface. Sulfate concentrations also decreased sharply with depth, suggesting bacterial sulfate reduction. The single sample that spiked for Cu at 25 cm depth probably represents sample contamination.

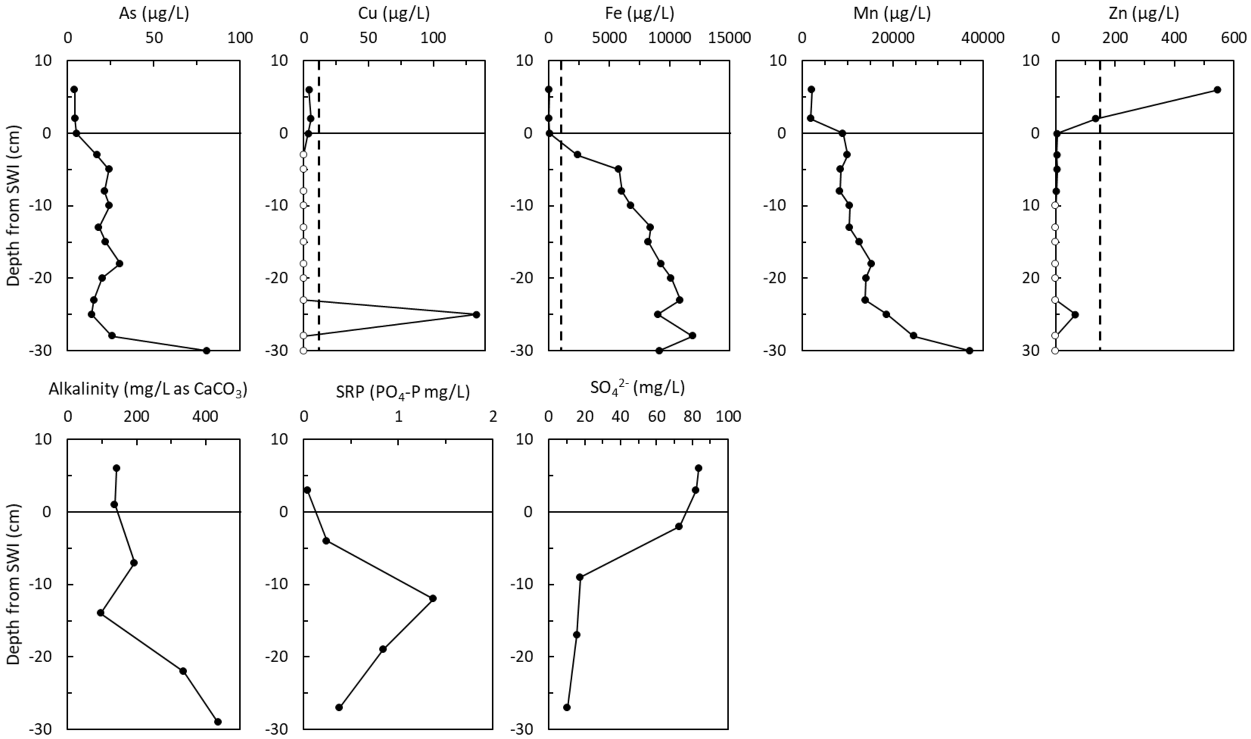


Figure 23. Peeper 14 results.

3.1.8. Peepers 16 and 17

Peepers 16 and 17 were installed on December 1, 2018 and sampled on December 17, 2018 (Figs. 24 and 25). These peepers were used to fill spatial data gaps in Blacktail Creek near the Butte KOA. Peeper 16 was installed in a sandy point bar near the northern creek bank. The upper 15 cm was silt with organic matter that graded into coarse sand. Peeper 17 was installed in the effluent from the pond south of I-90. The bed at peeper 17 was primarily organic matter and silt. The As, Fe, and Mn data for both peepers generally followed similar concentration trends except for higher concentrations in peeper 17. A possible reason for the differences could be the higher content of organic matter and fine sediment at peeper 17.

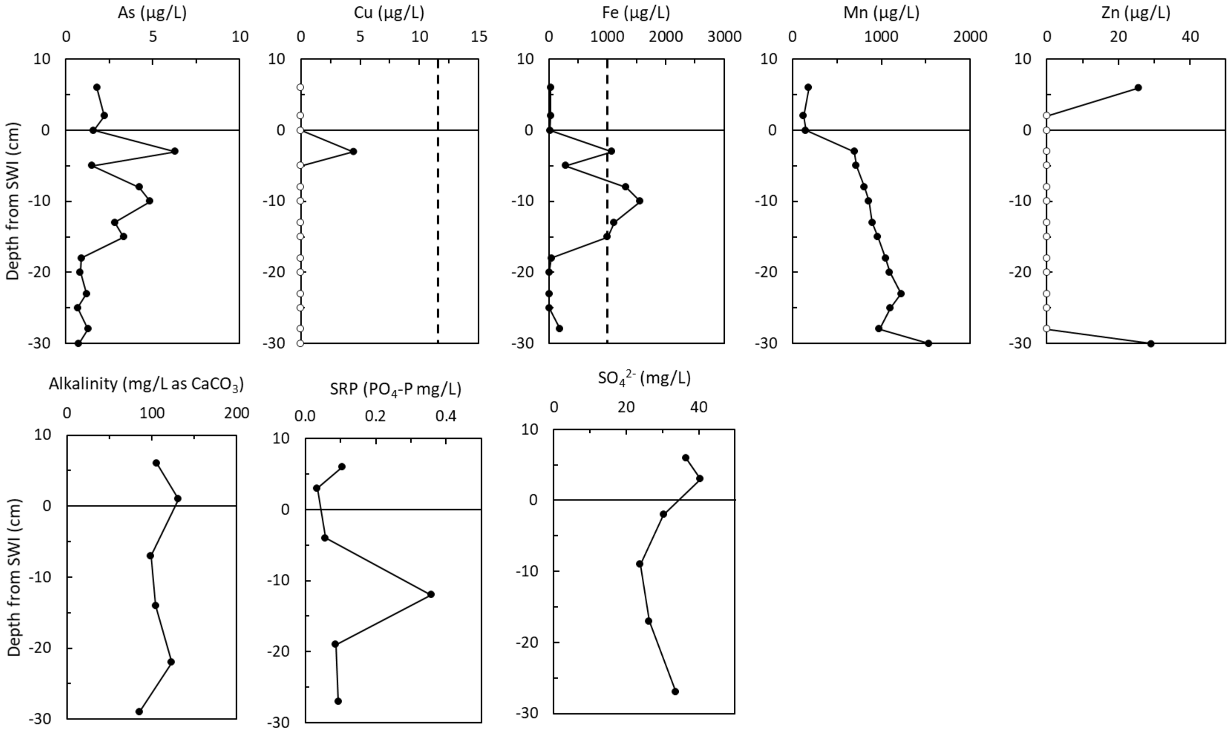


Figure 24. Peeper 16 results.

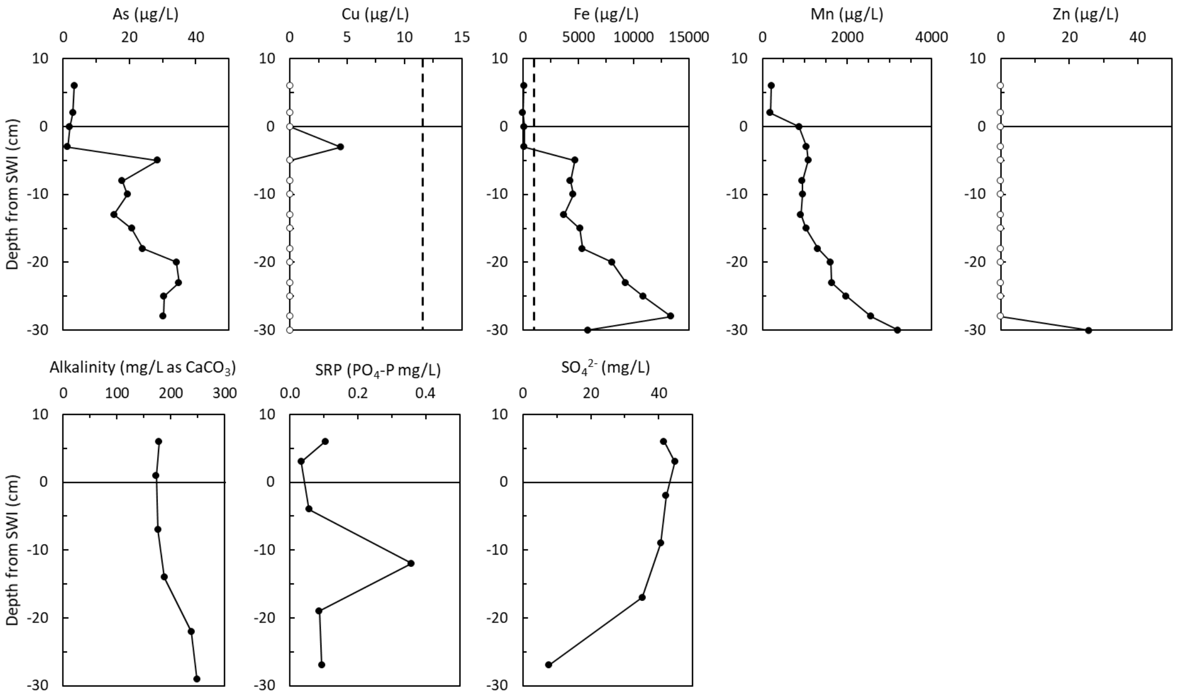


Figure 25. Peeper 17 results.

3.2. Water results by solute

The following sections provide results by solute. Boxplots provide the general chemical trends downstream starting at peeper 1 (Lexington Ave overpass) and ending at peeper 9 (near Rocker, MT), followed by the ponds and Grove Gulch (Fig. 26–34). The plots were designed so that the whiskers were the minimum and maximum values, the bottom of the box was the 25th percentile, the middle line was the median value, the top of the box was the 75th percentile, and the open circles represented outliers. For comparison, CDM Smith (2016) data for shallow groundwater are plotted with x-marks and surface water is designated with diamonds.

3.2.1. Alkalinity

Alkalinity for the surface water (cells 0–2) ranged from 121–216 mg/L as $CaCO_3$ (Fig. 26). The peepers with highest alkalinity, 10 and 11, were both sampled on the same day and located near the confluence of lower Blacktail and Upper Silver Bow creeks. Alkalinity in the sediment-pore water (cells 6–26) ranged from 31–673 mg/L as $CaCO_3$. Below the sediment-water interface, alkalinity values tended to increase with depth to around 200 mg/L $CaCO_3$, but went as high as 673 mg/L at peeper 11. Additionally, both ponds (peepers 6 and 7) had high alkalinity. Slag Canyon and Butte KOA generally had lower alkalinities. Complete tabulation of values is in Appendix A.

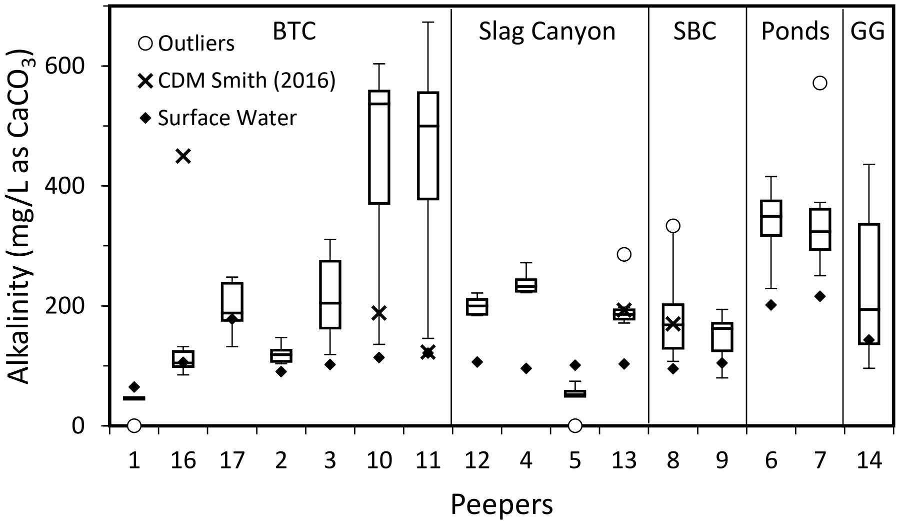


Figure 26. Boxplot of alkalinity concentrations. Blacktail Creek (BTC), Silver Bow Creek (SBC), and Grove Gulch (GG).

3.2.2. Phosphate

Phosphate concentrations ranged from 0–0.51 mg/L (as P) for surface water and 0–3.1 mg/L for pore water (Fig. 27). Highest concentrations were found in the pond pore water where peeper 6 was installed. In the creeks, Slag Canyon had the highest concentrations. Concentrations generally increased with depth in the sediment-pore water. A comparison between the HACH spectrophotometric and ICP-MS methods for P concentration is given in Figure 28. The comparison was made by using the ICP-MS cell closest to the cell used for SRP. If the ICP-MS cell was not close then an average value of the two closest ICP-MS cells was calculated. This method introduced additional errors and sharp gradients were probably inaccurately represented. Overall, the agreement is reasonable, especially at higher P concentrations. Phosphate from the HACH method might be higher if there was an interference with dissolved arsenate. Some of the points at low P concentration where the ICP-MS gave higher values than the HACH could possibly be explained by adsorption of phosphate onto hydrous ferric oxide forming in the Test-n-Tube vials after sampling and before analysis. This is also a problem with analysis of filtered but un-acidified samples for phosphate by IC (data not shown). The HACH phosphate data were used through the remainder of this thesis wherever P is discussed.

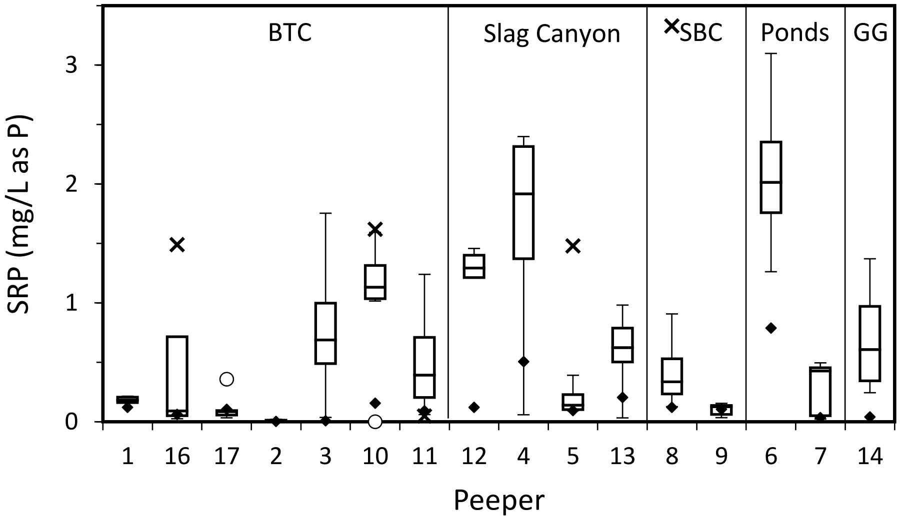


Figure 27. Boxplot of SRP concentration.

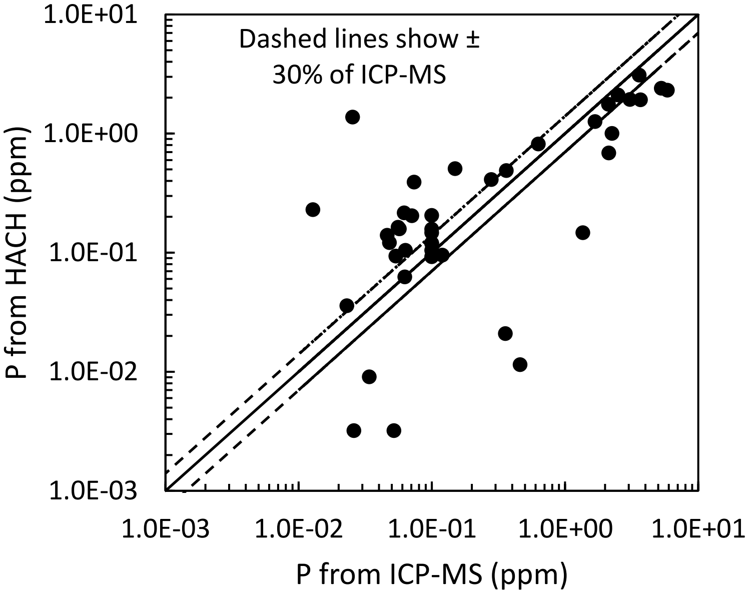


Figure 28. Comparison between phosphorus from ICP-MS vs HACH.

3.2.3. Sulfate and sulfide

Sulfate concentrations ranged from 14–91 mg/L for surface water and 1–2936 mg/L for pore water (Fig. 29). The highest concentrations were in Slag Canyon (peepers 4, 5, 12, and 13). Three different concentration-vs-depth trends were identified: (1) sulfate concentrations decreased with depth (peepers 6, 7, 8, 11, 14, and 17); (2) sulfate concentrations increased with depth (peepers 4, 5, and 12); and (3) no change in sulfate concentrations with depth (peepers 2, 9, 10, and 13). A decrease in sulfate concentration with depth is indirect evidence of bacterial sulfate reduction (see next chapter), whereas an increase in sulfate with depth could indicate the presence of buried mill tailings and/or upwelling alluvial groundwater that has high sulfate concentrations. There is currently no aquatic life standard for sulfate.

Sulfide concentrations ranged from 0–2.6 mg/L. Only a few locations had detectable levels of sulfide (peepers 4, 6, 7, 8, and 12). Because the HACH reagents for sulfide were added immediately after the peeper cells were sampled and filtered, any water with high concentrations of H_2S (e.g., > 0.1 mg/L) should have produced a blue color. The fact that most cells did not suggests that H_2S was either absent, or present at very low concentrations. The DEQ-7 aquatic life standard for sulfide is 2 µg/L. All of the peepers with detectable quantities of H_2S were over the standard.

3.2.4. Arsenic

Arsenic concentrations ranged from 2.00–17.7 µg/L for surface water and 1.43–2532 µg/L for pore water (Fig. 30). Highest concentrations were in Slag Canyon (peepers 5 and 12), near the Butte KOA (peepers 3 and 10), and the pond south of interstate 90 (peeper 7). Pore water As generally increased with depth. The Montana DEQ-7 aquatic life chronic standard is 150 µg/L and the human health standard for drinking water is 10 µg/L.

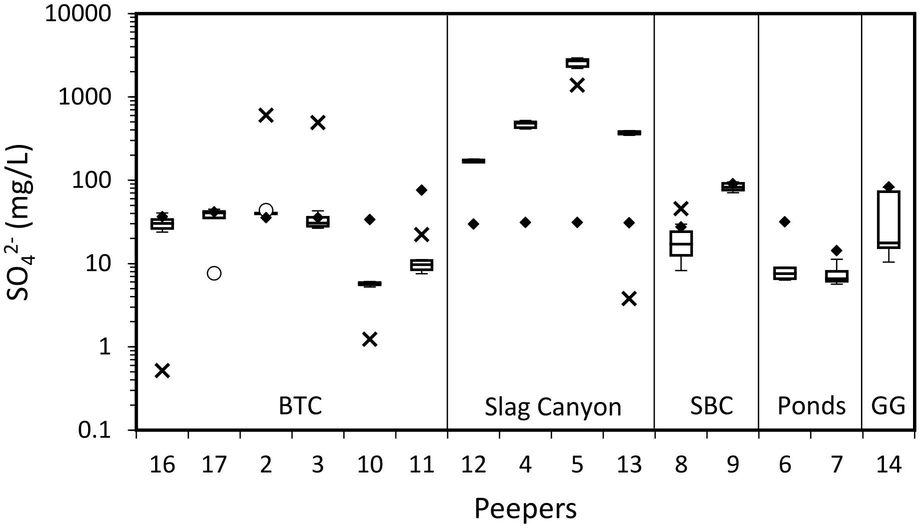


Figure 29. Boxplot of sulfate concentrations.

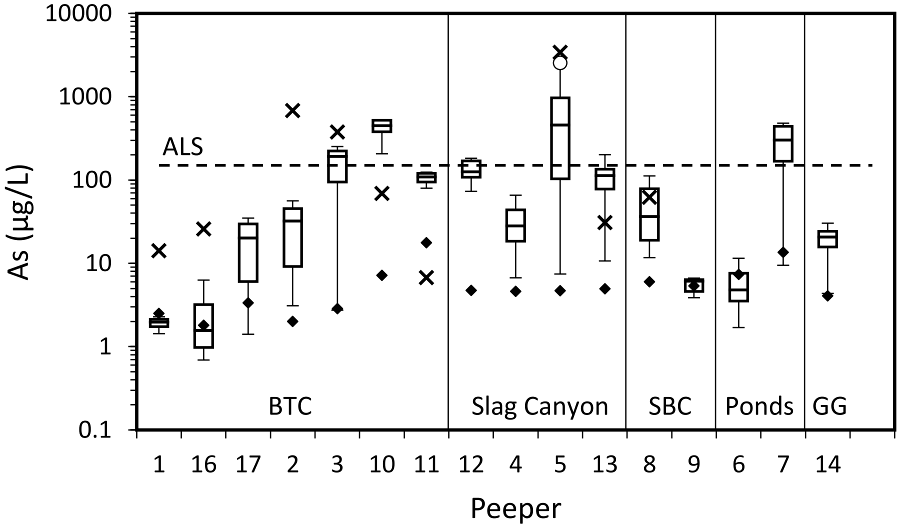


Figure 30. Boxplots of arsenic concentrations. Dotted line is the DEQ-7 chronic aquatic life standard (ALS).

3.2.5. Copper

Copper concentrations ranged from 0–11.6 µg/L for surface water and 0–17.7 µg/L for pore water (Fig. 31). Highest concentrations were located near the Butte KOA (peeper 2) and above the Montana Pole Treatment effluent (peeper 8). The ponds along Blacktail Creek did not have copper above the instrument detection limit (peepers 6 and 7). The concentrations generally decreased with depth (Figs. 9 and 15). The Montana DEQ-7 aquatic life chronic standard is alkalinity dependent. The peeper samples had an average alkalinity around 125 mg/L $CaCO_3$, which would make the Cu standard 11.6 µg/L. The surface water in the creeks and ponds never exceeded the aquatic life standard; however, four sediment-pore waters exceeded the standard (peepers 2, 8, and 9).

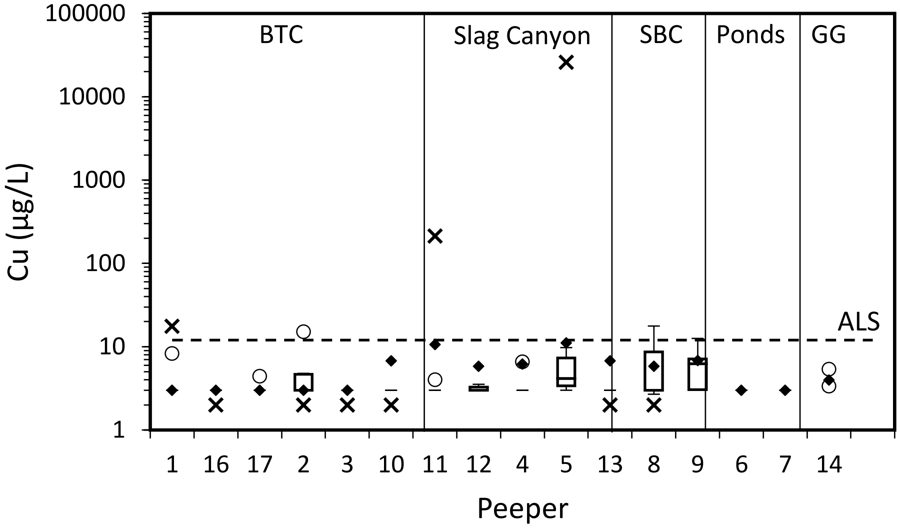


Figure 31. Boxplot of Cu concentrations.

3.2.6. Iron

Iron concentrations ranged from 10–390 µg/L for surface water and 0–609 mg/L for pore water (Fig. 32). Twelve of the 17 peepers had pore water that exceeded the Montana DEQ aquatic life chronic standard of 1000 µg/L. Iron concentrations tend to increase with depth. Many of the peepers had Fe-oxide staining at the sediment water interface (cells 4–6) indicating oxidizing conditions 2–3 cm into the sediment. Reducing conditions are present from 3–30 cm. Although no speciation data are available, it is likely that dissolved Fe was present as Fe^{2+} in the reduced sediment, especially considering the near-neutral pH's of the pore waters. Slag Canyon (peepers 4, 5, 12, and 13) tended to have the highest pore water concentrations.

