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Arsenic Geochemistry in Warm Spring Ponds: New Field and Experimental Results

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ARSENIC GEOCHMISTRY IN WARM SPRING PONDS: NEW FIELD AND EXPERIMENTAL RESULTS

by

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requirements for the degree of

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Abstract

Silver Bow Creek (SBC) flows into the Warm Springs Ponds Operable Unit (WSPOU), where various containment cells are used to precipitate copper and other metals (e.g., Cd, Cu, Mn, Pb, Zn). Lime is added seasonally to increase the pH and assist in removal of metals from the water column. Although the WSPOU is effective at removing copper and other cationic trace metals, concentrations of dissolved arsenic exiting the facility are often above the site specific standard, 20 μg/L, during low-flow periods each summer and fall.

This thesis is a continuation of arsenic geochemistry studies by Montana Tech in the WSPOU. Field work focused on Pond 3, the largest and first in the series of treatment ponds. Shallow groundwater was sampled from 8 PVC piezometers located near the south end of Pond 3. Three sediment pore-water diffusion samplers ("peepers") were also deployed at the south end of Pond 3 to examine vertical gradients in chemistry in the top 25 cm of the pond sediment. In general, the pH and Eh values of the shallow groundwater and sediment pore-water were less than in the pond water. Concentrations of arsenic were generally higher in subsurface water, and tended to pass through a maximum (up to 530 μg/L) about 10 cm below the sediment-water interface. In the peeper cells, there was a strong positive correlation between dissolved As and dissolved Fe, and an inverse correlation with sulfate. Therefore, the zone of arsenic release corresponds to a zone of bacterial Fe and sulfate reduction in the shallow, organic-rich sediment. Redox speciation of arsenic shows that arsenate (As(V)) is dominant in the pond, and arsenite (As(III)) is dominant in the subsurface water.

A series of laboratory experiments with pH adjustment were completed using SBC water collected near the inlet to the WSPOU as well as water and shallow sediment collected from Pond 3. Water ± sediment mesocosms were set up in 1-L Nalgene bottles (closed system) or a 20-L aquarium (open system), both with continuous stirring. The pH of the mesocosm was adjusted by addition of NaOH or HNO_3 acid. The closed system provided better pH control since the water was not in contact with the atmosphere, which prevented exchange of carbon dioxide. In both the closed and open systems, dissolved arsenic concentrations either decreased or stayed roughly the same with increase in pH to values > 11. Therefore, the release of dissolved As into the treatment ponds in low-flow periods is not due to changes in pH alone.

All of these results support the hypothesis that the arsenic release in WSPOU is linked to microbial reduction of ferric oxide minerals in the organic-rich sediment. Upwards diffusion of dissolved As from the sediment pore-water into the pond water is the most likely explanation for the increase in As concentration of the WSPOU in low-flow periods.

Keywords:

Arsenic Speciation, Lime Treatment, Iron Reducing Bacteria, Sulfate Reducing Bacteria, Peepers, Geochemical Modeling

Dedication

I dedicate this master's thesis to my family. They have been my cheerleaders all along this road believing that I could achieve this significant accomplishment. I want to extend my sincere gratitude to my parents, Dick and Debbie Crockford, for their unconditional love and words of encouragement and raising me with the attitude that anything is possible with perseverance and motivation. I want to acknowledge my husband, Chauncey, for his love and support and his patience when there were unexpected changes in my schedule on this project and he needed to step up and fulfill duties as mom and dad to our two sons. I want to thank my two amazing sons, Liam and Quincey Boese, who have taught me much along this road and love me for who I am. They always brighten my day with their humor and remind me that tomorrow is a whole new day; I love that they are so inquisitive and love to learn. And last, but definitely not least, I want to thank my sisters, Rebecca Combs and Theresa Unbehend, and my aunt, Mary Ellen Crockford, whom provided me with inspiration and support whenever I needed it.

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I want to thank Dr. Chris Gammons for providing me this amazing opportunity to work with him on this stimulating project. He shared an enormous amount of knowledge with me and patiently guided me throughout the process - his dedication to his students is unsurpassed. Also, I would like to thank Dr. Kumar Ganesan, Jeanne Larson, and Gary Wyss whom served on my committee and provided me with words of wisdom as well as edited my thesis. I’d like to give additional appreciation to the Environmental Engineering Department who funded my graduate schooling and opened more doors for my professional career by providing me this opportunity. My project would not have been successful without the help of Gary Wyss who gladly helped me operate the ICP-OES and assisted me with preparation of my lab samples. I’d like to thank Seth Reedy, Corey Swisher, and Angela Bolton, fellow graduate students, for assisting me in the field and in the lab during this project. I’m appreciative of the help provided by the operators at the Warm Springs Ponds during field work. Finally, I want to thank Jim Chatham with ARCO/BP for funding this thesis project; the support provided by companies such as ARCO/BP is tremendously appreciated by the students and Montana Tech and hopefully the symbiotic relationship continues far into the future. The learning opportunities on projects like these provide an unmeasurable amount of education and practical experience as well as a valuable springboard for our careers.