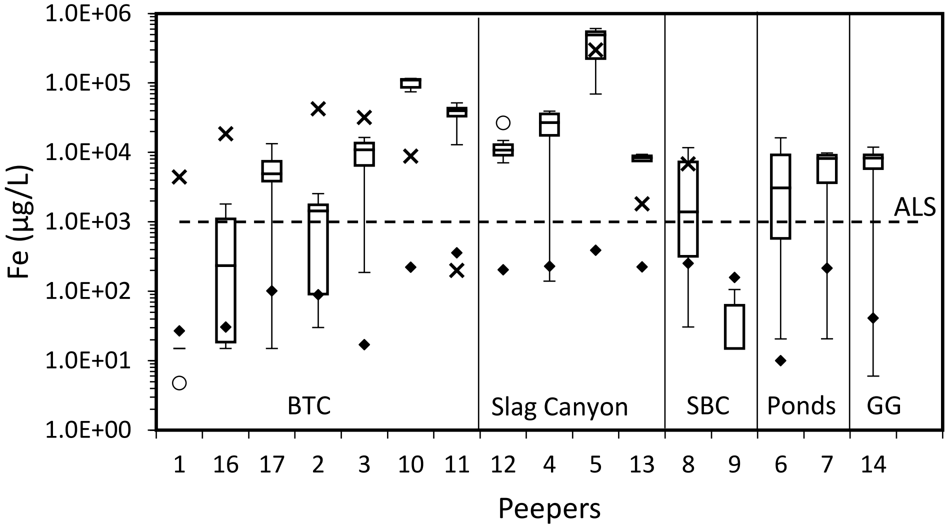


Figure 32. Boxplot of Fe concentrations.

3.2.7. Manganese

Manganese concentrations ranged from 0–85 µg/L for surface water and 0–57.4 mg/L for pore water (Fig. 33). The highest concentrations are clustered in Slag Canyon and Grove Gulch (peepers 4, 5, 12, 13, and 14). Dissolved manganese concentrations generally increased with sediment depth, and it is likely that any dissolved manganese was present as Mn^{2+}. There is currently not a Montana DEQ-7 aquatic life standard for Mn. However, pore water concentrations are much higher than the secondary drinking water standard MCL of 50 µg/L.

3.2.8. Zinc

Zinc concentrations ranged from 0–544 µg/L for surface water and 0–27.8 mg/L for pore water (Fig. 34). Grove Gulch had the highest surface-water Zn concentration (peeper 14; Fig. 22), whereas Slag Canyon had the highest pore water values (peeper 5; Fig. 12). The zinc concentration in peepers 2, 5, and 8 passes through a sharp maximum at shallow depths, decreasing both downwards into the sediment and upwards into the water column. The Montana DEQ-7 aquatic life chronic standard for Zn is alkalinity dependent: at 125 mg/L as $CaCO_3$, the value is 148.7 μg/L Zn. Grove Gulch (peeper 14) had the only surface water exceedances. The pore water in Slag Canyon (peeper 4 and 5) and peeper 2 had a combined eight exceedances.

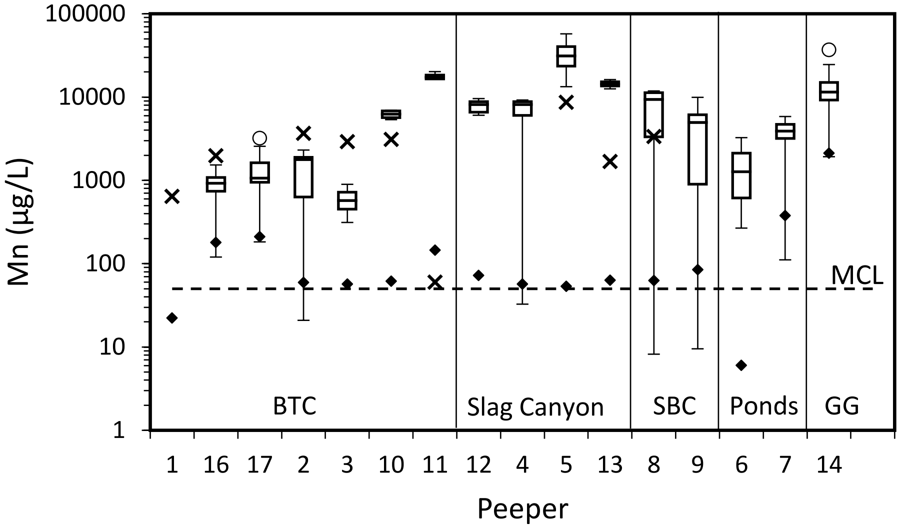


Figure 33. Boxplot of Mn concentrations.

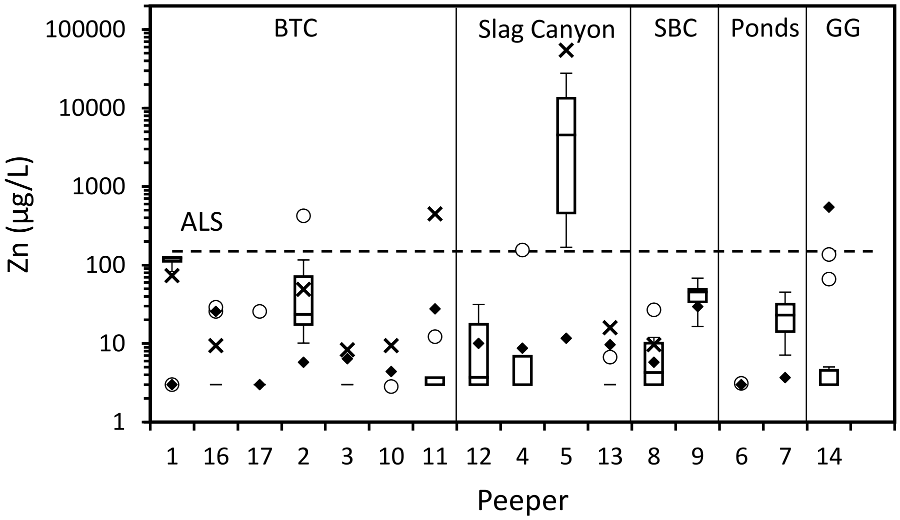


Figure 34. Boxplot of Zn concentrations.

3.3. Sediment

3.3.1. X-ray diffraction

The dominant minerals in peeper 12 were oligoclase (plagioclase), quartz, and muscovite, all of which are present in the weathered and/or hydrothermally altered Butte Granite (Fig. 35;

Table II). The minor minerals identified were calcite and pyrite. The detailed profile for peeper 12 shows an increase in pyrite content (up to 8 wt%) with depth, indicating the possible presence of buried mill tailings in the Slag Canyon area. In the same sediment column, calcite was identified from 22–26 cm depth. This may have been a zone where more acidic, Ca-rich water at depth interacted with higher-pH pore-water in the shallower sediment.

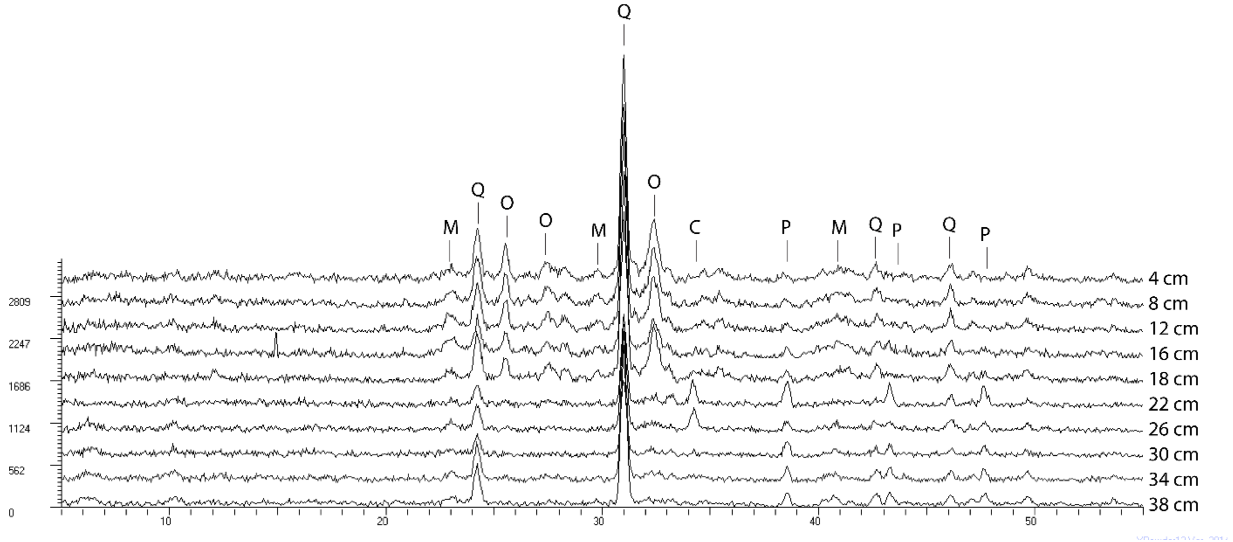


Figure 35. Stacked diffraction pattern for peeper 12.
Major peaks are labeled with interpreted minerals, calcite (c), muscovite (M), oligoclase (O), pyrite (P), quartz (Q).

Table II. Quantified weight percentage of crystalline phases (% W Xtl) for peeper 12.

Depth (cm)	Quartz (% W Xtl)	Calcite (% W Xtl)	Oligoclase (% W Xtl)	Muscovite/Illite (% W Xtl)	Pyrite (% W Xtl)
0	30	0.0	57	13	0.0
-4	28	0.0	57	14	0.0
-8	16	0.0	36	48	0.0
-12	24	2.0	43	29	1.9
-18	22	1.2	50	17	1.0
-22	32	15	0.0	34	8.4
-26	30	10	0.0	44	3.8
-30	32	6.0	0.0	43	5.6
-34	43	3.7	0.0	39	4.3
-38	53	0.0	0.0	34	5.2

3.3.2. X-ray fluorescence

Metal concentrations in sediment samples collected at the peeper sites were measured using X-ray fluorescence (XRF). Sediment cores were taken as close as possible to the peeper and named after the respective peeper. No cores were collected in the ponds. Metals of interest (As, Cu, Fe, Mn, Zn) from peepers 12–14 cores are plotted in Figure 36. Additional sediment core data are tabulated in Table III. These cores were selected because they had the most extensive sediment profiles. Sediment from Blacktail and Silver Bow creek had concentrations for many of the constituents of concern that were well above Silver Bow County background soil concentrations (Hydrometrics, 2013). Metal concentrations generally increased with depth except for Zn which stayed relatively consistent. Slag Canyon (peeper 12) had the highest concentrations of As, Cu, and Fe; whereas, Grove Gulch (peeper 14) had higher concentrations of Mn and Zn.

Table III. Average concentrations (mg/kg) and standard deviation (σ) for selected elements from sediment cores.

Peeper	As		Cu		Fe		Mn		Zn	
	avg.	1-σ	avg.	1-σ	avg.	1-σ	avg.	1-σ	avg.	1-σ
bkgd[1]	30		77		18700		974		105	
2	72	39	289	156	26700	8840	567	289	1970	1280
3	35	16	175	62	27400	7260	561	274	429	210
5	1035	653	1040	218	61800	17500	860	267	3230	1740
12	225	158	4580	3900	25100	5760	1670	758	2510	705
13	173	62	1440	431	60200	9970	1600	198	2470	494
14	230	69	487	194	21400	10200	7640	3750	3170	913

[1] Background soil in Silver Bow County (Hydrometrics, 2013)

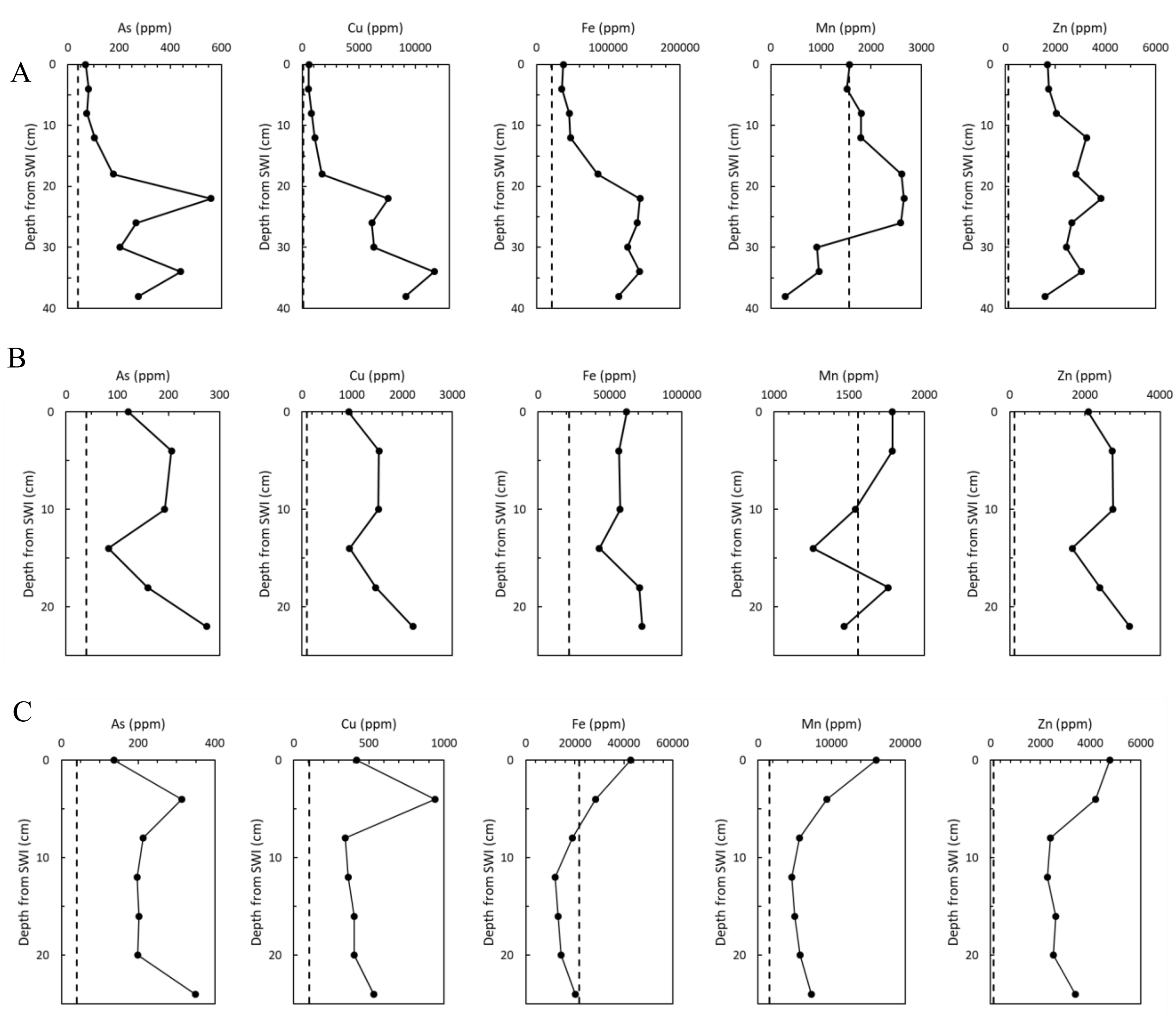


Figure 36. XRF data. (A) peeper 12 , (B) peeper 13, and (C) peeper 14. Dotted line shows background values for Silver Bow County (Hydrometrics, 2013).

4. Discussion

4.1. Reactions controlling pore water chemistry

4.1.1. Aerobic decay of organic matter

In organic-rich sediment, dissolved oxygen is rapidly consumed through aerobic decay of organic matter (rewritten from Drever, 1997):

$$C_{106}H_{263}O_{110}N_{16}P + 106O_2 \rightarrow 92CO_2 + 14HCO_3^- + 16NH_4^+ + HPO_4^{2-} + 92H_2O \qquad (1)$$

This reaction produces alkalinity and releases phosphate and ammonium to the water. Thus, high concentrations of ammonia and SRP may indicate areas where decomposition of organic matter is occurring. The peeper profiles for SRP in this thesis show this trend and most indicate that phosphate should be diffusing upward into the surface water from the stream sediment (Fig. 37). However, not all the phosphate released is a product of aerobic processes. Another process is dissolution of Fe- and Mn-oxides that have phosphate adsorbed to them (see next section).

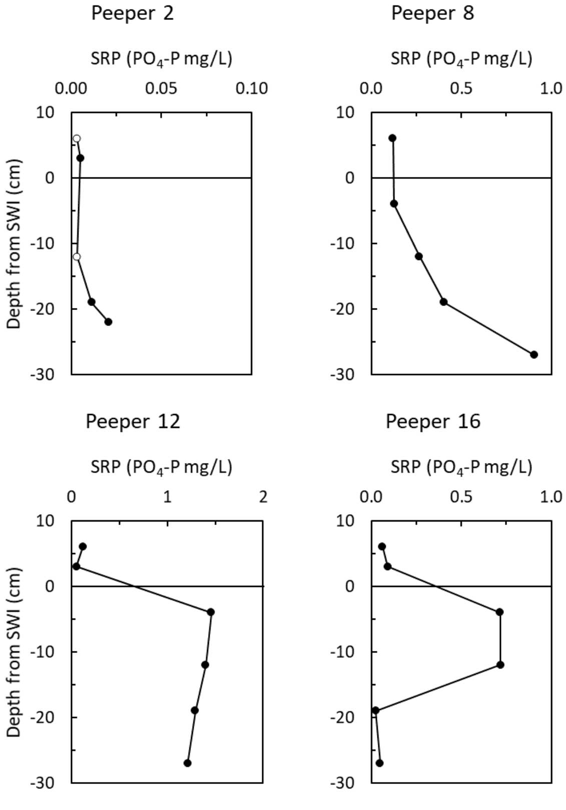


Figure 37. Soluble reactive phosphate trends recorded in selected peepers.

4.1.2. Reductive dissolution of Fe and Mn oxides

Iron and manganese are sensitive to redox conditions. Phosphate and trace metals can adsorb onto the surfaces of the oxides (Drever, 1997; Langmuir, 1997). When the Fe- or Mn-oxides are reduced, they can release dissolved metals and nutrients (e.g., AsO_4^{3-} and PO_4^{3-}) to the pore water (Langmuir, 1997). These reactions also consume protons and produce alkalinity (Drever, 1997). The reactions are as follows:

$$2MnO_2 + C_{organic} + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + H_2O \qquad (2)$$

$$4FeOOH + C_{organic} + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 5H_2O \qquad (3)$$

Manganese oxide reduction is thermodynamically favored to take place before iron oxide reduction as redox state is lowered (Langmuir, 1997). This trend was identified in peepers 2 and 8 (Fig. 38). Dissolved Mn concentrations increased around 5 cm below the sediment-water interface, whereas Fe concentrations did not begin increasing until around 10 cm depth. Because of the concentration gradients, both Fe^{2+} and Mn^{2+} will diffuse upwards towards the sediment-water interface. If DO is present, Fe^{2+} will oxidize to Fe-oxide, explaining the orange-red staining observed near some of the peeper sites (e.g., in Slag Canyon). If the Fe-oxides form, then they will be a sink for any dissolved phosphate or arsenate that will adsorb strongly onto them. Re-oxidation of Mn^{2+}, on the other hand, is kinetically inhibited so that Mn^{2+} may mix into the water column of the stream (Benner et al., 1995).

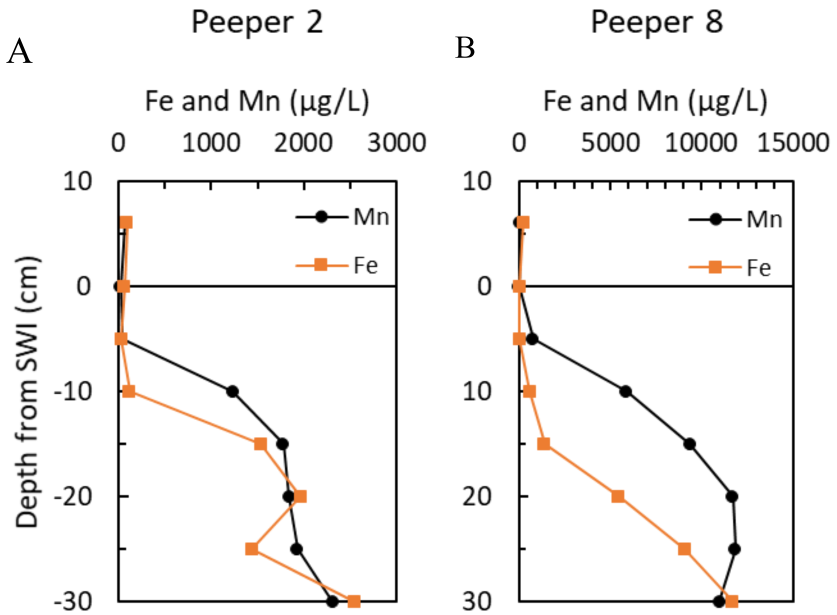


Figure 38. (A) Fe and Mn in peeper 2. (B) Fe and Mn in peeper 8. Note the different scale between A and B.

The importance of Fe and Mn redox reactions on pore-water chemistry is explored further in the solute cross-plots of Figure 39. Figures 39a and 39c show the expected trends of increase in pore-water arsenic and phosphate with increase in dissolved Fe^{2+} due to reductive dissolution of Fe-oxides. Most of the pore waters had dissolved Fe:As ratios that fell between 10 and 1000, and Fe:P ratios between 0.1 and 10. As mentioned above, phosphate can also be released by aerobic decay of organic matter, which helps to explain some of the low Fe:P ratios. A similar plot of Mn vs. Fe (Fig. 39b) shows that the pore waters had Fe:Mn ratios between about 0.1 and 10. Waters with elevated Mn but low Fe could be explained several different ways: 1) by preferential reduction of Mn-oxides before Fe-oxides; 2) by preferential oxidation of Fe^{2+} to Fe-oxide without oxidation of Mn^{2+}; and 3) by precipitation of Fe-sulfides or Fe-carbonate (siderite). Precipitation of Mn-sulfide (alabandite, MnS) is not thermodynamically favorable given the high solubility of this phase (Langmuir, 1997). Finally, Figure 39d shows a generally positive relationship between alkalinity and dissolved Fe^{2+}. However, the trend is not as robust as for the other diagrams. This is because there are many other reactions that can influence alkalinity other than reductive dissolution of Fe-oxide, such as aerobic decay of organic matter, bacterial sulfate reduction, and calcite dissolution or precipitation.

Previous work using peepers in the Warm Springs settling ponds identified reductive dissolution of Fe-oxides as a source of dissolved As to sediment pore water (Lee, 2012; Boese, 2015). The same relationships were found in this study. The covariance of Fe and As discussed above is even more convincing if results from individual peepers are examined (Fig. 40). This correlation, although not as strong, was also evident between Fe and P (Fig. 41). Based on these profiles, Fe^{2+}, phosphate, and dissolved As should all be diffusing upwards from the sediment into the creeks. However, if Fe^{2+} precipitates as Fe-oxides near the sediment-water interface, then As and P may adsorb onto the Fe-oxides and not make it to the creek.

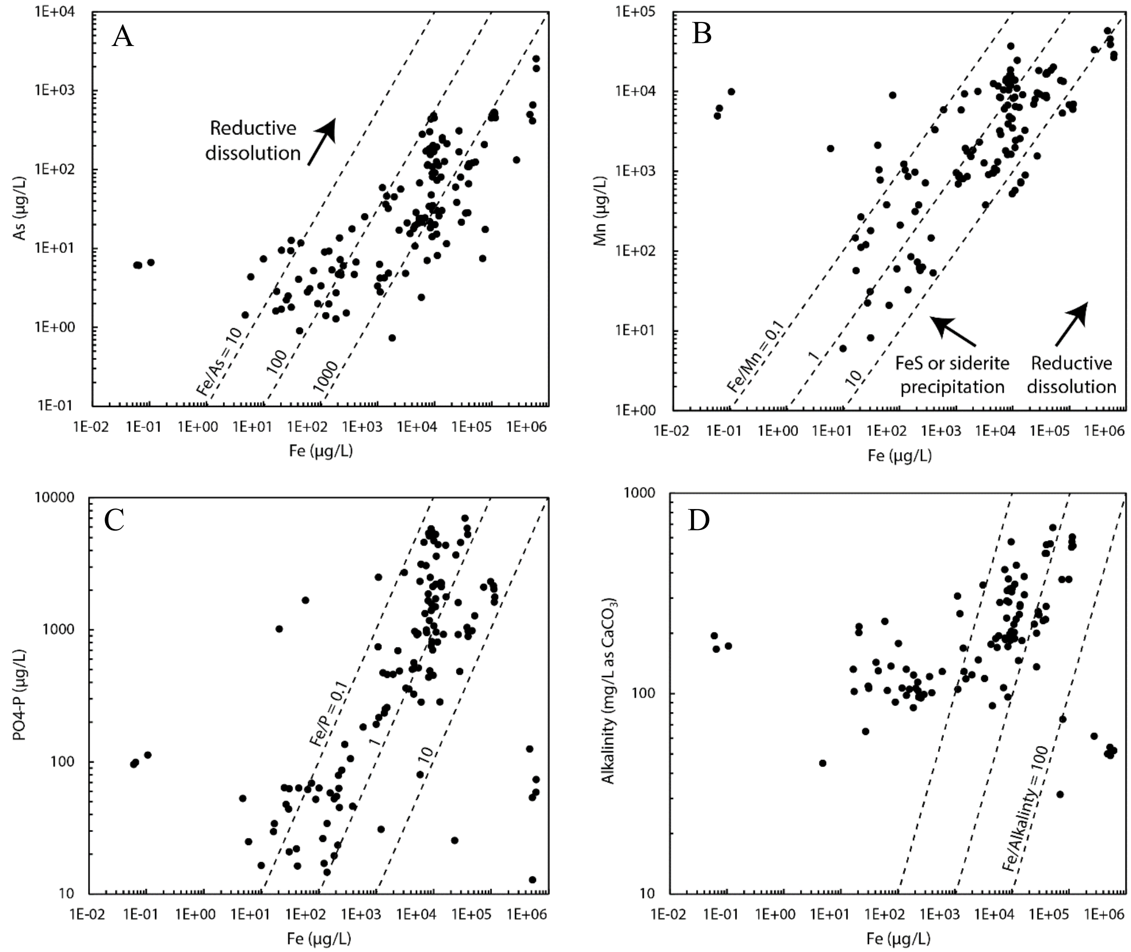


Figure 39. Comparison between dissolved concentrations of iron and (A) As, (B) Mn, (C) P, and (D) alkalinity.

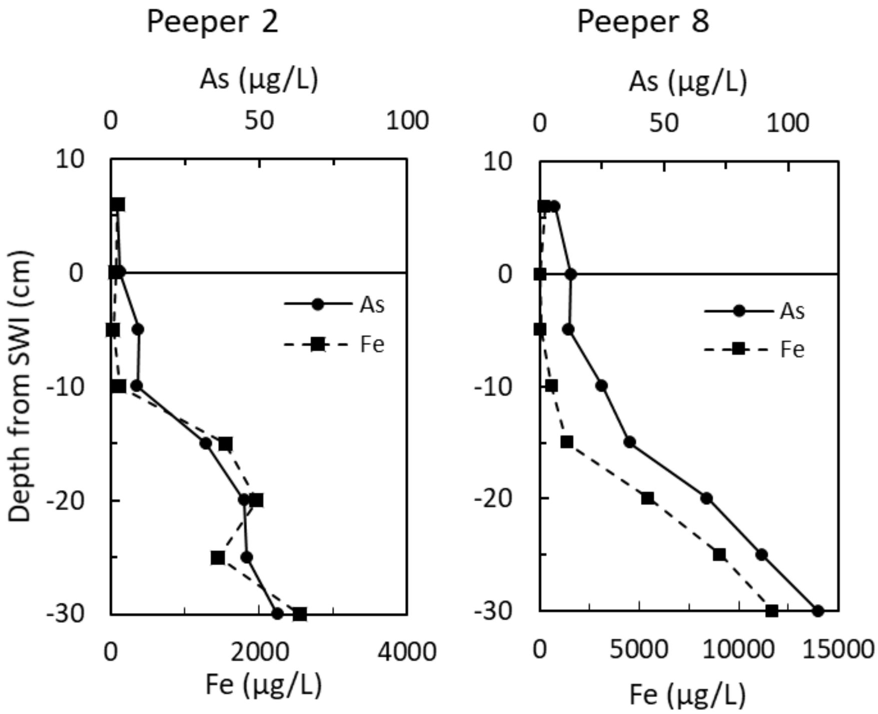


Figure 40. Relationship between As and Fe in peepers 2 and 8.

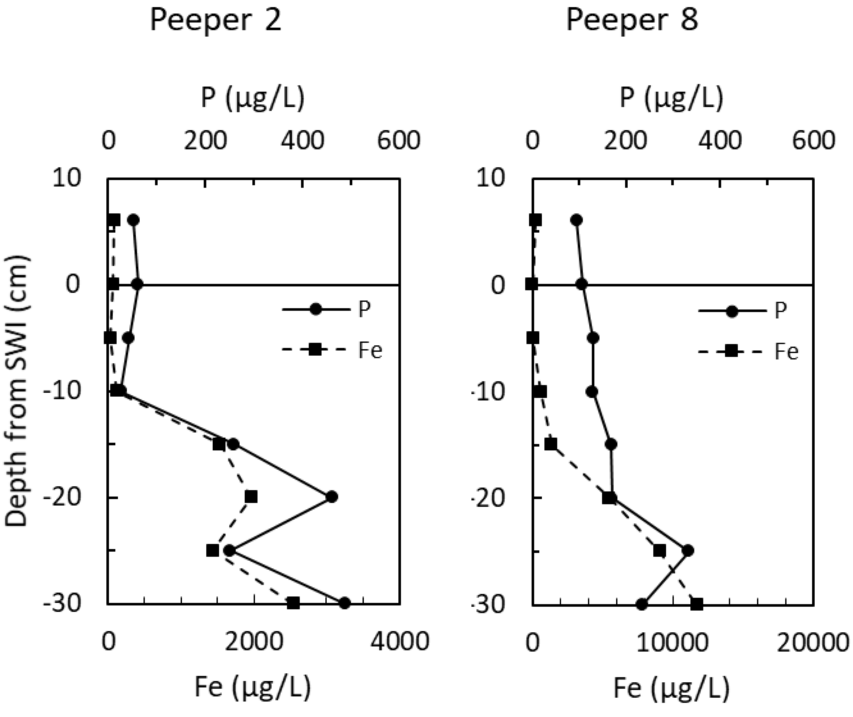


Figure 41. Relationship between P and Fe in peepers 2 and 8.

4.1.3. Reactions involving arsenic

As discussed in the previous section, arsenic can be adsorbed strongly to Fe-oxides (Langmuir, 1997). When Fe-oxides undergo reductive dissolution, As (V) is released and is subsequently reduced to As(III) in anoxic environments (Nagorski and Moore, 1999). This correlation is supported by As and Fe concentrations following similar concentration profiles for many of the peepers (Fig. 39). Further support for reduced Fe-oxides releasing As to the pore water and not from the groundwater comes from the sediment data.

Arsenic concentrations in Peeper 12 sediment were compared against the pore water concentrations (Fig. 42). When As concentration was high in the sediment, As concentration was low in the pore water, and vice versa. This may indicate that in areas of elevated pore water As, the sediment has undergone enough reduction to release As from the Fe-oxides. Speciation of dissolved arsenic between As(III) and As(V) in the pore water would have been helpful in understanding the mechanisms of As mobility, but was outside the scope of this study. In a study of pore-water chemistry in sediment from Warm Springs Ponds, Lee (2012) found that As(V) was the dominant form of dissolved As in the surface water, whereas As(III) was dominant in the organic-rich sediment. Other studies of mining impacted lakes drew similar conclusions as to arsenic redox behavior in sediment-pore water (e.g., Martin and Pedersen, 2002; Andrade et al., 2010).

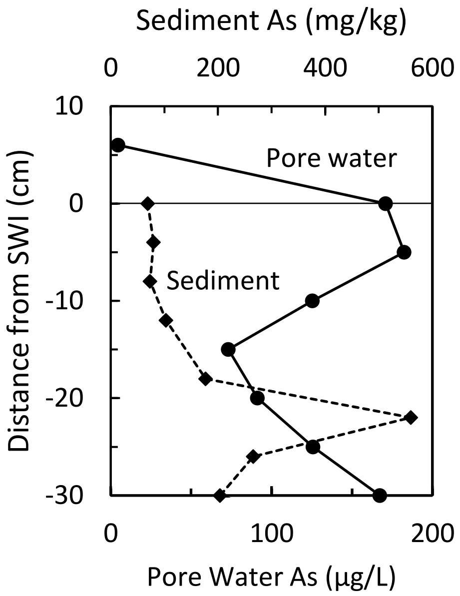


Figure 42. Peeper 12 comparison between dissolved and solid As.

4.1.4. Sulfate reduction

This study expected sulfate reduction to occur once the conditions were sufficiently reducing (Drever, 1997). In the absence of dissolved oxygen and in the presence of organic carbon, dissolved sulfate is reduced to hydrogen sulfide by sulfate reducing bacteria (e.g., *Desulfovibrio desulfuricans*). The reaction taking place can be written:

$$SO_4^{2-} + 2C_{organic} + 2H_2O \rightarrow H_2S + 2HCO_3^- \qquad (4)$$

Decreases in sulfate concentration with depth were noted in several peeper profiles (Fig. 43a), and correlated with a rise in alkalinity and H_2S concentrations (Figs. 43b and 44). However, whereas the drop in sulfate concentration was often on the order of 20 to 50 mg/L, none of the pore waters had H_2S concentrations greater than 2.5 mg/L. This suggests that H_2S is precipitating out as quickly as it forms, e.g., by formation of insoluble sulfide minerals of Fe, Cu, Zn, and other metals by reactions such as:

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \qquad (5)$$

$$Zn^{2+} + H_2S \rightarrow ZnS + 2H^+ \quad (6)$$

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \quad (7)$$

In contrast, MnS (alabandite) is more soluble and is not expected to precipitate at low levels of H_2S. The order of solubility of the sulfide minerals is: Mn > Fe > Zn > Pb > (Cu, Cd) (Drever, 1997).

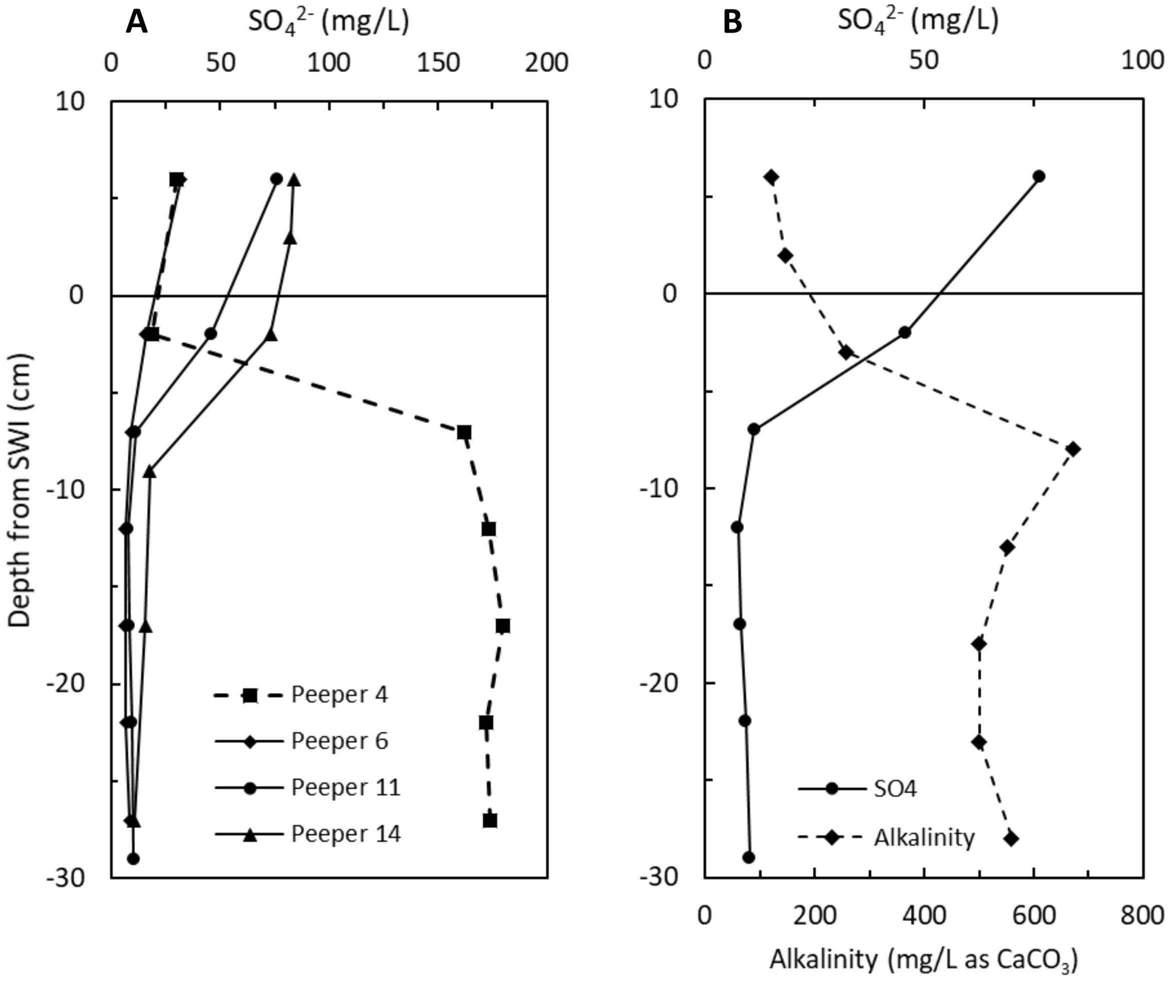


Figure 43. (A) Changes in sulfate concentration vs depth for selected peepers and (B) comparison between sulfate and alkalinity in peeper 11.

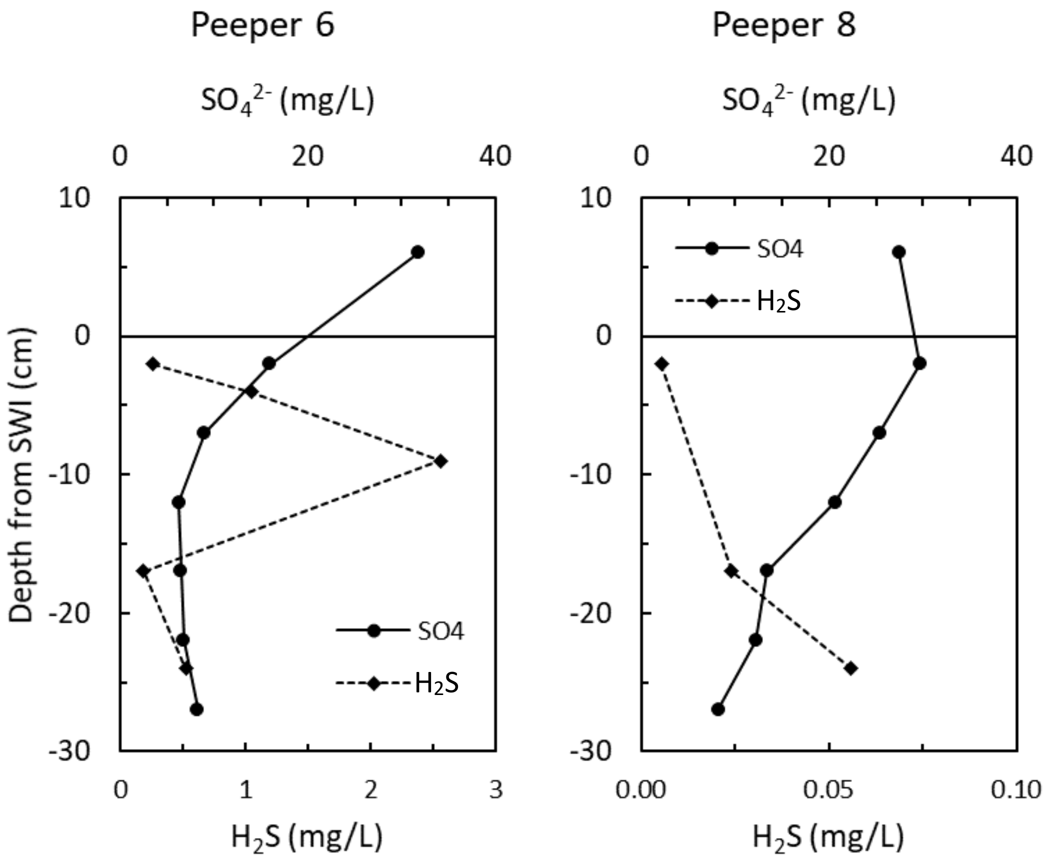


Figure 44. Comparison between sulfate and hydrogen sulfide for peepers 6 and 8.

4.1.5. Reoxidation of metals

DO diffusing into the sediment can oxidize sulfide minerals or reduced dissolved oxide minerals, causing the metals to be remobilized. The oxidation rate can be increased by storm events or bioturbation (e.g., feeding ducks) exposing fresh sediment previously in an anaerobic zone to an aerobic environment. In peepers 1, 2, 8, 14, and 17, there was a zone where dissolved Cu and/or Zn concentrations increase sharply in the top 2–6 cm of the sediment column. This could indicate oxidation of fine-grained sulfide minerals in the near surface pore water.

When dissolved Fe^{2+} and Mn^{2+} encounter oxygen, they undergo oxidation as follows:

$$2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+ \quad (8)$$

$$Fe^{2+} + \tfrac{1}{4}O_2 + 5/2\ H_2O \rightarrow FeOOH + 2H^+ \quad (9)$$

Formation of Fe-oxyhydroxides will occur first followed by Mn-oxides (Drever 1997). This order is the reverse of reduction. Oxidizing bacteria (e.g., Thiobacteria) were possibly responsible for increasing the rates of these reactions by as much as 5500 times above the abiotic rate (Langmuir, 1997). Ferrihydrite can form quickly when there are large concentrations of iron present (i.e., days to weeks; Langmuir, 1997). Mobile Fe^{3+} is not found in water with a pH of 5 to 10, but Fe^{3+} oxyhydroxides can occur in this pH range (Langmuir, 1997). Evidence of Fe oxidation staining in the top 5 cm of sediment was observed in many of the peeper membranes, especially in peeper 5. This qualitatively suggests that generally 5 cm beneath the sediment-water interface there was a reducing environment and above 5 cm there was an oxidizing environment. More accurate understanding of the redox conditions could have been possible with better Eh data.

4.1.1. Diffusion of solutes in and out of sediment

The understanding of diffusion gradients within the pore water is helpful for understanding the surface and groundwater interactions. Diffusing solutes will move from areas of high concentration to areas of lower concentration (Fetter et al., 2018). Depending on the slope of the vertical concentration profile, the diffusion direction could be into or out of the sediment.

4.2. Quantification of diffusive fluxes

Diffusive fluxes across the sediment-water interface were calculated for As and Zn to understand the magnitude of metal loading in the creeks and ponds. These metals were selected, because they should behave relatively conservatively as they diffuse through the pore water;

unlike Fe, which is expected to oxidize and reprecipitate. The diffusive flux of dissolved metals was calculated using Fick's first law (Tables 4 and 5; Santos-Echeandia et al., 2009):

$$J = \phi D_s \frac{dC}{dz} \tag{10}$$

where J is the specific diffusive flux of solute (μg cm^{-2} d^{-1}); ϕ is the sediment porosity (unitless); D_s is the diffusion coefficient (cm^2 sec^{-1}); C is the dissolved metal concentration (μg/L), and z is the distance from the sediment-water interface (cm).

The concentration gradient was calculated using the following equation:

$$\frac{dC}{dz} = \frac{C_{sw} - C_{pw}}{\Delta z} \tag{11}$$

where C_{pw} is the pore water concentration at 10 cm in the sediment, C_{sw} is the concentration in the stream directly above the sediment, and Δz is the distance (10 cm) between the two samples (Kalnejais et al., 2015). Positive values of *dC* indicate fluxes of dissolved metals into the stream; whereas, negative values indicate fluxes of metals into the sediment.

The diffusion coefficient (D_s) was calculated using:

$$D_s = \phi^2 D_0 \tag{12}$$

where D_0 is the diffusion coefficient for arsenate at 25°C (9.05×10^{-6} cm^2/sec) or Zn at 18°C (6.13×10^{-6} cm^2/sec; Li and Gregory,1974), and porosity (ϕ) was estimated to be around 0.3 for the fine sediment in the creeks (Fetter, 2001). D_s was calculated as 8.1×10^{-7} cm^2 sec^{-1} for As and 5.7×10^{-7} cm^2 sec^{-1} for Zn.

Once the average mass flux was calculated, the value was multiplied by the active area of the creeks (Eq. 13; Tables IV–VIII). The area for Blacktail and Silver Bow creeks was calculated by using Google Earth Pro 7.3 to measure the creek path between peepers 1 to 9 with a 6 m buffer (24,150 m^2). A 6 m buffer was selected as the average width of Blacktail and Silver Bow creeks based on five measurements from satellite imagery. The Grove Gulch area was estimated using the same approach as Blacktail and Silver Bow creeks, except with a 1.2 m buffer to represent the active portion of the creek and length from the Copper Mountain Sports Complex to the confluence with Blacktail Creek (2,058 m^{2}).

Table IV. As flux calculations.

Peeper	Δ Depth cm	As µg L^{1} 0 cm	As µg L^{-1} 10 cm	dC µg L-1	dC/dz µg L^{-1} cm^{-1}	D$_s$ * dC/dz µg sec^{-1} cm^{-2} 1000^{-1}	J µg sec^{-1} cm^{-2}	J µg d^{-1} m^{-2}
1	10	1.71	2.10	3.9E-01	3.9E-02	3.5E-10	9.5E-12	8.2E-03
2	10	3.1	9.00	5.9	5.9E-01	5.3E-09	1.4E-10	1.4E-01
3	10	2.74	169	1.7E+02	1.7E+01	1.5E-07	4.1E-09	3.5
4	10	9.2	65.8	5.7E+01	5.7	5.1E-08	1.4E-09	1.2
5	10	7.4	412	4.0E+02	4.0E+01	3.7E-07	9.9E-09	8.5
6	10	7.4	4.2	-3.2E+00	-3.2E-01	-2.9E-09	-7.8E-11	-6.8E-02
7	10	13.6	436	4.2E+02	4.2E+01	3.8E-07	1.0E-08	8.9
8	10	12.7	25.2	1.3E+01	1.3	1.1E-08	3.1E-10	2.6E-01
9	10	3.87	5.16	1.3	1.3E-01	1.2E-09	3.2E-11	2.7E-02
10	10	309	451	1.4E+02	1.4E+01	1.3E-07	3.5E-09	3.0
11	10	80.4	124	4.4E+01	4.4	4.0E-08	1.1E-09	9.3E-01
12	10	171	125	-4.6E+01	-4.6	-4.1E-08	-1.1E-09	-9.6E-01
13	10	10.7	154	1.4E+02	1.4E+01	1.3E-07	3.5E-09	3.0
14	10	5.2	24.4	1.9E+01	1.9	1.7E-08	4.7E-10	4.1E-01
16	10	1.61	4.23	2.6	2.6E-01	2.4E-09	6.4E-11	5.5E-02
17	10	1.98	17.8	1.6E+01	1.6	1.4E-08	3.9E-10	3.3E-01

Table V. Zn flux calculations.

Peeper	Δ Depth cm	Zn µg L^{-1} 0 cm	Zn µg L^{-1} 10 cm	dC µg L^{-1}	dC/dz µg L^{-1} cm^{-1}	Ds * dC/dz µg sec^{-1} cm^{-2} 1000^{-1}	J µg cm^{-2} sec^{-1}	J µg m^{-2} day^{-1}
1	10	126	125	-1.0	-1.0E-01	-9.1E-10	-1.7E-11	-1.5E-02
2	10	19.3	116	9.7E+01	9.7	8.8E-08	1.7E-09	1.4
3	10	6.4	0.0	-6.4	-6.4E-01	-5.8E-09	-1.1E-10	-9.4E-02
4	10	8.7	0.0	-8.7	-8.7E-01	-7.9E-09	-1.5E-10	-1.3E-01
5	10	8540	27800	1.9E+04	1.9E+03	1.7E-05	3.3E-07	2.8E+02
6	10	10.0	1100	1.1E+03	1.1E+02	9.9E-07	1.9E-08	1.6E+01
7	10	215.7	8640	8.4E+03	8.4E+02	7.6E-06	1.4E-07	1.2E+02
8	10	6.0	12	6.0	6.0E-01	5.4E-09	1.0E-10	8.8E-02
9	10	14	16	2.0	2.0E-01	1.8E-09	3.4E-11	2.9E-02
10	10	2.8	0.0	-2.8	-2.8E-01	-2.5E-09	-4.8E-11	-4.1E-02
11	10	12.2	0.0	-1.2E+01	-1.2	-1.1E-08	-2.1E-10	-1.8E-01
12	10	10.1	0.0	-1.0E+01	-1.0	-9.1E-09	-1.7E-10	-1.5E-01
13	10	6.7	0.0	-6.7E+00	-6.7E-01	-6.1E-09	-1.1E-10	-9.9E-02
14	10	544	0.0	-5.4E+02	-5.4E+01	-4.9E-07	-9.3E-09	-8.0
16	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0

The ponds were roughly traced with the path tool to find the area (12,000 and 62,000 m^2). The following equation was used to calculate the total diffusive flux for As and Zn:

$$F = J \cdot A \tag{13}$$

where F is the total diffusive flux (µg d^{-1}); J is the specific diffusive flux (µg m^{-2} d^{-1}); A is the area of the active channel (m^2).

Table VI. Average arsenic diffusive flux out of the sediment in Blacktail and Silver Bow creeks.

	As
Flux µg d^{-1}	3.53E+04
Flux mg d^{-1}	3.53E+01

Table VII. Zinc diffusive flux into the sediment in Grove Gulch (peeper 14).