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Glossary of Terms

As = arsenic

b.d. = below detect

Ca = calcium

cfs = cubic feet per second

Cu = copper

DOC = dissolved organic carbon

Eh = redox potential

EWC = East Wet Closure

FA = filtered-acidified

Fe = iron

FU = filtered-unacidified

GPS = global positioning satellite

GW = groundwater

ICP-MS = inductively coupled plasma-mass spectrometry

ICP-OES = inductively coupled plasma-optical emission spectrometry

MD=microwave digested

Mn = manganese

MS-5 = Minisonde 5

mV=milli-volts

N/A = not applicable

ORP = oxidation reduction potential

PES = polyestersulfone (filter)

PPB = part per billion

PPM = part per million

PVC = polyvinyl chloride

QA/QC =quality assurance/quality control

RA=raw-acidified

RU = raw-unacidified

SC = specific conductivity (μS/cm)

SBC = Silver Bow Creek

SWI = sediment water interface

SWL = static water level

TR=total recoverable

TSS=total suspended solids

WSPOU = Warm Springs Ponds Operable Unit

WWC = West Wet Closure

Zn = zinc

1. Introduction

Arsenic (As) is a highly toxic naturally-occurring element with average concentration in soil of 6 ppb (LaGrega, Buckingham, and Evans, 1994); however, due to the historic processes of metal extraction and lack of environmental considerations and regulations, arsenic concentrations are often found deposited around the source as well as carried downwind and downstream in concentrations that can pose a threat to human or aquatic health. The Butte-Anaconda area of SW Montana, in particular, has elevated arsenic contamination that was caused by over 150 years of mining and smelting of the rich ore deposits of Butte (Moore and Luoma, 1990). Reclamation activities have been on-going for several decades and have mitigated some of the environmental damage, although reclamation continues today. The present thesis addresses the geochemistry of arsenic in the Warm Spring Ponds Operable Unit (WSPOU), which is one of the operable units of the greater Butte-Upper Clark Fork Superfund Complex. Specific objectives of this thesis are given at the end of this chapter following a review of the history and previous work at the WSPOU.

1.1. Background

Gold, silver, and copper, as well as other metals, were discovered in the Butte, Montana area during the mid-1800’s and heavily mined from then to the present day. Due to high costs to ship and smelt the ore, mills and smelters were built in Butte and Anaconda, Montana (Glasscock, 1971). Mine tailings produced from milling and smelting activities were disposed into Silver Bow Creek (SBC) and severely contaminated the creek with metals, including arsenic, which is often a by-product of sulfide ores (Moore and Luoma, 1990). Three ponds were built at the lower end of Silver Bow Creek approximately 25 miles downstream of Butte, MT during the early to mid-1900’s to prevent these mine tailings and dissolved metals from entering the Clark Fork River. These ponds are known as the Warm Springs Ponds Operable Unit (WSPOU) and are roughly 2,700 acres in total area (EPA, 1992).

1.2. WSPOU Layout

Figure 1 shows the general layout of the WSPOU complex. Silver Bow Creek enters the WSPOU from the south near sampling site SS-01 and flows into Pond 3, the largest and most recently constructed settling pond at the site. Lime is added at the inlet to Pond 3 as needed, usually during the fall, winter, and early spring, to increase the pH and assist in settling the metals (EPA, 1992). Lime is typically not added in the summer because photosynthesis by plants and algae in the ponds causes the pH to remain above 9. From Pond 3, the flow is distributed northward into the West Wet Closure (WWC), the East Wet Closure (EWC), and Pond 2. The WWC and EWC are shallow ponds that are underlain by streamside tailings. Pond 2 was originally constructed to capture sediment travelling down SBC, but eventually filled to near-capacity, creating the need for Pond 3. Water exits the WSPOU at the northwest corner of Pond 2 at sampling site SS-05, where it flows as lower Silver Bow Creek for about a mile, at which point Warm Springs Creek enters from the west and the combined flow becomes the upper Clark Fork River.