	Zn
Flux µg d^{-1}	-1.65E+04
Flux mg d^{-1}	-1.65E+01

Table VIII. Average arsenic diffusive flux in the ponds. Pond 6 refers to location of peeper 6 and pond 7 refers to the location of peeper 7.

	Pond 6 As	Pond 7 As
Flux µg d-1	1.75E+04	9.06E+04
Flux mg d-1	1.75E+01	9.06E+01

The increase in solute concentration in the surface water due to diffusion of solutes from sediment-porewater was calculated using:

$$\Delta C = \frac{F}{d} \tag{14}$$

where ΔC is the change in solute concentration in the creek due to diffusion (µg L^{-1}); F is the diffusive flux of metal (µg d^{-1}); d is the creek discharge (L d^{-1}). The discharge values from USGS Gauging station 12323240 near the end of Blacktail Creek were used to calculate the increase in As concentration in Blacktail and Silver Bow creeks. Average monthly discharge values were used from October 2016 to October 2017 (Fig. 45). The discharge values from Lund (2018) were used for calculating Zn concentration in Grove Gulch. During periods of decreased discharge, the diffusing solutes will have a larger impact on the surface water concentrations, and during times of increased discharge the diffusing solutes will diluted (Table IX). Thus, diffusing solutes from the sediment-pore water will have the largest impact during the low flow periods in late summer and winter (Table IX; Fig. 46).

The range of discharge measurements for Grove Gulch were taken from Lund (2018; Table X; Fig. 47). The correlation between discharge and concentration was the same in Grove Gulch as in Blacktail and Silver Bow creeks; however, the sediment in Grove Gulch acted as a sink for dissolved Zn in the surface water represented by the negative value. Reducing the Zn concentration in the creek could directly reduce the amount of Zn stored in the sediment-pore water. This could possibly be a simple remedial solution for at least this part of the Grove Gulch reach.

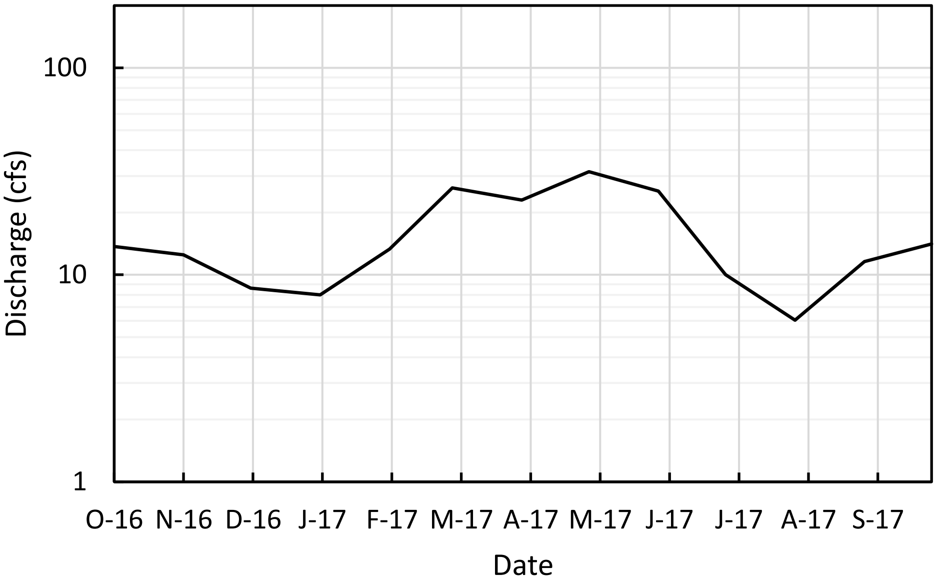


Figure 45. Monthly Blacktail Creek discharge at USGS gauging station (12323240) from 2016–2017.

Table IX. Predicted increase in dissolved As concentration in Blacktail and Silver Bow creeks due to diffusive flux out of the sediment based on average monthly discharge from USGS gauging station (12323240) for water year 2016 to 2017.

Date	Discharge cfs	Discharge L/day	Δ As µg/L
Oct-16	13.7	3.4E7	9.4E-04
Nov-16	12.5	3.1E7	1.0E-03
Dec-16	8.6	2.1E7	1.5E-03
Jan-17	8.0	2.0E7	1.6E-03
Feb-17	13.3	3.3E7	9.6E-04
Mar-17	26.3	6.4E7	4.9E-04
Apr-17	23.0	5.6E7	5.6E-04
May-17	31.5	7.7E7	4.1E-04
Jun-17	25.4	6.2E7	5.0E-04
Jul-17	10.0	2.4E7	1.3E-03
Aug-17	6.0	1.5E7	2.1E-03
Sep-17	11.6	2.8E7	1.1E-03
Oct-17	14.1	3.5E7	9.1E-04

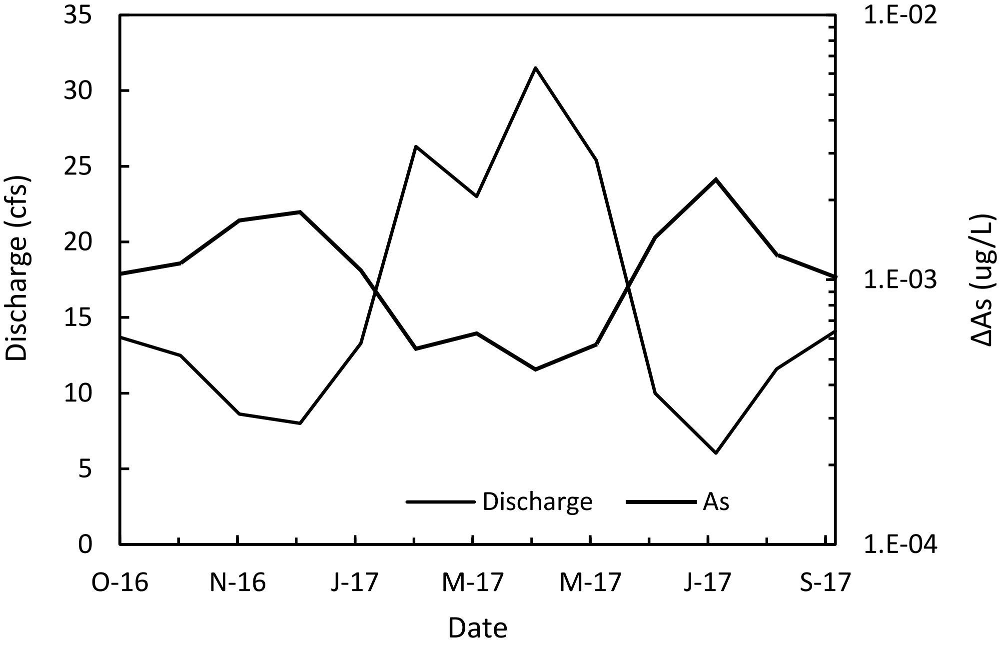


Figure 46. Comparison between discharge and load of As in Blacktail Creek and Silver Bow Creeks.

Table X. Predicted decrease in dissolved Zn concentration in Grove Gulch due to diffusive flux. Negative numbers indicate that the movement is from surface water into the sediment-pore water.

Discharge cfs	Discharge L day^{-1}	Δ Zn µg/L
1.0	2.4E6	-6.7E-03
0.8	2.0E6	-8.2E-03
0.6	1.5E6	-1.1E-02
0.4	9.8E5	-1.7E-02
0.2	5.0E5	-3.4E-02
0.1	2.4E5	-6.7E-02

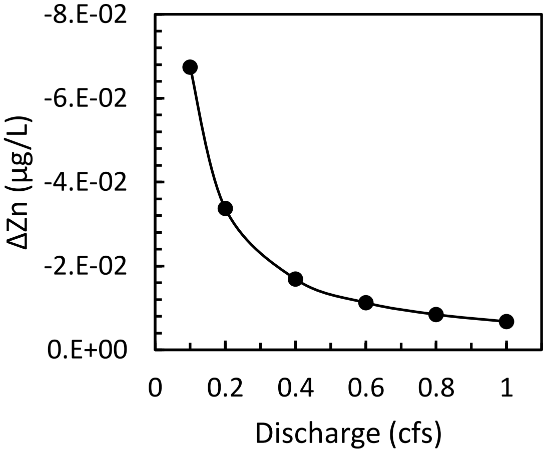


Figure 47. Grove Gulch Zn concentration and creek discharge.

Diffusive flux of dissolved solutes was calculated to be negligible for Blacktail and Silver Bow creeks (35 mg/day). The reaches contributing to the most As loading were the Slag Canyon and the Butte Chamber of Commerce area. The ponds had a diffusive flux of 91 mg/day. This is four orders of magnitude ($4.5x10^5$ mg/day) lower than the estimates from Warm Springs Ponds (WSP; Lee, 2012). WSPs have a significantly larger surface area, sediment volume, and a longer water retention time (weeks to months). This would allow As concentrations to increase in the surface water. In contrast, water probably takes a few hours to travel through the study site in the creeks. This short residence time would not be long enough for the slow diffusive flux of As from the sediment-pore water to increase the creek's surface water concentrations. The advective flux from groundwater is likely a larger contributor of metals to the creeks. The ponds have longer residence times as indicated by evaporated water isotopes (Appendix G). This could allow the As concentrations to build up in the ponds and could explain why the pond near Peeper 7, which showed the highest degree of evaporation based on isotopes, had elevated concentrations of As (13.7 μg/L) in its surface water.

The estimated decrease in Zn concentration in Grove Gulch due to the diffusion into the sediment was also relatively small. Additional peepers in Grove Gulch would help characterize the extent of the Zn loading into the sediment.

4.3. Conceptual model

The metal and nutrient concentrations studied in this project were probably occurring though several processes. One of the reactions increasing the sediment-pore water concentrations for As, Fe, Mn, and SRP was likely the reductive dissolution of Fe(III) and Mn(IV) oxides in the hyporheic zone which, when reduced, released trace metals (e.g., As) and nutrients (e.g., PO_4^{3-}) to the pore waters (Fig. 48). Another process occurring in the anerobic zone is the reduction of sulfate to sulfide. The released sulfide can then interact with the metals in the pore water forming insoluble sulfide minerals. The metals that are not captured by the sulfide can diffuse into the aerobic environment (~10 cm below the sediment-water interface) and can reoxidize or be suspended into the surface water. Contaminated groundwater was also a probable contributor of trace metals to the creeks (Fig. 49a). Support for sediment derived loading comes from the elevated metal concentrations (above Silver Bow County background levels) in the fine sediment fraction (< 74 µm; CDM Smith, 2016; Tetra Tech, 2016) and work in Warm Springs Ponds that identified elevated levels of As, Fe, and Mn in the sediment-pore waters (Fig. 49a; Lee, 2012; Boese, 2015). During high flow events or bioturbation, the fine sediment can be resuspended and carried away (Fig. 49b). Benner et al. (1995) estimated that 94% of the sediment-pore water in the hyporheic zone of Silver Bow Creek was from surface water. If this is the case in the study area, then surface water could flush dissolved metal out of the fine-sediment pore water (Fig. 49c). Disturbing the fine sediment exposes new sediment to oxidation and spreads metal-rich sediment downstream. The fine sediment in the creeks acts as a temporary sink for the metals that can be remobilized and distributed downstream during periods of high flow.

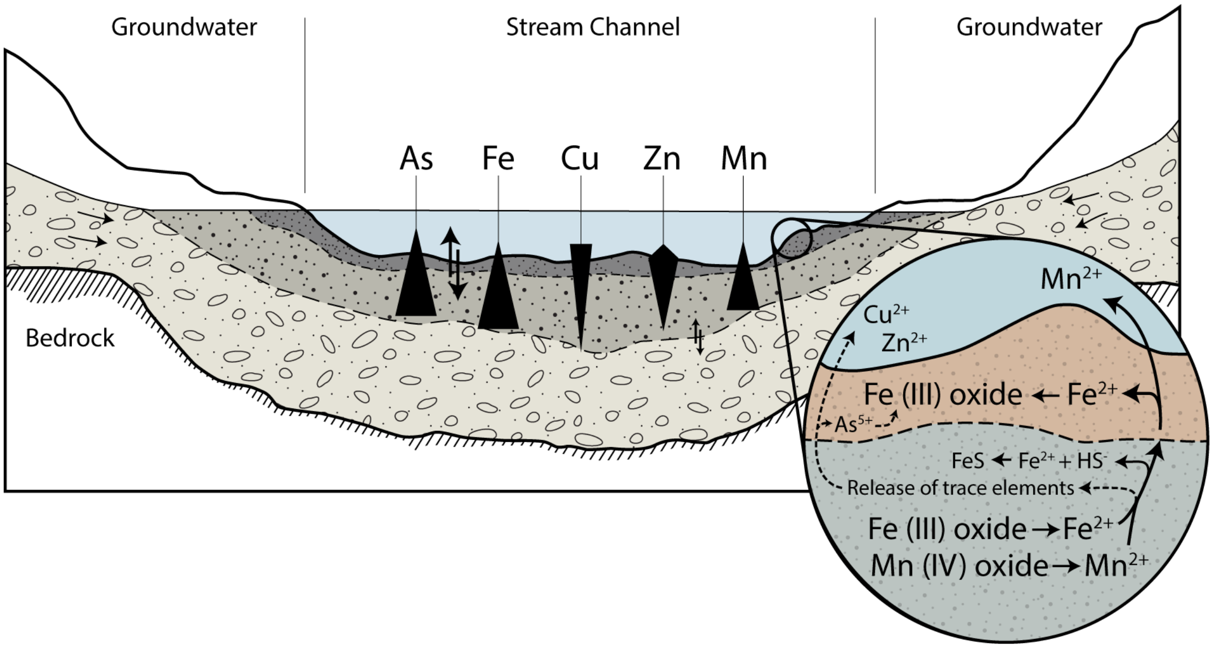


Figure 48. Conceptual model of metal concentrations within the creeks and the role Fe and Mn oxides play in trace metal mobility (modified from Triska et al., 1989; Stumm and Morgan, 1996). The relative sediment-pore water solute concentrations are indicated by the black triangles, the arrows indicate pore water can freely move between layers with the most exchange occurring near the sediment-water interface. The small arrows are on the stream water and groundwater interface.

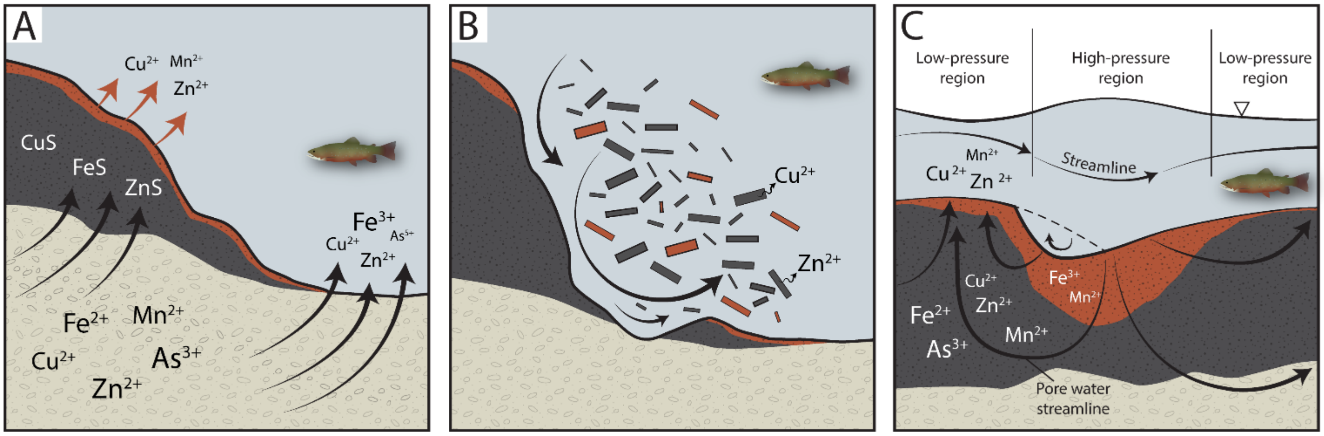


Figure 49. Hypothesized pathways for metal loading in the creeks.
(A) Contaminated groundwater enters the creeks from two pathways. The first pathway is directly into the creek; whereas, the other pathway is through fine sediment. The sediment may act as a temporary sink for metals. (B) Contaminated fine sediment is resuspended by high flow events and bioturbation. (C) Surface water actively flows through the shallow hyporheic zone.

5. Conclusions and Recommendations

5.1. Conclusions

This study conducted a high-resolution sampling of hyporheic pore water and sediment in Blacktail and Silver Bow creeks to characterize metal and nutrient concentrations. The important findings are as follows:

- Sediment-pore water samplers (peepers) were successful in a fluvial environment when the bed was fine grained. If the sediment was coarse grained, the peepers could not be installed successfully. The cm-scale resolution provided by the peepers allowed detailed profiling of metal and nutrient concentrations with depth across the sediment-water interface.
- Generally, pore water analytes increased in concentrations with depth below the sediment-water interface (e.g., As, Fe, Mn, SRP). The close parallels in the concentrations of As, Fe, Mn, and SRP support the idea that the reductive dissolution of Fe- and Mn-oxides was responsible for many of the solute trends in the pore water. Fe-and Mn-oxide minerals underwent reductive dissolution during the microbial decay of organic carbon with Mn-oxide reduction occurring first followed by Fe-oxide. The adsorbed As and SRP on the oxides was then released to the pore water.
- The dissolved Fe was then precipitated as a sulfide (in the presence of H_2S) or reoxidized if the ion diffused into an oxidizing environment. If Fe-oxide re-precipitated, it could recapture the dissolved arsenic as it diffused upwards.
- Evidence of bacterial sulfate reduction was present in many of the peepers that showed a decrease in sulfate concentrations with depth. Sulfate was microbially reduced to hydrogen sulfide which then captured dissolved Cu, Fe, or Zn to form insoluble sulfide minerals in the anaerobic environment.

- Other peepers showed an increase in sulfate concentration with depth which is most likely due to upwelling of contaminated groundwater.
- The ponds had similar pore-water concentrations of Fe, Mn, and Zn as the creeks. The pond that peeper 7 was deployed in had elevated surface-water concentrations of As, possibly due to upwards diffusion of As from the sediment coupled with a long residence time of water in the shallow pond.
- Sediment cores from the creeks had elevated metal (e.g., As, Cu, Fe, Mn, Zn) concentrations compared to the established background levels for Silver Bow County soils. The metal concentrations in the sediment were heavily dependent on the sediment character. In areas with fine sediment (<0.06 mm) and high organic content, metal concentrations tended to be high; whereas, in areas of sand size particles (0.06–2 mm) to gravel (2–20 mm) the metal concentrations were lower. Generally, metal concentrations in sediment increased with depth below the sediment-water interface.
- The sediment core sample from the Slag Canyon (peeper 12) showed vertical changes in mineralogy based on XRD analyses. The top 22 cm of sediment were mainly oligoclase, quartz, and muscovite. Directly below 22 cm, the sediment had a thin band of elevated calcite with quartz, muscovite, and pyrite. The dominant minerals below 26 cm were quartz, muscovite, and pyrite. Pyrite constituted about 5% of the solid mass in these areas. The transition was interpreted as modern stream sediment covering older mill tailings.
- Diffusive fluxes of dissolved solutes such as As and Zn were calculated to be negligible for Blacktail and Silver Bow creeks. The areas contributing most to the loading were in the Slag Canyon and the Butte Chamber of Commerce area. The estimated arsenic diffusive flux of 35 mg/day for the creeks and 91 mg/day for ponds is four orders of magnitude (4.5×10^5 mg/day)

lower than the estimates from Warm Springs Ponds (Lee, 2012). This was reasonable, because the ponds have a much greater surface area, sediment volume, and a longer water residence time.

- The advective flux from influent groundwater is likely a much larger source of dissolved metal loading to the creeks than the diffusive flux from the sediment-pore water.
- On a timescale of months to years, the creeks act as temporary storage for fine, metal-rich sediment. High flow events (e.g., spring runoff, storm events) or bioturbation removes and mobilizes both reduced and oxidized sediment. This spreads contaminated sediments further downstream potentially recontaminating the previously remediated areas.

5.2. Recommendations

- This study has shown that peepers can be successfully deployed in mining impacted streams and could be applicable to other contaminated fluvial systems where detailed geochemical profiles are desirable. Some caveats when using peepers: the bed sediment must be relatively fine grained, peepers must be deoxygenated before installation and sampled in anoxic conditions, and peepers require 2–3 weeks to reach equilibrium.
- Any study utilizing peepers should take pH and Eh measurements if possible. Microelectrodes in this study proved to be fickle, but possibly a better method could be used. Having pH and Eh data would allow more accurate modeling of the geochemical processes in the hyporheic zone.
- Use temperature buttons (HOBO loggers) in all future deployments. This would help understand direction of advective fluxes.
- Beaver mimicry structures or small dams could be used to capture resuspended metal rich sediment that is mobilized during high flow events. The sediment could then be dredged or

siphoned from the creek channel. Beaver mimicry can dramatically alter the stream channel morphology for better or worse. Dredging of the sediment also can have negative environmental impacts. One of the benefits of this method would be that it is inexpensive to implement. The removal of the contaminated sediments from the stream channel and floodplain of Blacktail and Silver Bow creeks would reduce the amount of metal loading occurring during high flow and storm events.

- Many shallow hydrogeological systems show distinct differences in chemistry between seasons (e.g., summer and winter; Santos-Echeandia, 2009). To test for seasonal changes occurring in the sediment pore water of the creeks, it would be helpful to sample one or two locations every few months over a one-year cycle.
- This study did not investigate the amount of sulfide stored in the sediment; however, this information would be useful in quantifying the amount of metals potentially captured in the sediment as sulfides. This could be accomplished by an acid volatile sulfide test. The captured H_2S could be recovered and analysed for S-isotopes to test whether the sulfide in the sediment is detrital ("rock" sulfide) or biological.
- New wetlands built along the upper Silver Bow Creek corridor will likely have high accumulation of As, Fe, and Mn in their sediment-pore waters. Unlike the creeks, which have short water retention times, concentrations of dissolved As could build up in these ponds by upward diffusion out of the sediment.

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7. Appendix A: Field parameter data

Table XI. Sampling plan for peepers 1–13.

Cell	ICP-Metals	H_2S	SRP	NH4-N	Alkalinity	IC-Anions
0	🟩	🟦	🟧	🟨	🟩	🟦
1			A			
2					🟩	
3				A		
4	🟩					
5		A				B
6					🟩	
7			A			
8	🟩					
9				A		B
10					🟩	
11		A				
12	🟩					
13			A			B
14					🟩	
15				A		
16	🟩					
17		A				B
18					🟩	
19			A			
20	🟩					
21				A		B
22					🟩	
23		A				
24	🟩					
25			A			B
26					🟩	
27				A		
28	🟩					

Table XII. Sampling plan for peepers 14–17.

Cell	ICP-Metals	H_2S	SRP	Alkalinity	IC-Anions
0	🟩	🟦	🟧	A & B	🟦
1			A		B
2	🟩				
3				A & B	
4	🟩				
5		A			B
6	🟩				
7			A		
8	🟩				
9				A & B	
10	🟩				
11		A			B
12	🟩				
13			A		
14	🟩				
15				A & B	
16	🟩				
17		A			B
18	🟩				
19			A		
20	🟩				
21				A & B	
22	🟩				
23		A			
24	🟩				
25			A		B
26	🟩				
27				A & B	
28	🟩				

Table XIII. Alkalinity (continued on next page). SWI stands for depth below the sediment-water interface.

Sample	SWI (cm)	Alkalinity ppm CaCO3	Sample	SWI (cm)	Alkalinity ppm CaCO3	Sample	SWI (cm)	Alkalinity ppm CaCO3
1.00	6	65	6.02	2	201	11.06	-3	257
1.02	2	54	6.06	-3	229	11.10	-8	673
1.06	-3	48	6.10	-8	307	11.14	-13	552
1.10	-8	46	6.14	-13	348	11.18	-18	500
1.14	-13	44	6.18	-18	416	11.22	-23	500
1.18	-18	44	6.22	-23	351	11.26	-28	559
1.22	-23	44	6.26	-28	383	12.00	6	106
1.26	-28	45	7.02	2	216	12.02	2	107
2.00	6	91	7.06	-3	250	12.06	-3	290
2.02	2	104	7.10	-8	373	12.10	-8	221
2.06	-3	109	7.14	-13	571	12.14	-13	188
2.10	-8	106	7.18	-18	326	12.18	-18	200
2.14	-13	118	7.22	-23	285	12.22	-23	184
2.18	-18	124	7.26	-28	322	12.26	-28	200
2.22	-23	129	8.00	6	95	13.00	6	103
2.26	-28	147	8.02	2	108	13.02	2	87
3.00	6	102	8.06	-3	130	13.06	-3	184
3.02	2	124	8.10	-8	129	13.10	-8	171
3.06	-3	119	8.14	-13	168	13.14	-13	189
3.10	-8	204	8.18	-18	170	13.18	-18	186
3.14	-13	202	8.22	-23	333	13.22	-23	198
3.18	-18	272	8.26	-28	235	13.26	-28	286
3.22	-23	278	9.00	10	105	14.00	6	143
3.26	-28	311	9.02	8	21	14.03	1	137
4.00	6	96	9.06	4	80	14.09	-7	194
4.02	2	98	9.10	-2	114	14.15	-14	96
4.06	-4	—	9.14	-5	158	14.21	-22	336
4.10	-8	272	9.18	-10	194	14.27	-29	436
4.14	-13	247	9.22	-15	167	16.00	6	106
4.18	-18	234	9.26	-20	173	16.03	1	132
4.22	-23	222	10.00	6	114	16.09	-7	99
4.26	-28	231	10.02	2	136	16.15	-14	105
5.00	6	101	10.06	-3	370	16.21	-22	124
5.02	2	31	10.10	-8	545	16.27	-29	85
5.07	-4	74	10.14	-13	604	17.00	6	178
5.10	-8	61	10.18	-18	571	17.03	1	173
5.14	-13	54	10.22	-23	537	17.09	-7	176
5.18	-18	50	10.26	-28	371	17.15	-14	188
5.22	-23	49	11.00	6	121	17.21	-22	238
5.26	-28	52	11.02	2	146	17.27	-29	248

Table XIV. Soluble reactive phosphate from HACH method (continued on next page).

Sample	SWI (cm)	SRP as PO4 ppm	SRP as P ppm	Sample	SWI (cm)	SRP as PO4 ppm	SRP as P ppm
1.00	6	0.37	0.12	PZ-3	—	1.26	0.41
1.01	3	—	—	PZ-4	—	2.50	0.82
1.07	-4	0.49	0.16	7.00	6	0.11	0.04
1.13	-12	0.50	0.16	7.01	3	0.08	0.02
1.19	-19	0.63	0.20	7.07	-4	0.16	0.05
1.25	-27	0.66	0.22	7.13	-12	1.64	0.50
2.00	6	0.01	0.00	7.19	-19	1.53	0.45
2.01	3	0.02	0.01	7.25	-27	1.44	0.43
2.07	-4	—	—	8.00	6	0.37	0.12
2.13	-12	0.01	0.00	8.01	3	—	—
2.19	-19	0.04	0.01	8.07	-4	0.39	0.13
2.21	-22	0.06	0.02	8.13	-12	0.82	0.27
3.00	6	0.03	0.01	8.19	-19	1.24	0.40
3.01	3	0.11	0.04	8.25	-27	2.78	0.91
3.07	-4	1.50	0.49	9.00	10	0.32	0.10
3.13	-12	2.11	0.69	9.01	9	0.19	0.06
3.19	-19	5.38	1.75	9.07	3	0.11	0.03
3.25	-27	3.06	1.00	9.13	-4	0.39	0.13
4.00	6	1.55	0.51	9.19	-11	0.42	0.14
4.01	3	0.18	0.06	9.25	-18	0.48	0.16
4.07	-4	4.20	1.37	10.00	6	0.48	0.16
4.13	-12	7.36	2.40	10.01	3	—	—
4.19	-19	7.10	2.31	10.07	-4	3.11	1.02
4.25	-27	5.88	1.92	10.13	-12	3.74	1.22
5.00	6	0.29	0.10	10.19	-19	4.89	1.59
5.01	3	0.43	0.14	10.25	-27	3.20	1.04
5.07	-4	0.31	0.10	11.00	6	0.28	0.09
5.11	-12	0.29	0.09	11.01	3	0.19	0.06
5.19	-19	0.70	0.23	11.07	-4	0.78	0.25
5.25	-27	1.20	0.39	11.13	-12	3.80	1.24
6.01	3	2.52	0.79	11.19	-19	1.64	0.53
6.07	-4	4.03	1.26	11.25	-27	—	—
6.13	-12	1.51	2.10	12.00	6	0.37	0.12
6.19	-19	1.26	1.92	12.01	3	0.17	0.06
6.25	-27	1.96	3.10	12.07	-4	4.47	1.46
PZ-1	—	0.45	0.15	12.13	-12	4.30	1.40
PZ-2	—	0.45	0.15	12.19	-19	3.97	1.29

Table XV. Soluble reactive phosphate.

Sample	SWI (cm)	SRP as PO4 ppm	SRP as P ppm
12.25	-27	3.72	1.21
13.00	6	0.63	0.20
13.01	3	0.10	0.03
13.07	-4	1.54	0.50
13.13	-12	3.01	0.98
13.19	-19	1.92	0.63
13.25	-27	2.42	0.79
14.00	6	—	—
14.01	3	0.12	0.04
14.07	-5	0.75	0.24
14.13	-12	4.20	1.37
14.19	-19	2.57	0.84
14.25	-24	1.16	0.38
16.00	6	0.19	0.06
16.01	3	0.28	0.09
16.07	-5	2.20	0.72
16.13	-12	2.20	0.72
16.19	-19	0.08	0.03
16.25	-24	0.15	0.05
17.00	6	0.32	0.10
17.01	3	0.10	0.03
17.07	-5	0.17	0.06
17.13	-12	1.10	0.36
17.19	-19	0.26	0.09
17.25	-24	0.29	0.09

Table XVI. H_2S data for sampled peepers.

Sample	SWI (cm)	H_2S (mg/L)	Corrected H_2S (mg/L)
1.05	-2	Under-range for dilution	—
1.11	-9	Under-range for dilution	—
1.17	-17	Under-range for dilution	—
1.23	-24	Under-range for dilution	—
4.05	-2	—	—
4.11	-9	0.006	2.99E-05
4.17	-17	0.014	3.67E-03
4.23	-24	0.012	3.24E-03
6.05	-2	0.064	0.266
6.07	-4	0.275	1.050
6.11A	-9	0.028	0.105
6.11B	-9	0.641	2.562
6.17	-17	0.045	0.188
6.23	-24	0.145	0.530
PZ-1	—	0.01	0.010
PZ-2	—	0.001	0.001
PZ-3	—	0.568	0.568
PZ-4	—	0.018	0.018
7.05	-2	0.001	0.004
7.11	-9	0.002	0.008
7.17	-17	0.002	0.008
7.23	-24	0.000	0.000
8.05	-2	0.001	0.005
8.17	-17	0.004	0.024
8.23	-24	0.011	0.056
12.05	-2	Under-range for dilution	—
12.11	-9	Under-range for dilution	—
12.17	-17	0.001	0.0064
12.23	-24	0.001	0.0061
14.05	-2	Under-range for dilution	—
14.11	-9	Under-range for dilution	—
14.17	-17	Under-range for dilution	—
14.23	-24	Under-range for dilution	—

8. Appendix B: IC, ICP-MS, and ICP-OES data

Table XVII. IC data for peepers.

	Sulfate	SWI		Sulfate	SWI		Sulfate	SWI
Sample	mg/L	cm	Sample	mg/L	cm	Sample	mg/L	cm
2.00	35.5	6	6.21	6.8	-22	12.05	18.8	-2
2.01+2.03	40.0	-1	6.25	8.3	-27	12.09	162	-7
2.05+2.07	37.9	-5	7.00	14.3	6	12.13	174	-12
2.09+2.11	39.7	-8	7.05	11.2	-2	12.19	180	-17
2.13+2.15	39.4	-10	7.09	6.2	-7	12.21	172	-22
2.17+2.19	39.7	-18	7.13	5.7	-12	12.25	174	-27
2.23	43.7	-24	7.17	6.1	-17	13.00	30.8	6
2.25+2.27	40.3	-25	7.21	6.9	-22	13.05	393	-2
3.00	35.7	6	7.25	8.4	-27	13.07	387	-7
3.05	42.9	-2	8.00	27.5	6	13.13	382	-12
3.09	29.8	-7	8.05	29.7	-2	13.19	354	-17
3.13	27.3	-12	8.09	25.4	-7	13.21	364	-22
3.17	31.5	-17	8.13	20.7	-12	13.25	346	-27
3.21	37.3	-22	8.17+8.19	13.4	-18	14.00	83.5	6
3.25	26.5	-27	8.21	12.3	-22	14.01	82.2	3
4.00	31.2	6	8.25	8.2	-27	14.05	72.9	-2
4.03	38.7	-2	9.00	90.9	10	14.11	17.6	-9
4.09	412	-7	9.05	95.2	5	14.17	15.5	-17
4.13	505	-12	9.09	94.6	1	14.25	10.4	-27
4.17	521	-17	9.13	83.0	-4	16.00	36.5	6
4.21	494	-22	9.17	70.8	-8	16.01	40.4	3
4.25	474	-27	9.21	74.0	-13	16.05	30.3	-2
5.00	31.3	6	9.25	81.2	-18	16.11	23.8	-9
5.03	327	-2	10.00	33.7	6	16.17	26.3	-17
5.09	2197	-7	10.05	5.7	-2	16.25	33.6	-27
5.13	2936	-12	10.09	5.5	-7	17.00	41.6	6
5.17	2701	-17	10.13	6.1	-12	17.01	44.8	3
5.21	2739	-22	10.15	5.2	-17	17.05	42.2	-2
5.25	2843	-27	10.23	5.8	-22	17.11	40.7	-9
PZ-1	24.9	—	10.25	6.0	-27	17.17	35.2	-17
PZ-2	1.5	—	11.00	76.3	6	17.25	7.6	-27
PZ-3	77.6	—	11.05	45.7	-2			
PZ-4	0.968	—	11.09	11.1	-7			
6.00	31.8	6	11.13	7.6	-12			
6.05	16.0	-2	11.17	8.1	-17			
6.09	9.1	-7	11.21	9.3	-22			
6.13	6.3	-12	11.27	10.1	-29			
6.17	6.5	-17	12.00	29.7	6			

Table XVIII. ICP-MS data for peepers 1–3. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI cm	7Li µg/L	11B µg/L	27Al µg/L	(31P) µg/L	(19K) mg/L	(20Ca) mg/L	49Ti µg/L	51V µg/L	55Mn mg/L	56Fe mg/L	59Co µg/L	60Ni µg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
1.00	6	< 1.7	20.8	< 1.7	48	2.7	36.6	< 1.7	2.8	0.022	0.027	< 1.7	< 1.7
1.04	0	< 2.5	17.4	< 2.5	39	2.8	29.3	< 2.6	5.1	< 0.01	< 0.026	< 2.6	< 2.6
1.08	-5	6.1	17.8	< 1.5	57	2.6	29.8	< 1.5	4.6	< 0.006	< 0.015	< 1.5	< 1.5
1.12	-10	6.0	17.4	< 1.2	56	2.6	29.3	< 1.3	4.5	< 0.005	< 0.013	< 1.3	< 1.3
1.16	-15	6.2	17.5	< 1.2	64	2.6	29.5	< 1.3	3.8	< 0.005	< 0.013	< 1.3	< 1.3
1.20	-20	5.8	16.5	< 1.2	71	2.5	29.2	< 1.3	3.0	< 0.005	< 0.013	< 1.3	< 1.3
1.24	-24	6.1	16.9	1.3	71	2.5	28.8	< 1.2	3.7	< 0.005	< 0.012	< 1.2	< 1.2
1.28	-30	6.1	17.1	2.9	53	2.5	28.7	< 1.2	3.0	0.003	0.005	< 1.2	< 1.2
2.00	6	8.9	25.4	6.1	52	3.4	35.4	2.4	2.3	0.060	0.089	< 1.0	< 1.0
2.04	0	9.5	27.6	1.2	62	3.6	35.7	< 1.0	2.0	0.021	0.065	< 1.0	< 1.0
2.08	-5	14.6	33.2	< 1.0	44	3.2	32.3	< 1.0	2.7	0.031	0.030	< 1.0	< 1.0
2.12	-10	32.4	46.2	< 1.0	26	3.0	35.9	< 1.0	< 1.0	1.23	0.118	< 1.0	< 1.0
2.16	-15	38.7	54.1	1.7	259	3.4	37.8	< 1.0	< 1.0	1.78	1.54	< 1.0	< 1.0
2.20	-20	38.5	52.4	< 1.0	461	3.5	38.1	< 1.0	< 1.0	1.84	1.97	< 1.0	< 1.0
2.24	-24	41.8	61.7	1.5	252	3.9	41.0	< 1.0	< 1.0	1.94	1.44	< 1.0	< 1.0
2.28	-30	28.0	78.2	2.1	489	5.1	46.0	< 1.0	< 1.0	2.32	2.55	< 1.0	< 1.0
3.00	6	173	140	< 1.0	34	3.0	37.5	< 1.0	2.4	0.057	0.017	< 1.0	< 1.0
3.04	0	38.2	49.3	< 1.0	20	3.4	38.6	< 1.0	< 1.0	0.313	0.187	< 1.0	< 1.0
3.08	-5	37.5	58.9	< 1.0	363	4.3	40.1	< 1.0	< 1.0	0.379	3.30	< 1.0	< 1.0
3.12	-10	27.1	182	< 1.0	2130	11.3	45.5	< 1.0	2.9	0.522	9.71	< 1.0	< 1.0
3.16	-15	25.7	309	< 1.0	2220	16.8	50.3	< 1.0	2.9	0.575	10.9	< 1.0	< 1.0
3.20	-20	32.9	512	< 1.0	2120	22.9	64.5	< 1.0	2.7	0.714	13.7	< 1.0	< 1.0
3.24	-24	29.4	565	< 1.0	2250	29.4	62.4	< 1.0	2.6	0.736	13.7	< 1.0	< 1.0
3.28	-30	30.2	733	1.5	1780	32.8	66.2	< 1.0	2.7	0.897	16.4	< 1.0	< 1.0

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XIX. ICP-MS data for peepers 1–3.

	SWI cm	63Cu µg/L	66Zn µg/L	71Ga µg/L	75As µg/L	85Rb µg/L	88Sr µg/L	98Mo µg/L	111Cd µg/L	137Ba µg/L	182W µg/L	Total Pb µg/L	238U µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
1.00	6	< 3	< 3	2.7	2.5	< 1.7	226	5.8	<0.7	49	< 0.7	< 0.7	4.3
1.04	0	< 5	126	< 2.6	1.7	< 2.6	180	11.3	1.1	25	1.6	< 1.0	< 1.0
1.08	-5	8	129	< 1.5	2.0	< 1.5	189	12.8	< 0.6	24	1.8	< 0.6	1.3
1.12	-10	< 3	125	< 1.3	2.1	< 1.3	188	12.3	< 0.5	24	1.7	< 0.5	1.4
1.16	-15	< 3	123	< 1.3	2.3	< 1.3	192	11.7	< 0.5	24	1.7	< 0.5	1.2
1.20	-20	< 3	112	< 1.3	2.1	< 1.3	190	10.9	< 0.5	23	1.6	< 0.5	1.1
1.24	-24	< 2	111	< 1.2	1.8	< 1.2	190	10.3	0.8	22	1.4	< 0.5	1.3
1.28	-30	< 2	83	1.3	1.4	< 1.2	185	10.0	< 0.5	25	1.3	< 0.5	1.1
2.00	6	< 2	6	2.6	2.0	1.4	203	5.7	< 0.5	50	< 0.5	< 0.5	4.3
2.04	0	5	19	2.4	3.1	< 1.0	209	7.2	< 0.5	49	< 0.5	< 0.5	4.3
2.08	-5	15	422	2.9	9.4	< 1.0	184	6.2	1.1	55	< 0.5	0.8	4.2
2.12	-10	5	116	3.9	9.0	< 1.0	207	10.0	< 0.5	76	1.0	< 0.5	5.9
2.16	-15	< 2	24	3.8	32	< 1.0	229	11.7	< 0.5	74	1.7	0.7	5.8
2.20	-20	< 2	10	4.0	45	< 1.0	237	11.1	< 0.5	75	1.8	< 0.5	5.3
2.24	-24	< 2	27	3.6	46	< 1.0	263	9.4	< 0.5	70	1.8	< 0.5	5.1
2.28	-30	< 2	16	4.1	56	< 1.0	324	3.8	< 0.5	80	2.2	0.6	2.8
3.00	6	< 2	6	3.0	2.9	< 1.0	215	5.5	< 0.5	58	0.6	< 0.5	4.5
3.04	0	< 2	< 2	2.8	2.7	< 1.0	219	6.2	< 0.5	53	0.6	< 0.5	3.1
3.08	-5	< 2	< 2	3.3	21	< 1.0	237	5.9	< 0.5	66	0.9	< 0.5	2.6
3.12	-10	< 2	< 2	5.3	169	2.9	336	3.2	< 0.5	104	2.1	< 0.5	1.1
3.16	-15	< 2	< 2	6.4	193	4.1	391	2.3	< 0.5	124	2.5	< 0.5	0.7
3.20	-20	< 2	< 2	7.1	253	5.6	518	3.4	< 0.5	135	3.1	< 0.5	1.8
3.24	-24	< 2	< 2	6.0	235	5.7	494	3.6	< 0.5	118	3.1	< 0.5	1.5
3.28	-30	< 2	< 2	6.3	213	5.6	528	2.9	< 0.5	123	3.2	< 0.5	1.3

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XX. ICP-MS data for peepers 4–6. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI	7Li	11B	27Al	(31P)	(19K)	(20Ca)	49Ti	51V	55Mn	56Fe	59Co	60Ni
	cm	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
4.00	6	2.8	11.8	7.23	45	0.1	10.6	< 1.5	1.8	0.1	0.23	< 1.5	< 1.5
4.04	0	3.0	8.6	5.76	34	0.1	11.4	< 1.5	2.1	0.0	0.14	< 1.5	< 1.5
4.06	-3	5.3	13.8	< 1.5	< 15	0.2	17.8	< 1.5	< 1.5	3.0	0.42	0.6	< 1.5
4.08	-5	13.7	71.5	< 1.5	26	0.7	42.0	< 1.5	< 1.5	6.5	23	1.0	< 1.5
4.12	-10	24.1	163	0.656	5280	1.6	81.1	< 1.5	3.3	8.2	39	0.7	< 1.5
4.16	-15	25.4	211	3.52	4590	1.8	86.6	< 1.5	2.8	9.0	30	0.7	< 1.5
4.20	-20	22.1	201	1.46	5880	1.7	83.2	< 1.5	3.2	8.9	38	0.8	< 1.5
4.24	-25	22.6	206	6.32	3690	1.9	83.9	< 1.5	1.8	7.9	24	0.7	< 1.5
4.28	-30	21.4	197	2.12	7020	2.1	79.2	< 1.5	3.8	8.4	35	0.6	< 1.5
5.00	6	2.8	7.2	42.7	46	0.1	10.4	< 1.5	2.1	0.1	0.39	< 1.5	< 1.5
5.04	0	11.8	28.4	46.5	< 15	0.6	46.1	< 1.5	< 1.5	12.8	69	15.7	13
5.06	-3	9.7	23.5	16.4	< 15	0.5	35.0	< 1.5	< 1.5	12.6	78	12.5	12
5.08	-5	13.3	31.7	21.5	< 15	0.6	60.5	< 1.5	< 1.5	32.1	274	26.0	26
5.12	-10	18.6	40.2	12.4	54	1.0	105	< 1.5	< 1.5	44.8	522	40.4	33
5.16	-15	19.5	44.2	2.10	125	0.8	123	< 1.5	< 1.5	54.9	471	32.2	12
5.20	-20	17.4	42.6	3.18	13	0.7	113	< 1.5	< 1.5	37.6	527	13.8	4
5.24	-25	19.4	48.4	3.16	74	0.6	123	< 1.5	< 1.5	29.6	609	7.7	< 1.5
5.28	-30	20.0	52.6	11.1	59	0.8	135	< 1.5	< 1.5	25.0	604	6.9	< 1.5
6.00	6	7.4	31.9	3.3	16	1.6	25.2	< 1.5	2.3	0.01	0.01	< 1.5	< 1.5
6.04	0	6.7	33.2	2.3	1020	4.4	40.1	< 1.5	< 1.5	0.27	0.02	< 1.5	< 1.5
6.08	-5	7.5	35.4	< 1.5	1680	5.7	48.9	< 1.5	< 1.5	0.38	0.06	< 1.5	< 1.5
6.12	-10	8.2	40.5	9.9	2510	6.8	61.3	< 1.5	< 1.5	0.85	1.10	< 1.5	< 1.5
6.16	-15	8.2	48.9	1.8	2720	6.8	70.6	< 1.5	< 1.5	1.27	3.10	< 1.5	< 1.5
6.20	-20	5.8	45.3	< 1.5	3070	6.2	65.2	< 1.5	< 1.5	1.81	7.41	< 1.5	< 1.5
6.24	-24	5.4	51.6	< 1.5	3620	14.7	70.1	< 1.5	< 1.5	2.44	11.1	< 1.5	< 1.5
6.28	-30	<1.5	54.4	2.4	4370	8.2	68.4	< 1.5	< 1.5	3.26	16.2	< 1.5	< 1.5

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXI. ICP-MS data for peepers 4–6.

	SWI	63Cu	66Zn	71Ga	75As	85Rb	88Sr	98Mo	111Cd	137Ba	182W	Total Pb	238U
	cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
4.00	6	6	9	1.6	1.6	< 1.5	185	6.2	< 0.2	13	< 0.2	< 0.6	3.6
4.04	0	7	< 2	1.7	3.2	< 1.5	198	5.9	< 0.2	13	< 0.2	< 0.6	3.9
4.06	-3	< 3	16	3.1	2.5	3.5	286	10.2	< 0.2	27	0.3	< 0.6	6.1
4.08	-5	< 3	< 2	6.9	21.5	8.9	724	9.4	< 0.2	59	1.4	< 0.6	7.3
4.12	-10	< 3	< 2	16.1	23.1	23.1	1530	< 1.5	< 0.2	137	1.0	< 0.6	0.7
4.16	-15	< 3	< 2	13.5	8.1	29.2	1520	< 1.5	< 0.2	127	1.0	< 0.6	< 0.6
4.20	-20	< 3	< 2	14.0	10.4	30.5	1450	< 1.5	< 0.2	128	1.0	< 0.6	< 0.6
4.24	-25	< 3	155	9.7	14.4	34.6	1460	4.0	< 0.2	95	0.8	< 0.6	< 0.6
4.28	-30	< 3	4	14.0	10.1	33.7	1460	< 1.5	< 0.2	121	1.0	< 0.6	< 0.6
5.00	6	11	12	1.8	1.6	< 1.5	187	7.8	< 0.2	14	< 0.2	1.6	3.7
5.04	0	10	8540	3.3	3.4	7.1	470	1.6	1.0	38	< 0.2	< 0.6	0.8
5.06	-3	3	10200	2.6	6.4	8.5	414	1.6	< 0.2	23	< 0.2	< 0.6	< 0.6
5.08	-5	< 3	22800	2.2	40.3	13.8	772	4.2	< 0.2	16	< 0.2	< 0.6	1.8
5.12	-10	8	27800	2.1	144	14.2	1150	10.1	< 0.2	20	0.3	< 0.6	7.5
5.16	-15	4	484	2.5	178	15.4	1340	12.1	< 0.2	24	0.6	1.1	14.7
5.20	-20	4	567	2.1	222	19.7	1170	7.1	< 0.2	19	0.3	< 0.6	13.5
5.24	-25	4	169	2.0	689	24.6	1060	5.6	< 0.2	20	0.4	1.0	8.6
5.28	-30	7	383	1.7	1050	28.1	977	4.6	< 0.2	20	0.4	1.1	6.5
6.00	6	< 3	< 3	10.6	7.4	< 1.5	182	6.7	< 0.6	243	2.8	< 0.6	3.9
6.04	0	< 3	< 3	12.5	1.7	< 1.5	245	< 1.5	< 0.6	275	0.6	< 0.6	0.6
6.08	-5	< 3	< 3	13.5	2.8	< 1.5	295	< 1.5	< 0.6	325	0.7	< 0.6	0.8
6.12	-10	< 3	3	16.3	4.2	< 1.5	374	< 1.5	< 0.6	385	0.7	< 0.6	0.9
6.16	-15	< 3	< 3	17.5	4.8	< 1.5	409	< 1.5	< 0.6	432	0.6	< 0.6	0.9
6.20	-20	< 3	< 3	17.6	7.0	< 1.5	396	1.3	< 0.6	421	0.6	< 0.6	0.9
6.24	-24	< 3	< 3	17.9	8.1	1.5	429	< 1.5	< 0.6	447	0.6	< 0.6	1.1
6.28	-30	< 3	< 3	24.2	11.5	< 1.5	452	< 1.5	< 0.6	575	0.9	< 0.6	0.7

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXII. ICP-MS data for peepers 7–9. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI	7Li	11B	27Al	(31P)	(19K)	(20Ca)	49Ti	51V	55Mn	56Fe	59Co	60Ni
	cm	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
7.00	6	12.2	67.4	1.9	23	9.0	66.8	< 1.5	< 1.5	0.38	0.22	< 1.5	< 1.5
7.04	0	13.1	73.3	< 1.5	< 15	10.2	67.3	< 1.5	< 1.5	0.11	0.02	< 1.5	< 1.5
7.08	-5	10.8	68.1	< 1.5	31	9.1	73.4	< 1.5	< 1.5	5.85	1.22	< 1.5	< 1.5
7.12	-10	7.7	68.2	< 1.5	490	10.3	72.3	< 1.5	< 1.5	4.83	8.64	< 1.5	< 1.5
7.16	-15	6.9	92.4	< 1.5	706	12.2	75.8	< 1.5	1.3	4.56	9.62	1.9	< 1.5
7.20	-20	<1.5	92.4	< 1.5	438	14.7	72.7	< 1.5	< 1.5	3.92	8.20	< 1.5	< 1.5
7.24	-24	<1.5	71.3	3.3	284	14.1	52.6	< 1.5	< 1.5	2.89	6.08	< 1.5	< 1.5
7.28	-30	<1.5	89.0	2.1	454	31.2	62.3	< 1.5	< 1.5	3.48	9.82	< 1.5	< 1.5
8.00	6	< 1.5	25.7	7.4	87	2.8	38.2	1.3	3.1	0.06	0.252	< 1.5	< 1.5
8.04	0	< 1.5	21.8	9.0	21	2.9	38.9	1.6	3.2	0.01	0.031	< 1.5	8.6
8.08	-5	< 1.5	18.1	7.4	64	3.3	38.8	1.3	2.6	0.78	0.045	< 1.5	< 1.5
8.12	-10	< 1.5	24.2	4.1	184	3.6	37.9	1.2	3.6	5.89	0.596	2.6	< 1.5
8.16	-15	< 1.5	29.6	4.0	235	4.5	42.8	1.1	2.6	9.36	1.39	3.9	< 1.5
8.20	-20	< 1.5	50.1	6.5	516	5.6	50.6	1.0	2.0	11.7	5.46	5.9	< 1.5
8.24	-24	< 1.5	55.6	7.1	754	5.6	48.8	1.1	1.7	11.9	9.10	7.0	< 1.5
8.28	-30	< 1.5	56.8	10.7	809	5.7	52.2	1.6	2.0	11.0	11.7	8.2	< 1.5
9.00	10	< 1.5	45.5	9.9	58	4.6	54.2	2.3	1.9	0.085	0.158	< 1.5	< 1.5
9.04	6	< 1.5	56.5	7.5	19	4.7	45.1	2.4	2.2	<0.006	< 0.015	< 1.5	< 1.5
9.08	2	< 1.5	51.0	4.3	16	4.7	42.7	2.6	2.2	<0.006	< 0.015	< 1.5	< 1.5
9.12	-2	< 1.5	44.7	3.0	34	5.6	58.2	2.1	1.5	0.01	< 0.015	< 1.5	< 1.5
9.16	-7	< 1.5	47.0	4.7	92	6.2	70.8	2.3	1.6	0.90	< 0.015	< 1.5	< 1.5
9.20	-12	< 1.5	48.0	3.3	96	5.6	65.5	2.0	3.6	4.95	0.060	< 1.5	2.4
9.24	-17	< 1.5	49.5	4.2	99	5.6	61.7	2.3	3.3	6.15	0.065	< 1.5	2.3
9.28	-22	16.6	55.7	6.6	113	6.2	72.0	2.6	3.7	9.93	0.106	1.4	2.3

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXIII. ICP-MS data for peepers 7–9.