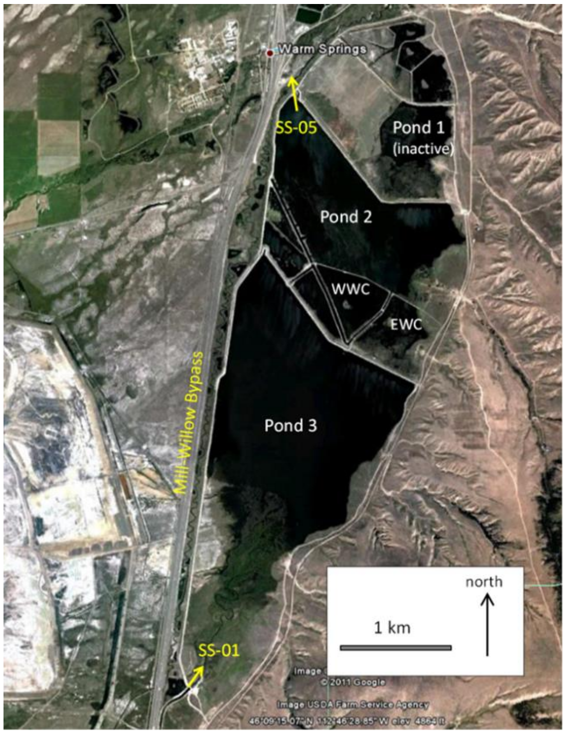


Figure 1. Warm Springs Ponds Operable Unit layout.

The WSPOU was originally constructed to remove toxic heavy metals, including copper (Cu), cadmium (Cd), manganese (Mn), lead (Pb), and zinc (Zn), prior to entry into the Clark Fork River. After several decades of monitoring (Pioneer Technical, 2005 and CDM, 2010), the WSPOU has proven to do an excellent job of removing these metals to meet State and Federal aquatic standards. However, arsenic enters the ponds primarily with suspended sediments during high-flow periods in spring runoff and summer thunderstorms, and exits the ponds primarily in dissolved form. The concentrations of arsenic exiting the ponds are particularly high during the summer and fall low-flow periods. Often the effluent concentrations exceed 50 μg/L As, which is 30 μg/L *more* than the site specific arsenic water standard of 20 μg/L. (For reference, the US EPA's drinking water standard for arsenic is 10 μg/L.) See Figure 2 below for semi-annual arsenic concentrations collected from the inlet and outlet of WSPOU.

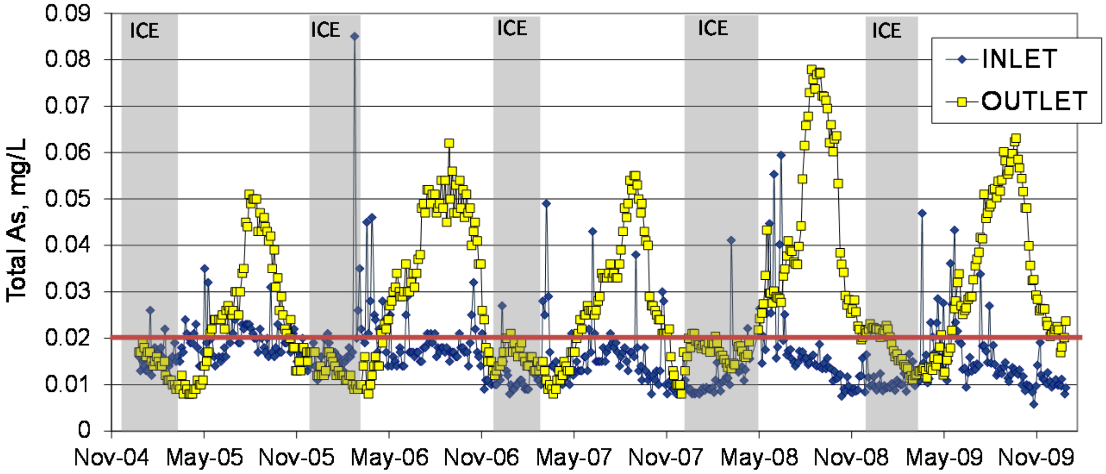


Figure 2. Bimonthly arsenic concentrations collected from the inlet (SS-01) and outlet (SS-05) of WSPOU from 2004 to 2010 (Data from Pioneer Technical, 2005 and CDM, 2010).

1.3. Possible causes of arsenic releases from the WSPOU

Previous and ongoing research at WSPOU has led to a number of hypothesis to explain the elevated concentrations of arsenic in the effluent of the ponds during the summer low-flow periods. These include: (1) influx of As-contaminated groundwater; (2) desorption of As bonded to suspended sediment due to the increase in pH from the addition of lime or the photosynthesis process; (3) mobilization of As from the benthic sediment; and (4) upwards diffusion of As from the sediment pore-water (the water in between the sediment particles) into the pond.

Describing these hypotheses a bit further, each one will be discussed in the order it is listed above. Groundwater may be a possible contributor to the increase in arsenic concentration since the ponds are located over historic tailings that contain arsenic and arsenic bearing materials. Depending on the vertical gradient in hydraulic head, groundwater may be flowing ‘upward’ or ‘downward’ into Pond 3 possibly affecting the As concentration. Because of the historic streamside tailings along SBC, suspended sediment may have arsenic attached to it thereby traveling continuously downstream and into the WSPOU. Once in the ponds, the increase in pH might possibly release this arsenic into the water in a dissolved form.

Arsenic geochemistry in various waters has been studied in great depths over the years. A recycling effect of adsorption and desorption between the arsenic and iron hydroxide within sediments of oxygenated bottom waters has been studied in anthropogenic impacted lakes (Belzile and Tessier, 1990; Couture, Gobeil, and Tessier 2010). Upon the iron binding with sulfur or carbon within the sediment, arsenic is allowed to diffuse from sediment pore-water through iron oxide rich sediments and travel into the overlying water column increasing arsenic concentrations in the lake (Martin and Pedersen, 2002).

1.4. Previous Work by Montana Tech

Previous research at the WSPOU conducted by Montana Tech includes Gammons C.H., Grant T.M., Nimick D.A., Parker S.R., DeGrandpre M.D. (2007) “Diel changes in water chemistry in an arsenic-rich stream and treatment-pond system”. This study measured the 24-hour changes in field parameters and concentrations of arsenic as well as heavy metals during two summer sampling events in 2004 and 2005 at the outlet to the WSPOU complex and in the Mill-Willow Bypass. The Mill-Willow Bypass diverts the adjoined Mill and Willow Creek from entering into the WSPOU and travels along the west side of the WSPOU. It was concluded that very few diel changes were noted in the ponds due to a lack of differences in temperature, dissolved oxygen (DO), and pH. Conversely, the Mill-Willow Bypass did show diel changes in As, Mn, iron (Fe), bicarbonate (HCO_3^-) and calcium (Ca) concentrations. As noted from the study, the chemical boundary layer across which diffusion of biological nutrients and waste products must take place is diminished in streams due to the flowing water.

Lauren Gordon completed her master's non-thesis project in 2011 focusing on a comparison of the sediment and sediment pore-water chemistry of two shallow ponds, the "Hog Hole" and the West Wet Closure (WWC), of the WSPOU. The Hog Hole is native material that was used as a borrow pit and the WWC has streamside tailings from SBC submerged below the water; both ponds receive surface water from Pond 3. It was concluded that the Hog Hole and the WWC both had low or undetectable concentrations of Cd, Cu, Pb, and Zn in the sediment pore-waters. Concentrations of As were as high as 300 µg/L in the WWC sediment pore-waters, but were not detected in the Hog Hole pore-waters. Elevated concentrations of Fe and Mn were measured in both the Hog Hole and WWC sediment. Concentrations of H_2S were barely detected in the WWC but were up to 9 mg/L in the Hog Hole sediment.

Joshua Lee focused his 2012 master's thesis project on the release mechanism of arsenic and the geochemistry of Pond 2 and the WWC (simultaneously studied during Gordon's project). The conclusion for Pond 2 was an increase in arsenic concentration either in the mid-nepheloid layer or near the bottom of this layer with arsenic continuing to increase as depth increased in the depth profile. As for the WWC, it was concluded that, generally, the arsenic concentration was the highest at the bottom of the nepheloid layer and then decreased with depth. Concentrations of dissolved metals from Pond 2 sediment pore-water were highly variable: Fe ranged from 0.1 to 1230 mg/L (avg. 176 mg/L), Mn from 0.02 to 38 mg/L (avg. 6.5 mg/L), and As from 0.02 to 3.40 mg/L (avg. 0.42 mg/L).