	SWI	63Cu	66Zn	71Ga	75As	85Rb	88Sr	98Mo	111Cd	137Ba	182W	Total Pb	238U
	cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
7.00	6	< 3	4	13.5	13.6	1.6	440	15.9	<0.6	327	< 0.6	< 0.6	6.1
7.04	0	< 3	8	16.4	9.5	1.9	489	25.0	<0.6	378	< 0.6	< 0.6	8.5
7.08	-5	< 3	7	18.4	59.0	2.0	515	37.7	<0.6	455	2.1	< 0.6	5.1
7.12	-10	< 3	20	17.3	436	3.1	516	39.4	<0.6	385	4.6	< 0.6	5.2
7.16	-15	< 3	45	19.4	481	3.5	538	57.0	<0.6	467	4.0	< 0.6	5.9
7.20	-20	< 3	29	14.7	301	3.5	459	55.5	<0.6	352	2.3	< 0.6	4.7
7.24	-24	< 3	23	16.3	279	3.3	361	50.2	<0.6	369	1.7	< 0.6	6.9
7.28	-30	< 3	34	20.5	449	4.9	462	80.3	<0.6	477	3.0	< 0.6	9.6
8.00	6	6	6	2.3	6.0	< 1.5	207	6.9	< 0.6	49	<0.6	< 0.6	4.1
8.04	0	18	< 3	< 1.5	12.7	< 1.5	199	6.6	< 0.6	28	<0.6	< 0.6	3.9
8.08	-5	14	27	< 1.5	11.7	1.6	222	6.5	< 0.6	47	0.7	< 0.6	3.3
8.12	-10	3	12	15.6	25.1	2.7	228	6.0	< 0.6	319	3.8	< 0.6	2.4
8.16	-15	< 3	4	6.4	36.3	3.8	286	7.2	< 0.6	138	5.3	< 0.6	2.9
8.20	-20	< 3	< 3	9.3	67.6	3.6	318	8.1	< 0.6	210	6.4	< 0.6	3.1
8.24	-24	< 3	< 3	9.9	89.4	3.5	320	8.5	< 0.6	212	7.4	< 0.6	2.8
8.28	-30	3	8	10.3	112	3.4	348	8.0	< 0.6	220	8.8	0.7	2.8
9.00	10	7	30	1.9	5.4	2.5	365	5.8	< 0.6	41	0.5	< 0.6	5.6
9.04	6	6	14	1.7	3.9	2.4	304	6.3	< 0.6	36	<0.6	< 0.6	4.6
9.08	2	7	13	1.8	4.0	2.5	289	6.4	< 0.6	36	0.7	< 0.6	4.4
9.12	-2	13	16	1.8	5.2	3.4	393	12.1	< 0.6	38	<0.6	< 0.6	6.6
9.16	-7	8	68	2.5	6.6	4.7	438	26.5	< 0.6	54	1.1	< 0.6	9.9
9.20	-12	3	46	2.9	6.1	4.5	407	25.2	< 0.6	66	2.4	0.6	11.7
9.24	-17	< 3	34	2.8	6.1	4.5	388	22.3	< 0.6	65	3.1	0.6	11.3
9.28	-22	< 3	49	3.5	6.6	5.4	510	18.9	< 0.6	84	3.3	0.6	10.1

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXIV. ICP-MS data for peepers 10–12. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI	7Li	11B	27Al	(31P)	(19K)	(20Ca)	49Ti	51V	55Mn	56Fe	59Co	60Ni
	cm	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
10.00	6	7.6	44.2	15.2	79	3.4	37.1	< 1.5	< 1.5	0.062	0.222	< 1.5	< 1.5
10.04	0	9.5	36.4	8.4	924	5.6	62.6	< 1.5	< 1.5	1.56	26.8	< 1.5	< 1.5
10.08	-5	14.2	38.6	9.9	2110	12.8	124	2.0	4.6	5.36	74.7	< 1.5	< 1.5
10.12	-10	22.8	68.5	9.2	1770	17.3	170	2.8	6.5	6.96	117	< 1.5	< 1.5
10.16	-15	19.3	84.4	9.6	1630	18.1	157	2.7	5.9	5.98	114	< 1.5	< 1.5
10.20	-20	15.9	102	5.3	2040	18.8	141	2.9	6.7	6.24	112	< 1.5	< 1.5
10.24	-24	14.2	125	12.0	2160	17.4	128	3.2	7.6	6.78	110	< 1.5	< 1.5
10.28	-30	14.5	153	12.4	2320	16.7	117	3.0	6.1	6.82	98.8	< 1.5	< 1.5
11.00	6	61.7	157	21.6	106	6.2	48.5	< 1.5	2.7	0.146	0.358	< 1.5	< 1.5
11.04	0	71.3	116	12.0	285	8.4	63.3	< 1.5	1.9	6.33	12.9	< 1.5	< 1.5
11.08	-5	75.6	150	13.6	484	14.9	129	< 1.5	1.9	18.2	28.6	< 1.5	< 1.5
11.12	-10	80.6	169	13.5	1280	18.1	153	< 1.5	2.0	20.2	51.8	< 1.5	< 1.5
11.16	-15	64.2	152	9.7	980	14.9	118	< 1.5	1.8	16.6	40.0	< 1.5	< 1.5
11.20	-20	63.5	149	11.6	1050	14.7	128	< 1.5	1.4	16.5	38.1	< 1.5	< 1.5
11.24	-24	62.1	145	12.1	894	14.9	129	< 1.5	1.7	17.3	40.0	< 1.5	< 1.5
11.28	-30	63.2	143	14.4	987	16.3	150	< 1.5	< 1.5	18.5	46.8	< 1.5	< 1.5
12.00	6	7.8	21.7	11.0	55	3.8	36.7	< 1.5	2.3	0.073	0.205	< 1.5	< 1.5
12.04	0	12.2	58.2	8.4	1330	6.6	52.8	< 1.5	3.6	6.05	7.09	< 1.5	< 1.5
12.08	-5	29.3	202	7.8	1870	11.7	74.5	1.8	3.6	6.74	8.11	1.6	< 1.5
12.12	-10	54.5	308	6.7	1500	12.1	139	2.7	2.2	8.49	10.8	2.0	< 1.5
12.16	-15	59.3	305	11.5	962	11.5	131	3.1	1.9	6.47	11.1	2.5	< 1.5
12.20	-20	55.1	283	8.2	1080	11.6	127	2.6	2.4	8.18	10.1	3.2	< 1.5
12.24	-24	59.6	275	7.0	926	12.1	148	2.6	2.5	9.11	14.9	5.8	< 1.5
12.28	-30	59.7	280	8.5	1610	12.9	139	2.7	3.8	9.60	26.8	3.1	< 1.5

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXV. ICP-MS data for peepers 10–12.

	SWI	63Cu	66Zn	71Ga	75As	85Rb	88Sr	98Mo	111Cd	137Ba	182W	Total Pb	238U
	cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
10.00	6	7	4	3.9	7.2	< 1.5	256	12.4	< 0.6	66	0.9	< 0.6	4.6
10.04	0	< 3	3	9.5	309	2.2	489	8.8	< 0.6	162	3.8	< 0.6	< 0.6
10.08	-5	< 3	< 3	32.0	207	6.9	1160	3.2	< 0.6	516	1.8	< 0.6	0.7
10.12	-10	< 3	< 3	63.6	451	8.7	1600	2.9	< 0.6	952	2.5	< 0.6	0.6
10.16	-15	< 3	< 3	61.8	511	8.5	1570	2.5	< 0.6	926	2.1	< 0.6	< 0.6
10.20	-20	< 3	< 3	55.3	529	9.6	1420	<1.5	< 0.6	804	1.5	< 0.6	< 0.6
10.24	-24	< 3	< 3	51.0	530	10.3	1280	1.8	< 0.6	770	1.4	< 0.6	< 0.6
10.28	-30	< 3	< 3	41.4	450	10.5	1180	2.3	< 0.6	690	1.6	< 0.6	< 0.6
11.00	6	11	28	< 1.5	17.7	3.1	360	21.0	< 0.6	19	1.6	0.8	3.6
11.04	0	4	12	8.5	80.4	4.8	633	45.1	< 0.6	144	11.2	< 0.6	4.1
11.08	-5	< 3	4	31.4	79.8	11.2	1390	22.6	< 0.6	497	10.9	< 0.6	3.2
11.12	-10	< 3	< 3	37.1	124	12.7	1540	31.3	< 0.6	626	12.7	< 0.6	1.5
11.16	-15	< 3	< 3	28.1	109	11.6	1200	52.1	< 0.6	466	13.5	< 0.6	1.3
11.20	-20	< 3	< 3	28.2	109	10.8	1190	56.1	< 0.6	464	13.1	< 0.6	0.7
11.24	-24	< 3	4	27.9	118	11.1	1330	64.9	< 0.6	460	13.0	0.8	1.7
11.28	-30	< 3	< 3	29.9	122	11.8	1510	64.8	< 0.6	480	12.8	< 0.6	1.0
12.00	6	6	10	3.1	4.7	< 1.5	244	10.2	< 0.6	52	<0.6	< 0.6	3.6
12.04	0	< 3	< 3	8.2	171	3.9	370	19.6	< 0.6	146	18.2	< 0.6	2.9
12.08	-5	< 3	< 3	18.7	183	9.5	845	12.9	< 0.6	340	19.7	< 0.6	4.0
12.12	-10	< 3	< 3	18.2	125	9.9	855	19.9	< 0.6	329	11.6	< 0.6	2.3
12.16	-15	< 3	4	15.6	73.1	8.4	752	14.0	< 0.6	279	5.6	< 0.6	2.0
12.20	-20	< 3	14	15.7	91.2	8.9	743	14.9	< 0.6	271	7.6	< 0.6	2.2
12.24	-24	5	31	16.8	126	10.4	783	16.3	< 0.6	287	10.8	< 0.6	2.9
12.28	-30	4	21	19.9	168	12.3	767	24.6	< 0.6	336	14.4	< 0.6	2.6

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXVI. ICP-MS data for peepers 13–14. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI	7Li	11B	27Al	(31P)	(19K)	(20Ca)	49Ti	51V	55Mn	56Fe	59Co	60Ni
	cm	μg/L	μg/L	μg/L	μg/L	mg/L	mg/L	μg/L	μg/L	mg/L	mg/L	μg/L	μg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
13.00	6	9.5	31.4	7.7	63	4.0	38.5	< 1.5	2.5	0.063	0.224	< 1.5	< 1.5
13.04	0	147	285	5.7	326	36.7	208	5.6	< 1.5	12.6	4.51	< 1.5	< 1.5
13.08	-5	189	439	6.1	815	67.4	229	6.3	< 1.5	14.8	9.39	< 1.5	< 1.5
13.12	-10	181	378	8.7	1180	59.7	216	5.8	< 1.5	13.6	8.43	< 1.5	< 1.5
13.16	-15	174	363	5.9	1000	58.2	208	5.6	< 1.5	13.6	7.48	< 1.5	< 1.5
13.20	-20	183	399	6.7	954	63.2	222	5.9	< 1.5	14.3	7.62	< 1.5	< 1.5
13.24	-24	184	383	7.2	1400	70.3	249	5.9	< 1.5	16.2	9.10	< 1.5	< 1.5
13.28	-30	201	404	6.0	2500	66.4	235	6.2	< 1.5	15.9	8.71	< 1.5	< 1.5
14.00	6	11.1	42.2	< 1.5	22	4.9	44.1	1.5	< 1.5	2.12	0.041	< 1.5	< 1.5
14.02	2	14.2	62.6	< 1.5	25	5.6	49.3	< 1.5	< 1.5	1.93	< 0.015	< 1.5	< 1.5
14.04	0	13.3	48.6	< 1.5	69	5.0	49.2	< 1.5	< 1.5	8.95	0.075	< 1.5	< 1.5
14.06	-3	13.0	42.8	< 1.5	696	5.2	48.3	< 1.5	< 1.5	10.0	2.39	< 1.5	< 1.5
14.08	-5	11.8	35.4	2.5	2330	4.5	43.0	< 1.5	2.1	8.50	5.80	< 1.5	< 1.5
14.10	-8	9.7	32.4	1.5	3150	4.2	42.5	< 1.5	2.1	8.36	6.04	< 1.5	< 1.5
14.12	-10	9.6	38.4	< 2.0	4610	4.6	52.1	< 2.0	2.7	10.5	6.80	< 2.0	< 2.0
14.14	-13	10.7	35.9	< 1.5	5130	4.5	55.8	1.9	3.1	10.4	8.44	< 1.5	< 1.5
14.16	-15	11.5	34.2	< 1.5	5400	5.0	64.5	< 1.5	3.3	12.6	8.23	< 1.5	< 1.5
14.18	-18	13.2	36.7	1.4	5590	5.7	59.8	1.6	3.4	15.3	9.30	< 1.5	< 1.5
14.20	-20	15.0	58.8	< 3.0	4740	6.4	69.3	< 3.0	< 3.0	14.1	10.1	< 3.0	< 3.0
14.22	-23	14.1	57.4	< 3.0	5290	7.0	68.9	< 3.0	< 3.0	13.9	10.9	< 3.0	< 3.5
14.24	-25	18.7	60.6	2.6	5840	8.7	87.8	< 2.5	2.7	18.7	9.04	< 2.5	< 3.0
14.26	-28	23.8	80.8	< 3.5	4430	8.6	104	< 3.5	< 3.5	24.6	11.9	< 3.5	< 3.5
14.28	-30	24.2	76.0	< 4.0	1580	8.7	116	< 4.0	< 4.0	37.0	9.16	< 4.0	< 4.0

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXVII. ICP-MS data for peepers 13–14.

	SWI	63Cu	66Zn	71Ga	75As	85Rb	88Sr	98Mo	111Cd	137Ba	182W	Total Pb	238U
	cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
13.00	6	7	10	3.3	4.9	< 1.5	236	7.4	< 0.6	57	< 0.6	< 0.6	3.9
13.04	0	< 3	7	25.0	10.7	19.5	1199	5.7	< 0.6	415	21.7	< 0.6	2.5
13.08	-5	< 3	< 3	23.0	202	72.9	1300	12.2	< 0.6	398	335	< 0.6	17.3
13.12	-10	< 3	< 3	19.5	154	79.8	1180	8.4	< 0.6	342	299	< 0.6	12.6
13.16	-15	< 3	< 3	19.9	113	75.0	1150	6.9	< 0.6	347	290	< 0.6	13.6
13.20	-20	< 3	< 3	19.5	115	81.3	1180	9.5	< 0.6	349	332	< 0.6	13.9
13.24	-24	< 3	< 3	22.7	108	78.7	1300	8.5	< 0.6	410	360	< 0.6	11.7
13.28	-30	< 3	< 3	27.9	47.7	77.3	1240	5.2	< 0.6	466	179	< 0.6	4.4
14.00	6	4	544	2.0	4.1	< 1.5	279	27.6	< 0.6	35	< 0.6	< 0.6	2.2
14.02	2	5	136	2.9	4.4	< 1.5	301	25.8	< 0.6	53	< 0.6	< 0.6	2.9
14.04	0	3	5	6.8	5.2	< 1.5	301	25.4	< 0.6	121	1.3	< 0.6	1.5
14.06	-3	< 3	4	10.0	17.1	< 1.5	304	21.3	< 0.6	177	2.5	< 0.6	0.7
14.08	-5	< 3	5	16.6	24.1	< 1.5	301	15.8	< 0.6	288	3.1	< 0.6	< 0.6
14.10	-8	< 3	3	14.9	21.4	< 1.5	293	11.2	< 0.6	260	3.0	< 0.6	< 0.6
14.12	-10	< 4	< 4	16.1	24.4	< 2.0	332	12.6	< 0.8	285	4.0	< 0.8	< 0.8
14.14	-13	< 3	< 3	16.2	18.2	< 1.5	368	8.7	< 0.6	288	3.3	< 0.6	< 0.6
14.16	-15	< 3	< 3	17.6	22.0	< 1.5	381	6.3	< 0.6	312	3.7	< 0.6	< 0.6
14.18	-18	< 3	< 3	21.2	30.3	1.4	438	5.0	< 0.6	384	4.1	< 0.6	< 0.6
14.20	-20	< 6	< 6	22.5	20.0	< 3.0	515	6.2	< 1.2	400	4.2	< 1.2	< 1.2
14.22	-23	< 7	< 7	23.1	15.2	< 3.5	432	< 3.6	< 1.4	394	2.9	< 1.4	< 1.4
14.24	-25	133	66	24.9	14.0	< 2.5	541	< 2.5	< 1.0	431	3.4	4.3	< 1.0
14.26	-28	< 7	< 7	29.5	25.8	< 3.5	658	< 3.5	< 1.4	516	3.1	< 1.4	< 1.4
14.28	-30	< 8	< 8	36.4	80.7	< 4.0	766	7.6	< 1.6	632	6.5	< 1.6	< 1.6

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXVIII. ICP-MS data for peeper 16. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI	7Li	11B	27Al	(31P)	(19K)	(20Ca)	49Ti	51V	55Mn	56Fe	59Co	60Ni
	cm	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
16.00	6	7.8	120	2.5	63	3.38	38.3	< 1.5	4.3	0.181	0.031	< 1.5	< 1.5
16.02	2	8.1	108	2.5	64	3.70	40.5	< 1.5	4.7	0.120	0.025	< 1.5	< 1.5
16.04	0	8.8	109	1.9	30	3.76	42.2	< 1.5	3.1	0.147	0.016	< 1.5	< 1.5
16.06	-3	10.3	100	2.6	745	3.38	37.1	< 1.5	< 1.5	0.694	1.08	< 1.5	< 1.5
16.08	-5	10.6	111	2.3	136	3.45	36.7	< 1.5	< 1.5	0.716	0.28	< 1.5	< 1.5
16.10	-8	11.0	115	3.2	474	3.59	33.9	< 1.5	< 1.5	0.807	1.32	< 1.5	< 1.5
16.12	-10	10.7	110	5.8	461	3.47	31.7	< 1.5	< 1.5	0.859	1.56	< 1.5	< 1.5
16.14	-13	10.9	106	3.4	217	3.48	31.7	< 1.5	< 1.5	0.897	1.11	< 1.5	< 1.5
16.16	-15	11.0	112	3.1	193	3.53	31.5	< 1.5	< 1.5	0.960	1.00	< 1.5	< 1.5
16.18	-18	10.5	109	2.6	16	3.52	31.2	< 1.5	< 1.5	1.05	0.043	< 1.5	< 1.5
16.20	-20	10.9	97.1	2.8	< 15	3.76	33.1	< 1.5	< 1.5	1.09	< 0.015	< 1.5	< 1.5
16.22	-23	10.6	111	3.3	28	3.38	29.7	< 1.5	< 1.5	1.22	< 0.015	< 1.5	< 1.5
16.24	-25	10.7	106	4.0	18	3.65	32.1	< 1.5	< 1.5	1.10	< 0.015	< 1.5	< 1.5
16.26	-28	11.2	110	4.4	53	3.56	33.1	< 1.5	< 1.5	0.975	0.186	< 1.5	< 1.5
16.28	-30	18.1	143	24	< 15	6.42	52.9	< 1.5	< 1.5	1.53	1.81	< 1.5	< 1.5

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXIX. ICP-MS data for peeper 16.

	SWI	63Cu	66Zn	71Ga	75As	85Rb	88Sr	98Mo	111Cd	137Ba	182W	Total Pb	238U
	cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
16.00	6	< 3	26	4.4	1.8	< 1.5	223	8.7	< 0.6	71	0.8	< 0.6	6.1
16.02	2	< 3	< 3	4.2	2.2	< 1.5	223	8.8	< 0.6	69	0.7	< 0.6	6.8
16.04	0	< 3	< 3	4.7	1.6	< 1.5	220	10.7	< 0.6	76	0.7	< 0.6	5.4
16.06	-3	< 3	< 3	3.0	6.3	< 1.5	200	4.0	< 0.6	49	0.8	< 0.6	1.8
16.08	-5	< 3	< 3	5.4	1.5	< 1.5	202	6.2	< 0.6	85	0.6	< 0.6	1.5
16.10	-8	< 3	< 3	4.9	4.2	< 1.5	200	8.7	< 0.6	79	1.0	< 0.6	1.1
16.12	-10	< 3	< 3	4.1	4.9	< 1.5	192	10.7	< 0.6	65	1.1	< 0.6	1.2
16.14	-13	< 3	< 3	3.9	2.8	< 1.5	188	11.5	< 0.6	63	1.0	< 0.6	1.0
16.16	-15	< 3	< 3	4.7	3.3	< 1.5	192	10.4	< 0.6	74	1.0	< 0.6	1.2
16.18	-18	< 3	< 3	4.5	0.9	1.4	185	11.9	< 0.6	75	1.0	< 0.6	1.5
16.20	-20	< 3	< 3	4.4	0.8	1.4	185	13.0	< 0.6	69	1.2	< 0.6	1.4
16.22	-23	< 3	< 3	3.8	1.2	< 1.5	187	10.9	< 0.6	60	1.3	< 0.6	1.7
16.24	-25	< 3	< 3	4.5	0.7	1.5	187	10.4	< 0.6	73	0.9	< 0.6	1.1
16.26	-28	< 3	< 3	4.4	1.3	1.5	198	6.2	< 0.6	72	0.9	< 0.6	0.9
16.28	-30	< 3	29	13.1	0.7	2.3	315	2.8	< 0.6	222	< 0.6	< 0.6	< 0.6

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXX. ICP-MS data for peeper 17. ( ) indicates not usually quantified by ICP-MS. Practical detection limits are listed in table.