1.5. Thesis Objectives

Objectives of this thesis project include a continuation of geochemistry studies, especially arsenic mobility, within the WSPOU focusing on Pond 3 as well as conducting lab experiments. The study of Pond 3 is significant because 1) Pond 3 is the largest of all of the ponds and 2) this is the first pond that SBC enters where lime treatment is performed within the WSPOU complex. By conducting lab experiments, arsenic mobility was studied from various angles such as different sampling locations of water collected, collecting samples at various streamflows, and adjusting pH of collected water which were testing hypotheses (2) and (3) from Section 1.3. Field work using piezometers and sediment pore-water samplers (aka “peepers”) was completed to also assist in answering the question of “what is causing the increase in arsenic concentration”. Field work completed using the peepers was designed to specifically test hypothesis (4) and builds on previous work of Gordon (2011) and Lee (2012). Hypothesis (1) was also examined with data collected from the field.

Methods used to determine the cause of the increase in arsenic are described in Chapter 2, results of the lab experiments and field work are presented in Chapter 3, results are explained in Chapter 4, conclusions and recommendations are listed in Chapter 5, references are listed following Chapter 5, and tables of analytical data and photographs are included in the appendices.

2. Methods

2.1. Laboratory experiment and sampling methods

Two different laboratory experiments were performed simulating an open system (Pond 3 water and sediment placed in a fish tank) as well as a closed system (bottled site water) to examine the effects of arsenic concentrations in water samples when pH was adjusted. Details of these experiments are discussed in the following sections.

2.1.1. Closed System Experiments and Sampling Methods

Water used in the ‘closed system’ was collected in two 1-liter Nalgene plastic bottles as well as two 60-mL plastic bottles (one filtered and one unfiltered) during sampling events from Silver Bow Creek near the inlet of Pond 3 during different streamflows. A total of sixteen 1-L bottles were collected over a period of approximately three months (April 4-July 7, 2014) and transported to a chemistry laboratory at MT Tech. Field measurements such as temperature, specific conductivity (SC), pH, oxidation-reduction potential (ORP), and dissolved oxygen were collected on-site during each water collection using a Hydrolab MiniSonde 5 (MS-5) (HACH Environmental). The MS-5 was calibrated each time prior to using it in the field and the lab.

In the laboratory, one of the 1-L bottles was placed on a stir plate for continuous stirring while the other 1-L bottle was placed in the refrigerator as a back-up sample. The temperature was allowed to raise to ambient room temperature within the lab. The MS-5 was inserted into the 1-L bottle of water and the pH was simultaneously measured as sodium hydroxide (NaOH) was added to increase the pH of the system by approximately 1 pH unit during each adjustment. The pH was increased roughly 2 to 3 pH standard units from the original pH measured instream. Upon each pH change the MS-5 was removed and two 15-mL samples of water were collected with a syringe. One sample was filtered using a 0.2 μm pore diameter PES filter and acidified (filtered acidified, FA) while the other sample was unfiltered and acidified (raw acidified, RA). Acidification was completed with 1% nitric acid (HNO_3) and placed in the refrigerator for preservation methods until analysis was performed on the ICP-OES (more detail of analysis is discussed in Section 2.3 Analytical Methods). After the samples were collected, the bottle was tightly capped and para-film was placed around the lid in order to prevent CO_2 from off-gassing. Approximately 48 hours was allowed to pass between additional pH changes. Figure 3 shows the laboratory experiment set-up of the ‘closed system’. Data collected from the closed system experiments can be found in Appendix A.

Figure 3. Bottled site water used for the "closed system".

The concentration of total suspended solids (TSS) of the SBC water samples was determined using raw water samples collected on-site at the inlet to WSPOU as well as the samples collected after the third pH adjustment. These samples were weighed (amount of water filtered), filtered (filter pre-weighed), and dried in an oven over night. Once drying was complete, the filter papers were re-weighed (filter and total suspended solids) and the TSS was determined (the filter weight was subtracted from the dried sediment and divided by the weight of water filtered) for each of the eight initial samples (HB1-8) as well as four samples collected from the final pH adjustments (HB5-3, HB6-3, HB7-3, and HB8-3).

2.1.2. Open System Experiments and Sampling Methods

Approximately 5-gallons of water and 1-liter of shallow, organic-rich sediment were collected in a 5-gallon bucket from Pond 3 and transported to a chemistry laboratory. This Pond 3 mixture was poured into a fish tank (approximately 5-gallon volume) and the circulation system was turned on for the duration of this experiment. Once the circulation system was operating, the water was pumped upwards inside a tube and over a weir allowing the water to fall approximately 3-6 inches back into the fish tank. This configuration somewhat simulated an ‘open system’ at the WSPOU because it was left open to the air. Three separate pH adjustment experiments were completed using water and shallow sediment collected from Pond 3; the order of the experiments was a pH increase, a pH decrease, and a second pH increase. Sodium hydroxide was used to increase the pH and nitric acid was used to decrease the pH of the system. For this experiment, the Hydrolab MS-5 was placed inside the fish tank for the duration of the experiment in order to measure pH and specific conductivity (SC). Upon each pH change, two 15-mL samples of water were collected in plastic bottles. These bottles were labeled “FA” and “RA” which are abbreviations for “filtered-acidified” and “raw-acidified”. The FA sample was filtered using a syringe and a 0.2 μm pore diameter PES filter while the RA sample was not filtered; both of these samples were preserved with 1% nitric acid and placed in the refrigerator prior to analysis for trace metals on the ICP-OES and ICP-MS (more detail of analysis is discussed in Section 2.3 Analytical Methods). Approximately 48 hours was allowed to pass between additional pH changes. Figure 4 shows the laboratory experiment set-up of the ‘open system’. Data collected from the open system experiments can be found in Appendix B.

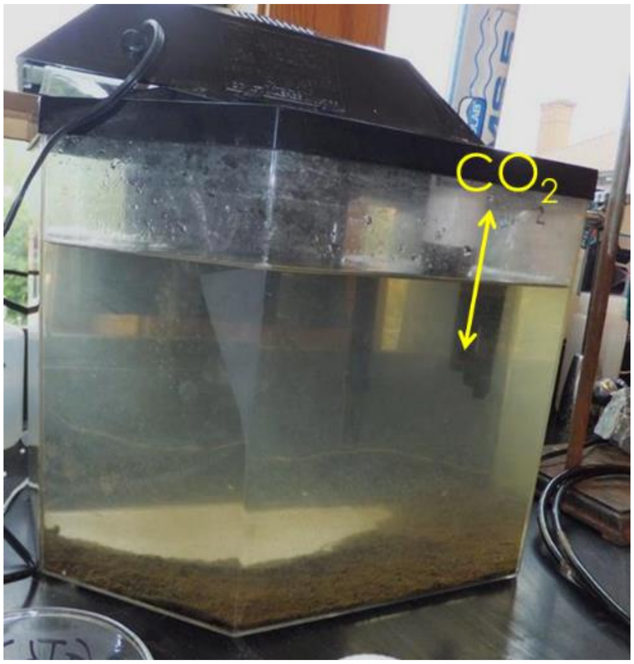


Figure 4. Fish tank used for the "open system".

2.2. Field Methods

Field work included installation of and sampling water collected from piezometers and pore-water diffusion samplers, known as “peepers”. Pond water samples were also collected near the piezometers for comparison purposes and were analyzed similarly as the piezometers and peepers. (More details are below.) Locations of the piezometers and peepers were determined using a Magellan eXplorist 300 Global Positioning System (GPS) handheld unit. GPS coordinates are located in Appendix C. Locations of piezometers and peepers installed in Pond 3 are found on Figure 5.

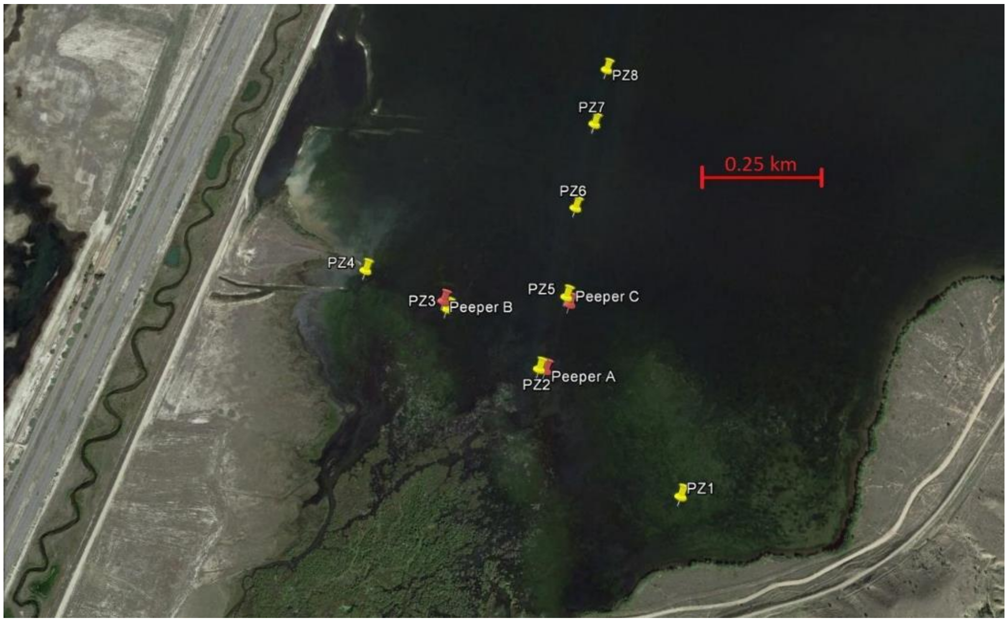


Figure 5. Locations of piezometers and peepers installed in Pond 3 of the Warm Springs Ponds.