	SWI	7Li	11B	27Al	(31P)	(19K)	(20Ca)	49Ti	51V	55Mn	56Fe	59Co	60Ni
	cm	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L
Instrum. detection limit		0.5	0.2	0.5	5	0.005	0.005	0.5	0.5	0.002	0.005	0.5	0.5
17.00	6	13.2	143	2.2	64	4.11	47.0	< 1.5	3.9	0.212	0.102	< 1.5	< 1.5
17.02	2	13.0	127	2.4	22	4.49	49.1	< 1.5	3.2	0.183	< 0.015	< 1.5	< 1.5
17.04	0	13.7	123	2.2	15	5.06	58.4	< 1.5	< 1.5	0.861	0.140	< 1.5	< 1.5
17.06	-3	13.2	117	2.7	17	5.15	51.9	< 1.5	< 1.5	1.04	0.124	< 1.5	< 1.5
17.08	-5	13.5	116	3.3	976	5.29	56.3	< 1.5	< 1.5	1.09	4.72	< 1.5	< 1.5
17.10	-8	13.1	121	4.1	503	5.22	65.0	< 1.5	< 1.5	0.944	4.28	< 1.5	< 1.5
17.12	-10	12.7	125	2.7	566	4.89	51.4	< 1.5	< 1.5	0.950	4.54	< 1.5	< 1.5
17.14	-13	12.3	108	1.8	356	5.21	56.3	< 1.5	< 1.5	0.910	3.71	< 1.5	< 1.5
17.16	-15	12.4	118	3.6	920	5.45	43.6	< 1.5	< 1.5	1.03	5.15	< 1.5	< 1.5
17.18	-18	11.1	119	2.5	938	5.71	38.4	< 1.5	< 1.5	1.31	5.36	< 1.5	< 1.5
17.20	-20	10.4	109	2.9	1660	6.36	71.5	< 1.5	< 1.5	1.61	8.04	< 1.5	< 1.5
17.22	-23	9.4	113	3.5	1420	6.10	71.5	< 1.5	1.4	1.63	9.26	< 1.5	< 1.5
17.24	-25	10.8	132	3.4	1720	6.61	74.5	< 1.5	1.5	1.98	10.9	< 1.5	< 1.5
17.26	-28	11.1	119	4.5	2290	6.56	76.3	< 1.5	2.2	2.57	13.4	< 1.5	< 1.5
17.28	-30	14.6	178	6.5	80	6.54	76.9	2.4	< 1.5	3.21	5.84	2.5	< 1.5

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXXI. ICP-MS data for peeper 17.

	SWI	63Cu	66Zn	71Ga	75As	85Rb	88Sr	98Mo	111Cd	137Ba	182W	Total Pb	238U
	cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Instrum. detection limit		1	1	0.5	0.2	0.5	1	0.5	0.2	1	0.2	0.2	0.2
17.00	6	< 3	< 3	7.0	3.4	< 1.5	306	8.1	< 0.6	110	2.9	< 0.6	10.2
17.02	2	< 3	< 3	6.4	3.0	< 1.5	289	7.3	< 0.6	105	2.4	< 0.6	10.2
17.04	0	< 3	< 3	5.9	2.0	< 1.5	299	7.3	< 0.6	96	2.1	< 0.6	6.0
17.06	-3	4	< 3	5.9	1.4	< 1.5	291	5.9	< 0.6	94	1.8	< 0.6	4.3
17.08	-5	< 3	< 3	8.0	28.5	< 1.5	299	6.0	< 0.6	128	2.1	< 0.6	2.1
17.10	-8	< 3	< 3	8.3	17.8	< 1.5	292	5.7	< 0.6	135	1.6	< 0.6	2.4
17.12	-10	< 3	< 3	8.9	19.4	< 1.5	286	5.5	< 0.6	144	1.6	< 0.6	2.5
17.14	-13	< 3	< 3	9.2	15.4	< 1.5	294	5.7	< 0.6	146	1.5	< 0.6	3.7
17.16	-15	< 3	< 3	10.3	20.8	< 1.5	299	4.9	< 0.6	169	1.6	< 0.6	2.7
17.18	-18	< 3	< 3	9.1	24.0	< 1.5	332	3.3	< 0.6	147	1.4	< 0.6	2.6
17.20	-20	< 3	< 3	11.4	34.2	< 1.5	364	1.7	< 0.6	183	1.3	< 0.6	2.1
17.22	-23	< 3	< 3	11.8	34.9	1.4	353	< 1.5	< 0.6	193	1.2	< 0.6	1.6
17.24	-25	< 3	< 3	13.3	30.4	1.6	395	< 1.5	< 0.6	229	1.1	< 0.6	1.9
17.26	-28	< 3	< 3	13.5	30.3	1.9	424	1.6	< 0.6	229	1.0	< 0.6	3.3
17.28	-30	< 3	26	17.6	2.4	2.5	454	3.4	< 0.6	286	< 0.6	< 0.6	1.4

Note: The following elements were below detection: Ag, Be, Cs, La, Nb, Nd, Pd, Pr, Sb, Se, Sn, Tl, Th, Zr

Table XXXII. ICP-OES data from peepers 2, 3, and 4 (continued next page).

	SWI cm	B mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	P mg/L	Si mg/L	Sr mg/L
MDL		0.0241	0.0079	0.0087	0.0112	0.0279	0.0035	0.0129	0.0065	0.0225	0.0101	0.006
2.00	6	< 0.06	0.0507	38.4	0.0810	3.75	9.79	0.0689	14.1	0.0603	12.3	0.207
2.04	0	< 0.06	0.0483	37.9	0.0480	3.90	10.2	< 0.04	14.8	0.0669	11.7	0.199
2.08	-5	< 0.06	0.0576	35.4	< 0.03	3.57	12.2	< 0.04	15.6	< 0.06	11.4	0.179
2.12	-10	< 0.06	0.0783	39.7	0.109	3.33	12.5	1.37	16.7	< 0.06	10.4	0.208
2.16	-15	< 0.06	0.0768	42.3	1.77	3.77	11.8	2.00	17.6	0.293	10.6	0.226
2.20	-20	< 0.06	0.0792	43.2	2.22	4.01	11.5	2.08	17.8	0.490	10.7	0.237
2.24	-25	< 0.06	0.0735	46.5	1.63	4.28	12.0	2.22	19.6	0.313	11.2	0.268
2.28	-30	0.0909	0.0830	51.8	2.91	5.67	12.9	2.63	20.6	0.457	12.4	0.327
3.00	6	0.170	0.0599	42.8	< 0.03	3.47	32.9	0.0661	32.9	0.0639	11.5	0.221
3.04	0	< 0.06	0.0562	44.2	0.204	3.92	13.6	0.360	21.0	< 0.06	10.9	0.233
3.08	-5	0.0679	0.0677	44.6	3.79	4.71	13.6	0.426	20.4	0.325	11.6	0.241
3.12	-10	0.229	0.103	51.6	11.4	12.8	14.4	0.598	17.3	2.24	15.2	0.346
3.16	-15	0.365	0.128	59.3	13.4	19.5	16.0	0.674	17.8	2.46	15.6	0.419
3.20	-20	0.601	0.136	72.7	15.9	25.6	19.5	0.809	19.8	2.25	15.7	0.527
3.24	-25	0.667	0.121	71.7	16.4	34.0	19.2	0.847	20.3	2.39	15.7	0.522
3.28	-30	0.885	0.124	78.0	20.1	37.9	20.9	1.07	20.3	2.00	17.5	0.560
4.00	6	< 0.06	< 0.023	30.8	0.311	3.31	7.70	< 0.04	14.3	0.146	9.94	0.194
4.04	0	< 0.06	< 0.023	33.3	< 0.03	3.80	8.13	< 0.04	15.3	0.149	9.03	0.207
4.06	-3	< 0.06	< 0.023	48.8	0.482	5.81	10.3	3.0	14.7	0.094	10.4	0.285
4.08	-5	0.225	0.154	117	23.3	19.6	18.7	6.5	26.4	0.158	18.0	0.744
4.12	-10	0.622	0.365	231	39.4	42.5	31.1	8.2	42.5	5.30	26.3	1.59

Table XXXIII. ICP-OES data for peeper 4 to 5.

	SWI cm	B mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	P mg/L	Si mg/L	Sr mg/L
MDL		0.0241	0.0079	0.0087	0.0112	0.0279	0.0035	0.0129	0.0065	0.0225	0.0101	0.006
4.16	-15	0.624	0.309	231	29.6	44.3	31.2	9.0	41.3	4.83	25.3	1.56
4.20	-20	0.618	0.325	225	38.5	44.7	30.9	8.9	41.4	5.96	26.0	1.52
4.24	-25	0.631	0.239	223	24.5	48.3	31.6	7.9	45.6	3.85	25.3	1.50
4.28	-30	0.607	0.320	221	35.1	56.8	31.2	8.4	44.9	6.91	27.2	1.46
5.00	6	< 0.06	< 0.023	30.4	0.465	3.30	7.89	< 0.04	15.0	0.124	9.85	0.180
5.04	0	< 0.06	0.074	102	69.5	11.3	12.0	12.8	15.7	0.0657	12.7	0.445
5.06	-3	< 0.06	< 0.023	95.9	77.5	12.5	11.1	12.6	15.0	0.0674	13.3	0.394
5.08	-5	< 0.06	< 0.023	198	274	20.3	18.0	32.1	16.3	0.0740	19.5	0.772
5.12	-10	0.085	< 0.023	299	522	26.1	26.0	44.8	17.7	0.0516	27.1	1.14
5.16	-15	< 0.06	< 0.023	345	471	21.7	32.2	54.9	18.5	0.124	23.1	1.34
5.20	-20	< 0.06	< 0.023	335	527	18.8	27.0	37.6	18.8	0.0847	23.3	1.13
5.24	-25	< 0.06	< 0.023	341	609	18.1	25.5	29.6	19.7	< 0.06	25.6	1.05
5.28	-30	< 0.06	< 0.023	325	604	19.6	24.3	25.0	20.7	< 0.06	24.6	0.958

9. Appendix C: Piezometer and Peeper 0 Data

Table XXXIV. Piezometers and ponds ICP-MS, ICP-OES, and field data (corrected for dilution).

Piezometer	Location	Mn µg/L	Fe µg/L	Cu µg/L	Zn µg/L	As µg/L	Alkalinity as CaCO3 mg/L	SO_4^{2-} mg/L	H_2S mg/L	SRP as P mg/L
PZ-1	Well	149	53.8	< 1	4.84	4.05	148	25.0	0.01	0.15
	Pond						112	32.0	0	0.06
PZ-2	Well	3150	11100	< 1	1.72	36.9	270	1.5	0.001	0.15
	Pond						112	32.0	0	0.06
PZ-3	Well	77.7	56.8	< 1	1.43	5.21	188	78.0	0.568	0.41
	Pond						112	32.0	0	0.06
PZ-4	Well	1640	21300	< 1	< 1	18.2	280	1.0	0.018	0.82
	Pond						184	14.0	0	0.15

Table XXXV. Piezometers and ponds field parameters.

Piezometer	Location	Static Water Level (cm)	SC (µS/cm)	pH	Temperature (°C)
PZ-1	Well	101	364	7.67	9.90
	Pond	39.0	447	7.66	12.4
PZ-2	Well	45.7	601	7.71	15.8
	Pond	43.6	321	9.98	16.3
PZ-3	Well	44.8	618	7.93	14.9
	Pond	37.2	441	7.51	—
PZ-4	Well	37.5	741	7.31	9.80
	Pond	36.0	727	7.85	13.9

Table XXXVI. Field parameters for peeper 0.

Descriptoin	Cell	pH	ORP mV, Ag/AgCl	True Eh mV, SHE	NH_4 mg/L as N	Alkalinity mg/L as $CaCO_3$
Nepheloid	2	7.55	-45	165		
Nepheloid	3				0.28	No sample
Nepheloid	4	7.50	-95	115		
Nepheloid	5					
Sediment	6	7.25	-187	23		
Sediment	7				1.50	96.3
Sediment	8	7.02	-174	36		
Sediment	9					
Sediment	10	6.98	-162	48		
Sediment	11				2.26	153.3
Sediment	12	6.96	-148	62		
Sediment	13					
Sediment	14	6.96	-135	75		
Sediment	15				2.16	181.5
Sediment	16	7.04	-102	108		
Sediment	17					
Sediment	18	7.02	-78	132		
Sediment	19				2.73	183.3
Sediment	20	7.05	-119	91		
Sediment	21					
Sediment	22	6.95	-66	144		
Sediment	23				2.93	181.5
Sediment	24	6.96	-77	133		
Sediment	25					
Sediment	26	6.96	-110	100		
Sediment	27				2.99	205.7
Sediment	28	6.90	-64	146		

Table XXXVII. Ion chromatograph results from peeper 0 (corrected for dilution).

	F	Cl	NO_2-N	NO_3-N	PO_4-P	SO_4
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PQL	0.05	0.3	0.1	0.07	0.5	0.6
0.01	0.52	5.7	< 0.6	< 0.5	< 3.0	35.4
0.05	0.52	5.7	< 0.4	< 0.3	< 1.5	33.4
0.13	0.46	9.3	< 0.4	< 0.3	< 1.5	3.7
0.21	0.51	8.6	< 0.4	< 0.3	< 1.5	2.4
0.25	0.39	5.6	< 0.4	< 0.3	< 1.5	2.4
Btail-out	0.51	6.8	< 0.1	< 0.07	< 0.5	39.7
Spring	0.48	6.1	< 0.1	0.29	< 0.5	43.3

PQL = Practical quantification instrument (varies with dilution factor)

Table XXXVIII. ICP-OES data (corrected for dilution) from peeper 0 (continued on next page).

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PQL	0.05	0.015	0.01	0.01	0.0005	0.1	0.004	0.005	0.005	0.005	0.08	0.5	0.05	0.1	0.001
0.02	< 0.15	< 0.045	< 0.03	0.05	< 0.0015	33.0	< 0.012	< 0.015	< 0.015	< 0.015	< 0.24	3.0	< 0.015	7.1	0.46
0.04	< 0.15	< 0.045	< 0.03	0.06	< 0.0015	35.4	< 0.012	< 0.015	< 0.015	< 0.015	< 0.24	2.9	< 0.015	7.6	0.56
0.06	< 0.15	< 0.045	< 0.03	0.08	< 0.0015	44.6	< 0.012	< 0.015	< 0.015	< 0.015	< 0.24	3.7	< 0.015	9.8	0.77
0.08	< 0.15	< 0.045	< 0.03	0.14	< 0.0015	73.8	< 0.012	< 0.015	< 0.015	< 0.015	0.42	5.8	< 0.015	17.4	1.20
0.10	< 0.15	< 0.045	0.03	0.19	< 0.0015	90.9	< 0.012	< 0.015	< 0.015	< 0.015	0.77	6.7	< 0.015	22.3	1.46
0.12	< 0.15	< 0.045	0.03	0.21	< 0.0015	97.7	< 0.012	< 0.015	< 0.015	< 0.015	0.81	6.9	< 0.015	24.4	1.46
0.14	< 0.15	< 0.045	< 0.03	0.22	< 0.0015	97.9	< 0.012	< 0.015	< 0.015	< 0.015	0.86	6.7	< 0.015	24.8	1.48
0.16	< 0.15	< 0.045	< 0.03	0.24	< 0.0015	97.7	< 0.012	< 0.015	< 0.015	< 0.015	1.01	6.9	< 0.015	25.0	1.51
0.18	< 0.15	< 0.045	< 0.03	0.26	< 0.0015	105	< 0.012	< 0.015	< 0.015	< 0.015	1.16	7.1	< 0.015	26.7	1.57
0.20	< 0.15	< 0.045	0.05	0.27	< 0.0015	107	< 0.012	< 0.015	< 0.015	< 0.015	1.42	7.4	< 0.015	27.2	1.63
0.22	< 0.15	< 0.045	0.04	0.27	< 0.0015	111	< 0.012	< 0.015	< 0.015	< 0.015	1.67	7.1	< 0.015	28.4	1.73
0.24	< 0.15	< 0.045	0.04	0.30	< 0.0015	117	< 0.012	< 0.015	< 0.015	< 0.015	2.08	7.6	< 0.015	30.0	1.90
0.26	< 0.15	< 0.045	0.04	0.32	< 0.0015	123	< 0.012	< 0.015	< 0.015	< 0.015	2.37	8.9	< 0.015	31.8	2.04
0.28	< 0.15	< 0.045	< 0.03	0.34	< 0.0015	120	< 0.012	< 0.015	< 0.015	< 0.015	2.19	47.8	< 0.015	31.4	2.08
Btrail out	< 0.05	< 0.015	0.02	0.02	< 0.005	34.8	< 0.004	< 0.005	< 0.005	< 0.005	< 0.08	3.5	< 0.005	8.0	0.14
Spring	< 0.05	< 0.015	0.02	0.02	<0.0005	28.9	< 0.004	< 0.005	< 0.005	< 0.005	< 0.08	2.8	< 0.005	7.5	0.07

PQL = Practical quantification instrument (varies with dilution factor)

Table XXXIX. ICP-OES data (corrected for dilution) from peeper 0.

	Mo	Na	Ni	P	Pb	S	Sb	Se	Si	Sn	Sr	Ti	Tl	V	Zn
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PQL	0.005	0.5	0.01	0.06	0.05	0.1	0.05	0.05	0.1	0.01	0.005	0.01	0.1	0.01	0.001
0.02	< 0.015	11.9	< 0.03	0.24	< 0.15	9.4	< 0.015	< 0.15	8.3	< 0.03	0.21	< 0.03	< 0.03	< 0.03	0.018
0.04	< 0.015	12.4	< 0.03	0.26	< 0.15	9.1	< 0.015	< 0.15	9.2	< 0.03	0.22	< 0.03	< 0.03	< 0.03	0.017
0.06	< 0.015	13.8	< 0.03	0.42	< 0.15	7.6	< 0.015	< 0.15	11.3	< 0.03	0.28	< 0.03	< 0.03	< 0.03	< 0.003
0.08	< 0.015	18.4	< 0.03	0.85	< 0.15	2.9	< 0.015	< 0.15	17.8	< 0.03	0.47	< 0.03	< 0.03	< 0.03	< 0.003
0.10	< 0.015	31.0	< 0.03	0.77	< 0.15	2.0	< 0.015	< 0.15	19.9	< 0.03	0.59	< 0.03	< 0.03	< 0.03	< 0.003
0.12	< 0.015	22.3	< 0.03	0.75	< 0.15	2.0	< 0.015	< 0.15	20.0	< 0.03	0.64	< 0.03	< 0.03	< 0.03	0.008
0.14	< 0.015	22.6	< 0.03	0.77	< 0.15	2.0	< 0.015	< 0.15	19.3	< 0.03	0.65	< 0.03	< 0.03	< 0.03	< 0.003
0.16	< 0.015	22.3	< 0.03	0.78	< 0.15	2.0	< 0.015	< 0.15	19.0	< 0.03	0.65	< 0.03	< 0.03	< 0.03	< 0.003
0.18	< 0.015	24.0	< 0.03	0.84	< 0.15	2.1	< 0.015	< 0.15	19.5	< 0.03	0.70	< 0.03	< 0.03	< 0.03	< 0.003
0.20	< 0.015	24.6	< 0.03	0.88	< 0.15	2.1	< 0.015	< 0.15	19.6	< 0.03	0.72	< 0.03	< 0.03	< 0.03	< 0.003
0.22	< 0.015	25.6	< 0.03	0.93	< 0.15	2.2	< 0.015	< 0.15	19.5	< 0.03	0.74	< 0.03	< 0.03	< 0.03	< 0.003
0.24	< 0.015	27.0	< 0.03	1.00	< 0.15	2.4	< 0.015	< 0.15	20.0	< 0.03	0.78	< 0.03	< 0.03	< 0.03	< 0.003
0.26	< 0.015	28.7	< 0.03	1.03	< 0.15	2.4	< 0.015	< 0.15	20.2	< 0.03	0.83	< 0.03	< 0.03	< 0.03	0.015
0.28	< 0.015	28.0	< 0.03	1.01	< 0.15	2.2	< 0.015	< 0.15	19.2	< 0.03	0.81	< 0.03	< 0.03	< 0.03	0.007
Btrail out	< 0.005	15.5	< 0.01	< 0.06	< 0.05	12.9	< 0.005	< 0.05	8.0	< 0.01	0.21	< 0.01	< 0.01	< 0.01	0.004
Spring	< 0.005	15.8	< 0.01	0.07	< 0.05	13.8	< 0.005	< 0.05	12.4	< 0.01	0.19	< 0.01	< 0.01	< 0.01	0.075

PQL = Practical quantification instrument (varies with dilution factor)

10. Appendix E: X-ray fluorescence data

Table XL. XRF for peepers 2, 3, and 5. S stands for sieved and R stands for unsieved (continued on next page).

Location	Sample depth (cm)	Note	Sr	Pb	As	Zn	Cu	Ni	Fe	Mn
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Sediment holder			< LOD	< LOD	< LOD	22.1	146	< LOD	764	1410
Peeper 2	0	R	378	161	58	738	344	36	23800	445
Peeper 2	0	R	401	176	166	1150	662	54	44000	640
Peeper 2	0	R	358	61	28	984	137	< LOD	12300	< LOD
Peeper 2	0	R	432	98	80	4210	236	48	28100	483
Peeper 2	0	R	336	69	46	1790	210	< LOD	17300	358
Peeper 2	0	R	397	91	107	2490	426	82	30800	471
Peeper 2	0	R	325	73	61	4150	215	< LOD	21800	204
Peeper 2	0	R	377	115	49	1330	190	34	34100	1230
Peeper 2	0	R	454	97	51	907	185	< LOD	27700	714
Peeper 3	0	R	429	80	43	323	224	< LOD	28400	523
Peeper 3	0	R	394	42	27	221	106	76	19800	309
Peeper 3	0	R	481	52	15	240	101	45	17400	275
Peeper 3	0	R	473	75	20	366	163	46	26500	466
Peeper 3	0	R	367	107	42	639	180	< LOD	34000	709
Peeper 3	0	R	322	114	63	783	275	< LOD	38100	1080
Peeper 5	0	S	199	484	165	814	843	109	96200	345
Peeper 5	0	S	348	413	1830	4210	1050	83	51400	964
Peeper 5	4	S	406	270	646	1450	754	61	55600	904
Peeper 5	8	S	391	574	1760	5030	1210	55	48500	972
Peeper 5	12	S	405	448	776	4630	1340	123	57500	1120

Note: The following elements were below detection: Ag, Au, Bi, Ce, Cl, Cr, Cs, Hf, Hg, La, Mo, Nb, P, Pd, Sb, Se, Sc, Sn, Rb, Re, Ta, Te, Th, U, V, W, Y, Zr

Table XLI. XRF for peepers 2, 3, and 5. S stands for sieved and R stands for unsieved.

Location	Sample depth (cm)	Note	Ti	Ca	K	S	Ba	Cd	Al	Si
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Sediment holder			44.0	< LOD	< LOD	< LOD	< LOD	< LOD	160000	2980
Peeper 2	0	R	2680	17100	17700	6070	753	27	58400	343000
Peeper 2	0	R	2230	31100	13000	57400	876	< LOD	48600	238500
Peeper 2	0	R	183	2380	10800	3730	930	81	7380	82100
Peeper 2	0	R	1570	14200	16400	15400	500	48	35800	231900
Peeper 2	0	R	830	12300	13800	5520	742	39	25200	243600
Peeper 2	0	R	2160	14000	14400	3770	1080	30	5860	56500
Peeper 2	0	R	429	18400	12400	3700	319	< LOD	4850	39000
Peeper 2	0	R	1580	13800	14800	4440	601	39	33200	234000
Peeper 2	0	R	1440	17600	13900	16700	908	37	27000	211000
Peeper 3	0	R	842	17400	24300	6100	417	< LOD	64200	393000
Peeper 3	0	R	1920	11200	26900	1640	593	21	14000	112000
Peeper 3	0	R	1640	19600	16800	9660	487	< LOD	51800	309000
Peeper 3	0	R	2800	21700	18500	7220	556	23	63600	319000
Peeper 3	0	R	693	21800	4820	42300	235	< LOD	19200	168000
Peeper 3	0	R	1830	70600	17200	125000	397	< LOD	44800	233000
Peeper 5	0	S	2980	4930	15700	5680	254	< LOD	11900	69000
Peeper 5	0	S	3140	19100	20700	6600	719	21	16800	101000
Peeper 5	4	S	2120	23100	17500	24300	726	< LOD	61600	335000
Peeper 5	8	S	3500	19010	19500	18000	725	24	58700	266000
Peeper 5	12	S	2710	20900	19400	29400	1020	< LOD	79700	342000

Note: The following elements were below detection: Ag, Au, Bi, Ce, Cl, Cr, Cs, Hf, Hg, La, Mo, Nb, P, Pd, Sb, Se, Sc, Sn, Rb, Re, Ta, Te, Th, U, V, W, Y, Zr

Table XLII. XRF data for peeper 12 (continued on next page).