2.2.1. Piezometers

Eight piezometers (PZ) were installed in the southern portion of Pond 3 in order to study the geochemistry of the groundwater. PZ 1 to 4 were placed in an easterly to westerly direction and PZ 5 to 8 extending perpendicular to PZ2 in a northerly direction.

The piezometers were created using 1" PVC pipe in five and ten foot lengths. The bottom 12 inches of the pipe were sawn to create a screen, the end was capped, and the bottom 1 to 2 feet was filled with coarse sand to act like a filter. These piezometers were installed 4 to 9 feet below the sediment-water interface (SWI) in 1 to 7.5 feet of water from an inflatable kayak by either pushing them into the pond sediment by hand or using a fence-post pounder.

2.2.1.1. Piezometer Sampling

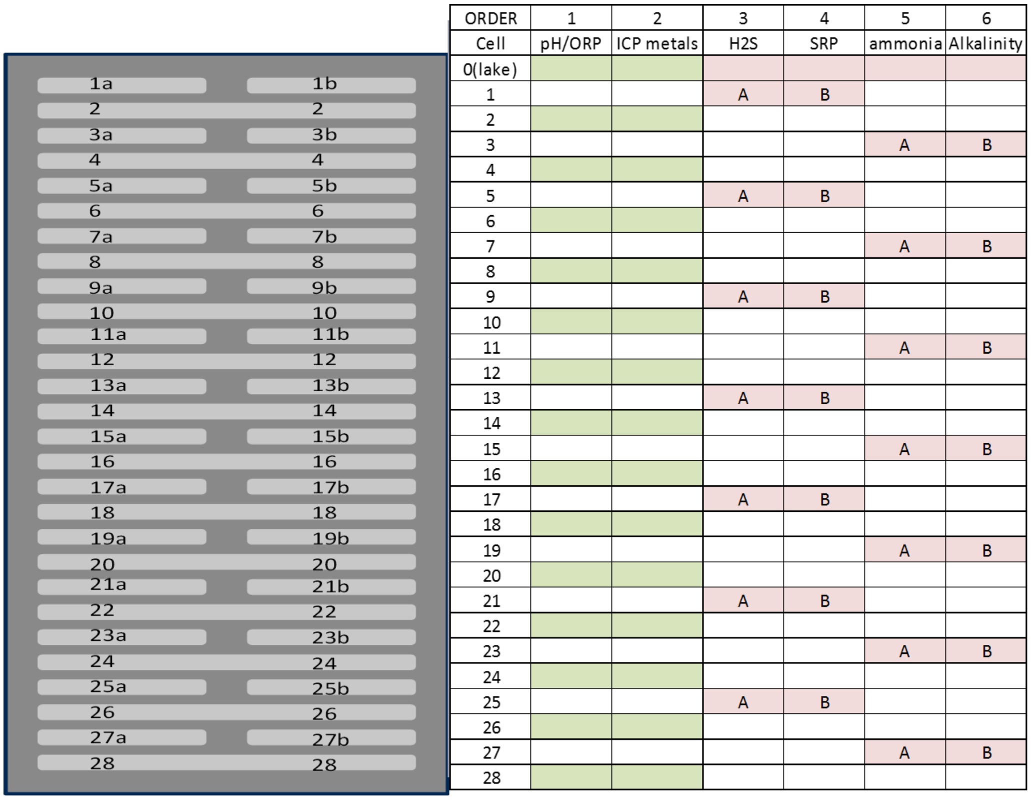
Once installation was complete, each piezometer was pumped dry with a peristaltic pump and flexible tubing. About one cubic foot of argon gas was then pumped back into the bottom of the piezometer to create a barrier to prevent oxidation from occurring as the water levels in the piezometers recovered. Oxidation is prevented because argon gas is heavier than air and will reside on top of the incoming groundwater inside the piezometer. Each piezometer was loosely capped to allow the argon gas to slowly escape as the water levels recovered. Sampling occurred after several days had passed allowing the water inside the piezometers to recharge. Prior to collecting samples, depth inside the piezometer to the static water level (SWL) and the depth outside the piezometer from the top of casing to the pond were measured. This estimated the vertical gradients in hydraulic head and to understand whether groundwater flow was directed upwards or downwards at this spot in the pond. Field measurements such as temperature, specific conductivity (SC), pH, oxidation-reduction potential (ORP), and dissolved oxygen were collected on-site during water collection using a Hydrolab MS-5 equipped with a flow cell. The MS-5 was calibrated each time prior to using it in the field. A peristaltic pump was used to collect samples which were collected in two 60-mL and one 120-mL Nalgene bottles. The 60-mL bottles were labeled “FA” and “FU” and the 120-mL bottle was labeled “RU”. The abbreviations on the bottles were for “filtered-acidified”, “filtered-unacidified”, and “raw-unacidified”. The FA sample was filtered using a syringe, a 0.2 µm pore diameter PES filter, and preserved with 1% nitric acid; this sample was analyzed for trace metals on the ICP-OES and ICP-MS. The FU sample was filtered, unacidified, and was analyzed for nutrients using a HACH spectrophotometer. The RU sample was unfiltered, unacidified, and was used for alkalinity titration using a digital titrator. Further details on instrumental analysis are discussed in Section 2.3. Field and laboratory data collected from the piezometers can be found in Appendix C.