Location	Sample depth (cm)	Note	Sr	Pb	As	Zn	Cu	Ni	Fe	Mn
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Peeper 12	0	R	316	350	58.7	1870	502	< LOD	35400	2200
Peeper 12	4	R	390	368	44.4	1740	596	77	34700	1860
Peeper 12	8	R	387	419	98.2	2150	975	54	44500	1860
Peeper 12	12	R	312	586	129	3460	1470	52	53900	2570
Peeper 12	18	R	426	306	53.2	1590	487	37	33400	1230
Peeper 12	22	R	313	214	119	2200	2840	69	72000	2900
Peeper 12	26	R	243	132	52.4	952	1230	36	32700	1040
Peeper 12	30	R	196	292	98.5	1970	4610	< LOD	118000	891
Peeper 12	34	R	203	235	194	2670	4370	87	85700	995
Peeper 12	38	R	171	263	243	1800	6150	< LOD	108000	385
Peeper 12	0	S	401	338	69.0	1690	583	80	37100	1570
Peeper 12	4	S	400	350	80.0	1740	552	82	35300	1520
Peeper 12	8	S	407	400	73.0	2040	818	85	45600	1800
Peeper 12	12	S	385	553	103	3250	1120	92	47300	1800
Peeper 12	18	S	392	476	177	2820	1750	98	85400	2610
Peeper 12	22	S	204	478	560	3820	7620	246	144000	2660
Peeper 12	26	S	209	314	266	2650	6150	< LOD	140000	2590
Peeper 12	30	S	186	265	204	2440	6350	78	127000	915
Peeper 12	34	S	174	452	440	3040	11700	< LOD	143000	959
Peeper 12	38	S	155	348	276	1600	9150	< LOD	114000	290

Note: The following elements were below detection: Ag, Au, Bi, Ce, Cl, Cr, Cs, Hf, Hg, La, Mo, Nb, P, Pd, Sb, Se, Sc, Sn, Rb, Re, Ta, Te, Th, U, V, W, Y, Zr

Table XLIII. XRF data for peeper 12.

Location	Sample depth (cm)	Note	Ti	Ca	K	S	Ba	Cd	Al	Si
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Peeper 12	0	R	889	16400	10300	18500	800	31	35500	226000
Peeper 12	4	R	1690	31200	12700	30700	962	43	33100	191000
Peeper 12	8	R	3180	23800	18300	24400	571	< LOD	52000	255000
Peeper 12	12	R	2470	26400	14400	38800	694	34.76	44400	211000
Peeper 12	18	R	1880	40600	16000	66400	440	< LOD	34100	185000
Peeper 12	22	R	2440	78300	14600	50300	931	< LOD	54200	202000
Peeper 12	26	R	1830	66600	21500	29900	486	< LOD	51200	297000
Peeper 12	30	R	3270	15400	28200	147000	859	< LOD	120200	321000
Peeper 12	34	R	3100	12900	34600	101000	507	< LOD	125000	398000
Peeper 12	38	R	2980	5640	27700	109000	859	< LOD	115000	381000
Peeper 12	0	S	3480	38100	26500	21400	884	24	95000	378000
Peeper 12	4	S	2970	28700	17800	16500	966	33	78000	330000
Peeper 12	8	S	2920	29300	18300	21800	1120	< LOD	853003	329000
Peeper 12	12	S	4070	27500	17200	33900	987	38	70500	286000
Peeper 12	18	S	3300	39500	19500	35300	1220	< LOD	96800	331000
Peeper 12	22	S	705	19300	3740	26300	154	< LOD	18000	72400
Peeper 12	26	S	4610	77800	26300	92500	772	< LOD	132000	305000
Peeper 12	30	S	4050	14100	30300	107000	790	< LOD	157000	371000
Peeper 12	34	S	4440	23600	28000	87200	778	< LOD	113000	320000
Peeper 12	38	S	3330	4560	25400	96500	851	< LOD	90900	326000

Note: The following elements were below detection: Ag, Au, Bi, Ce, Cl, Cr, Cs, Hf, Hg, La, Mo, Nb, P, Pd, Sb, Se, Sc, Sn, Rb, Re, Ta, Te, Th, U, V, W, Y, Zr

Table XLIV. XRF data for peepers 12 and 14 (continued on next page).

Location	Sample depth (cm)	Note	Sr ppm	Pb ppm	As ppm	Zn ppm	Cu ppm	Ni ppm	Fe ppm	Mn ppm
Peeper 13	0	R	456	340	78.6	1950	738	52	51900	2040
Peeper 13	6	R	334	577	192	2390	1240	37	52400	2470
Peeper 13	10	R	381	1010	196	2990	1540	39	56600	1710
Peeper 13	14	R	437	278	68.1	1450	941	58	43200	1860
Peeper 13	18	R	452	171	33.5	940	719	93	28500	936
Peeper 13	22	R	392	519	106	1760	1100	84	42300	982
Peeper 13	0	S	399	384	122	2090	930	59	61700	1790
Peeper 13	4	S	349	737	206	2730	1540	69	56400	1790
Peeper 13	10	S	362	738	193	2750	1530	< LOD	57200	1540
Peeper 13	14	S	387	413	83.0	1660	948	50	42600	1260
Peeper 13	18	S	388	492	159	2390	1470	< LOD	70700	1760
Peeper 13	22	S	359	608	275	3190	2210	< LOD	72500	1470
Peeper 14	0	R	230	306	137	4780	419	52	42800	16000
Peeper 14	4	R	148	1230	314	4200	941	< LOD	28500	9370
Peeper 14	8	R	142	533	214	2390	344	53	19100	5610
Peeper 14	12	R	113	518	198	2280	365	< LOD	11900	4540
Peeper 14	16	R	134	623	202	2620	402	< LOD	13100	5000
Peeper 14	20	R	144	625	199	2520	401	43	14300	5680
Peeper 14	24	R	129	942	350	3410	534	50	20300	7260

Note: The following elements were below detection: Ag, Au, Bi, Ce, Cl, Cr, Cs, Hf, Hg, La, Mo, Nb, P, Pd, Sb, Se, Sc, Sn, Rb, Re, Ta, Te, Th, U, V, W, Y, Zr

Table XLV. XRF data for peepers 13 and 14.

Location	Sample depth (cm)	Note	Ti	Ca	K	S	Ba	Cd	Al	Si
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Peeper 13	0	R	1780	49800	10300	94700	707	35	29400	152000
Peeper 13	6	R	2980	63500	12000	133000	682	< LOD	39800	165000
Peeper 13	10	R	1910	57400	11800	120000	885	44	31000	136000
Peeper 13	14	R	3510	27200	14900	39800	861	< LOD	44800	236000
Peeper 13	18	R	2160	25200	22900	9630	746	< LOD	70700	355000
Peeper 13	22	R	3260	22400	22800	14100	651	< LOD	72000	324000
Peeper 13	0	S	2950	27500	15900	17600	865	25	63700	295000
Peeper 13	4	S	3880	25400	16500	27000	1090	42	69400	289000
Peeper 13	10	S	2940	30000	17700	25900	754	60	60500	268000
Peeper 13	14	S	2110	30600	15200	12900	966	39	50200	263000
Peeper 13	18	S	2150	30100	15000	15600	1290	< LOD	48900	249000
Peeper 13	22	S	2640	22500	13600	23300	1520	30	61900	267000
Peeper 14	0	R	1920	37800	11000	74300	922	34	34300	207000
Peeper 14	4	R	1110	21500	11100	38100	1330	60	22500	206000
Peeper 14	8	R	911	10900	6900	23600	1190	49	23200	299000
Peeper 14	12	R	642	2540	5810	5600	992	29	5950	127000
Peeper 14	16	R	862	3220	7000	12600	998	32	19300	318000
Peeper 14	20	R	1650	7340	1070	19300	773	32	32700	392000
Peeper 14	24	R	1600	8560	12300	35100	974	36	< LOD	403000

Note: The following elements were below detection: Ag, Au, Bi, Ce, Cl, Cr, Cs, Hf, Hg, La, Mo, Nb, P, Pd, Sb, Se, Sc, Sn, Rb, Re, Ta, Te, Th, U, V, W, Y, Zr

11. Appendix F: HOBO temperature loggers

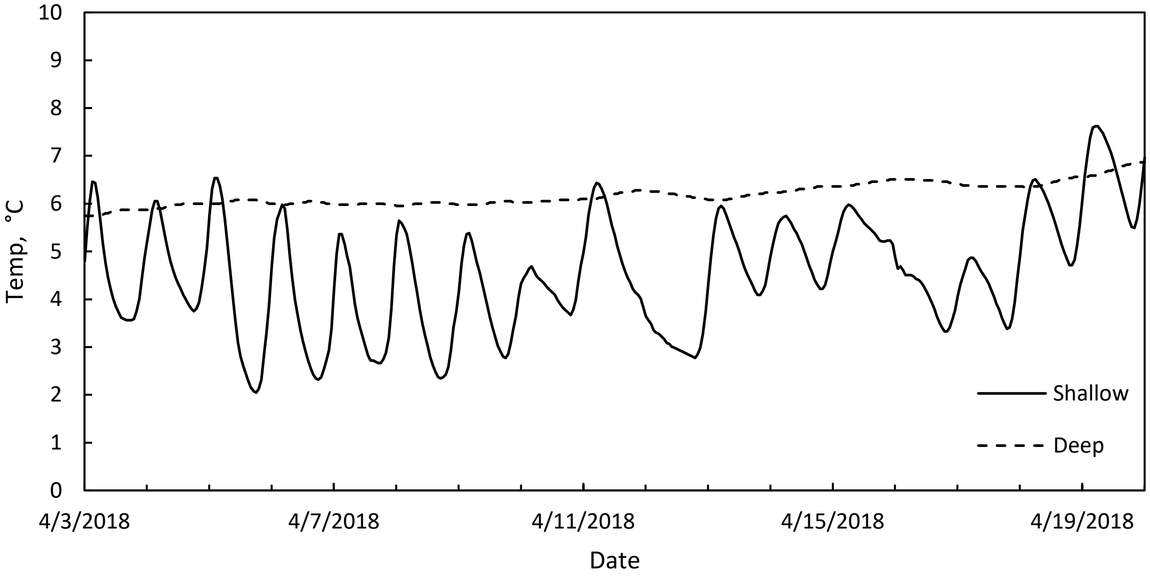

Figure 50. HOBO temperature logger data for peeper 4.

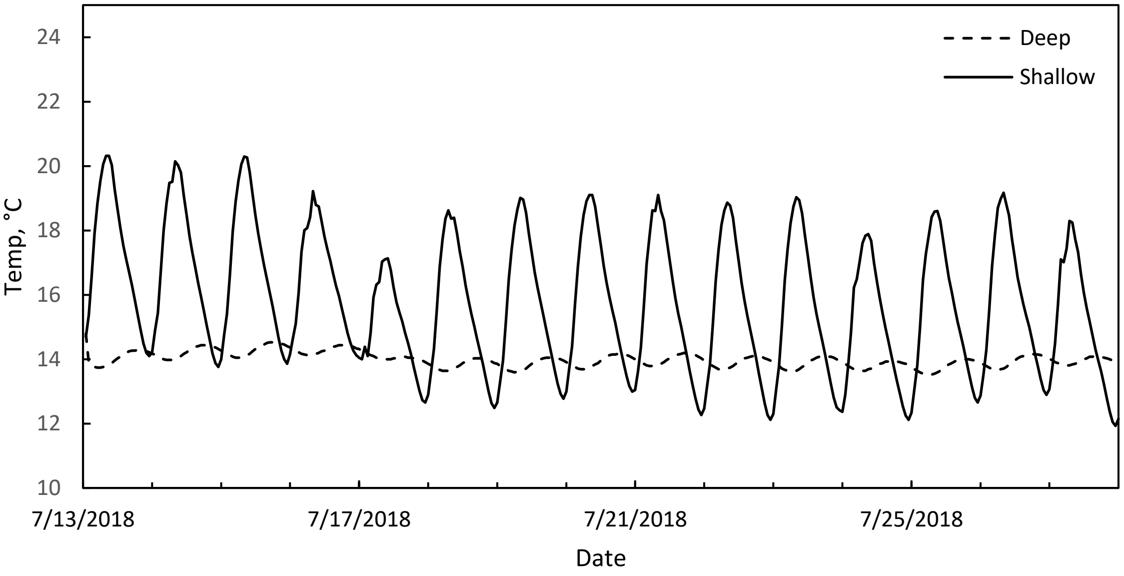

Figure 51. HOBO temperature logger data for peeper 8.

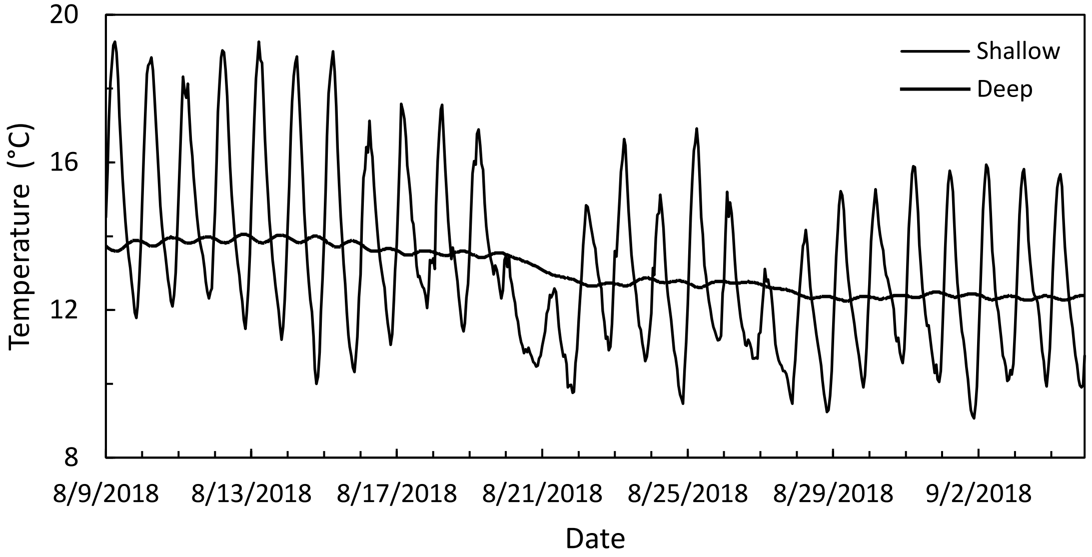

Figure 52. HOBO temperature logger data for peeper 10.

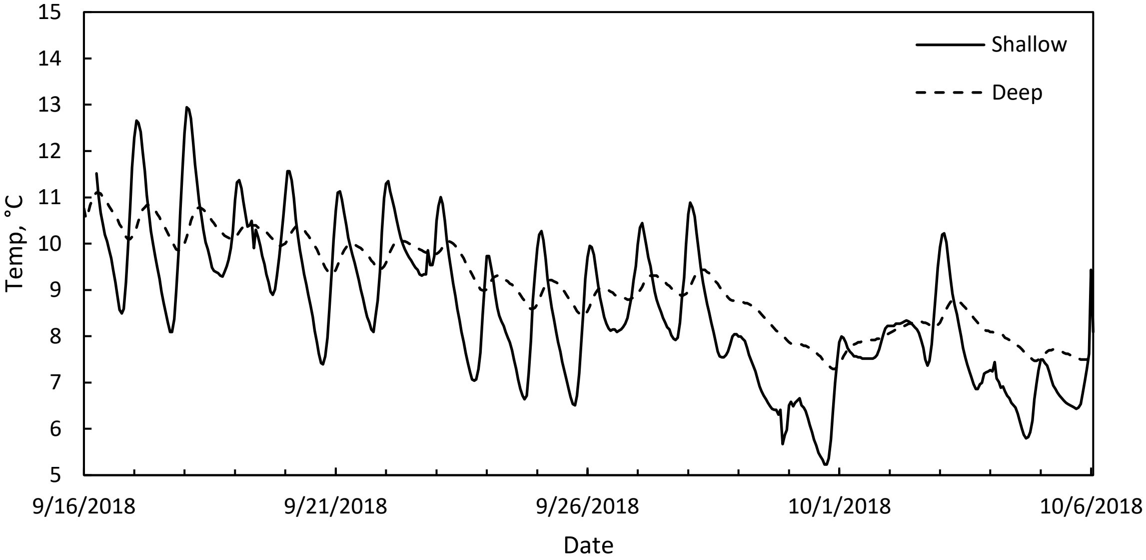

Figure 53. HOBO temperature logger data for peeper 12.

12. Appendix G: Water isotope study, peepers 6 and 7

During sampling of Peepers 6 and 7 and their associated piezometers, additional filtered samples were collected for analysis of stable isotopes of O and H. The samples were run by J. Timmer at the MBMG lab in Butte, Montana, using a Picarro water-isotope analyzer. The data are summarized in the following table, are plotted below, and are briefly interpreted.

Table XLVI. Water isotopes of ponds and piezometers near peepers 6 and 7.

Location	δ^{18}O, ‰	δD, ‰
Pond near Peeper 6	-15.1	-128
PZ-1	-17.6	-140
PZ-2	-15.0	-128
PZ-3	-17.1	-137
Pond near Peeper 7	-13.5	-118
PZ-4	-17.1	-138

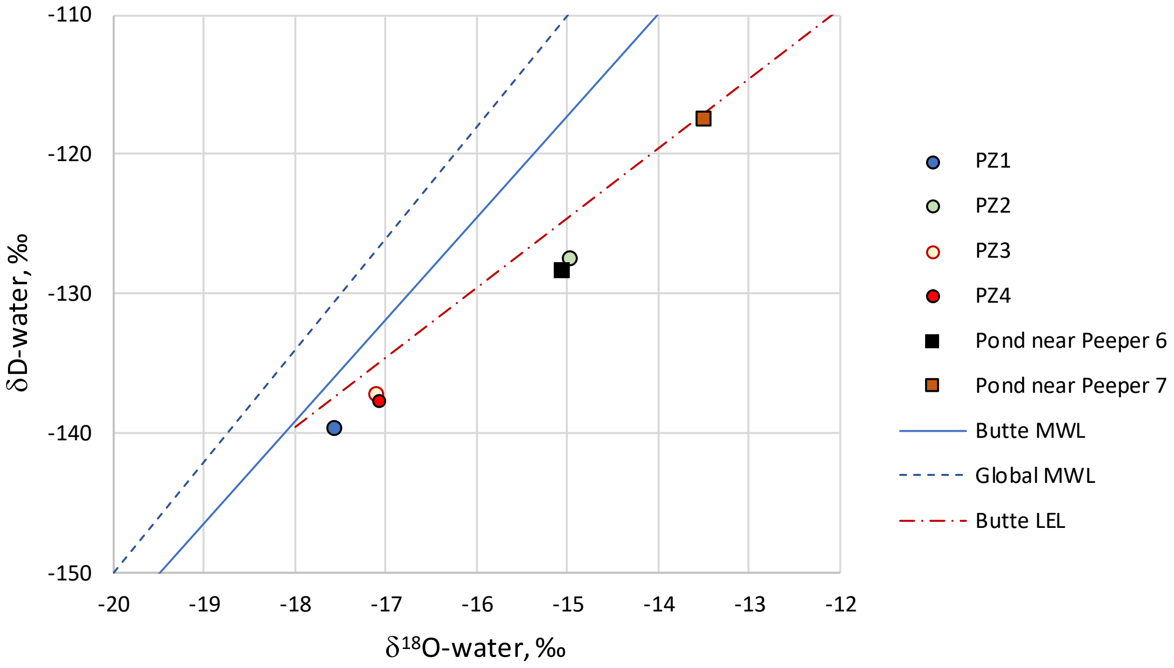

Figure 54. Water isotopes of ponds and piezometers near peepers 6 and 7.

From these data, it can be concluded that both ponds were significantly evaporated, since they are displaced from the Butte meteoric water line (MWL) along the Butte local evaporation line (LEL). Peeper 6 was deployed in a large pond, whereas Peeper 7 was in a much smaller pond. Within the large pond, piezometer PZ-2 had the same isotopic signature as the surface water in the pond, consistent with a downwards gradient of pore water at the north end of the pond near the embankment. The other two piezometers in the large pond (PZ-1 and PZ-3) were non-evaporated, consistent with their position at the south, recharging end of the pond. The small pond near Peeper 7 was highly evaporated. In contrast, the piezometer at the south end of the small pond (PZ-4) was non-evaporated, again consistent with upwelling water at this location.

13. Appendix H: Photographs

Figure 55. Peeper installation locations: (A) Sampling Peeper 1, (B) Sampling Peeper 2, (C) Sampling Peeper 3, (D) Peeper 4(looking upstream), (E) Installing Peeper 5, (F) Peeper 6 (looking NW) with PZ-2 in view.

Figure 56. Peeper installation locations: (A) sampling Peeper 6, (B) Peeper 7 location looking north, (C) Peeper 8 (looking downstream), (D) Peeper 9 (looking downstream), (E) Peeper 9 after sampling. Note coarse sand, (F) Sampling Peeper 10.

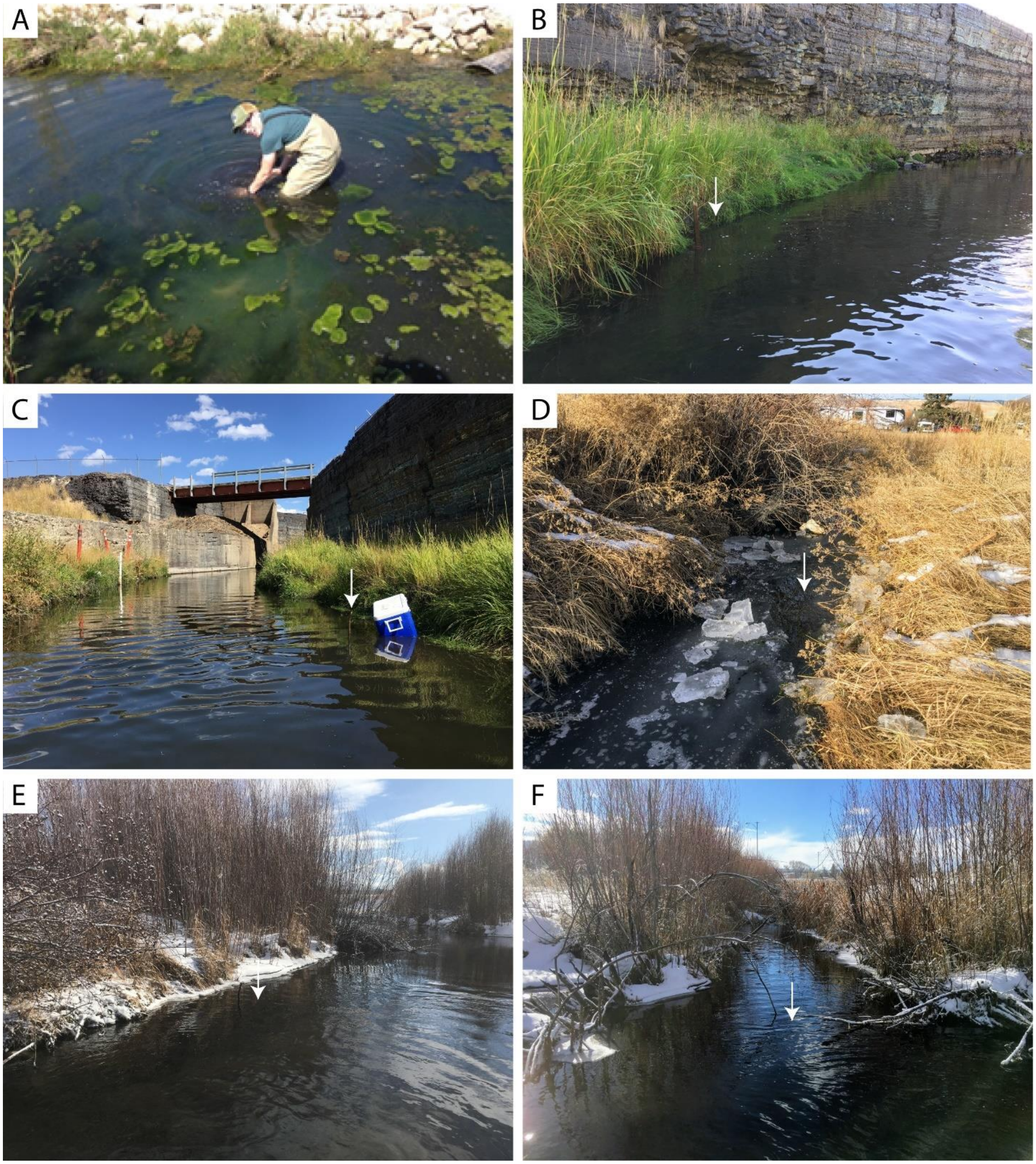

Figure 57. Peeper installation locations: (A) Sampling Peeper 11, (B) Peeper 12 (looking down stream), (C) Peeper 13 (looking upstream), (D) Peeper 14 (looking downstream), (E) Peeper 16 (looking upstream), (F) Peeper 17 (looking upstream).

SIGNATURE PAGE

This is to certify that the thesis prepared by Robert M. Rader entitled "Geochemistry of Metals and Nutrients in Fine-Sediment Pore Water in Blacktail and Silver Bow Creeks, Butte, Montana" has been examined and approved for acceptance by the Department of Geological Engineering, Montana Technological University, on this 19th day of April, 2019.

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