2.2.2. Peepers

Sediment pore-water was sampled at depths between 0 and 25 centimeters below the SWI using a modified Hesslein diffusion sampler (aka “peeper”). Figure 6 is a photo of one of the peepers used on this project. Hesslein (1976) describes these devices as highly suited to collect closely-spaced, vertical pore-water samples from sediment with very low hydraulic conductivity, such as pond sediment (e.g., Martin and Pederson, 2002). Peepers allow sediment pore-water to diffuse through a nylon membrane (5 μm pore diameter) that is placed between a solid acrylic rectangular shaped back with cells hollowed out and a matching acrylic front with holes that correspond in size and spacing to the cells. There are 28 horizontal cells vertically placed at 1 cm intervals from top to bottom of the peeper. The rows alternate between two side-by-side smaller cells (5 mL volume) and one larger cell (11 mL volume). Stainless steel screws are used in assembly along the perimeter and in the middle of the peeper.

Figure 6. Modified Hesslein diffusion sampler ("peeper").

Each peeper was assembled in a cooler partially filled with de-ionized (DI) water. Nitrogen gas was bubbled throughout the DI water to rid the water of dissolved oxygen. After the peeper was assembled, the lid of the cooler was closed and N_2 gas was continually bubbled in the water for at least 24-hours until the peeper was ready to deploy in the field. As the peepers were put together, it was carefully observed that no air bubbles were trapped within the peeper cells. During transportation, the nitrogen gas tank was turned off and a portable argon gas tank was used to keep the water in the cooler and peeper deoxygenated. The cooler and the portable argon tank were transported in the vehicle and then on the inflatable kayak until the peepers were deployed. Peepers A, B, and C were installed near piezometers 2, 3, and 5, respectively. Peepers were collected approximately 2 to 3 weeks after installation, which is the recommended time for equilibrium to be reached (e.g., Hesslein, 1976). As soon as the peepers were retrieved from the sediment, they were carefully placed in a makeshift glovebag consisting of two gallon-sized Ziploc bags taped together and duct taped at the end, with flexible tubing for flow of Ar gas inserted inside the bag. Once the peepers were collected and brought to the “work-bench” in the field, a syringe needle was inserted through the glovebag and nylon membrane to collect water from the individual cells according to the sampling plan (Figure 7). Oxidation-reduction potential (ORP), pH parameters, and ICP metal samples were collected from the even numbered cells, H_2S and ammonia samples were collected from column A and soluble reactive phosphate (SRP) and alkalinity were collected from column B. All sampling was completed as quickly as possible in the field since time was of the essence and this decreased the opportunities for the samples to oxidize.



ORDER	1	2	3	4	5	6
Cell	pH/ORP	ICP metals	H2S	SRP	ammonia	Alkalinity
0(lake)	🟩	🟩	🟥	🟥	🟥	🟥
1			A	B		
2	🟩	🟩				
3					A	B
4	🟩	🟩				
5			A	B		
6	🟩	🟩				
7					A	B
8	🟩	🟩				
9			A	B		
10	🟩	🟩				
11					A	B
12	🟩	🟩				
13			A	B		
14	🟩	🟩				
15					A	B
16	🟩	🟩				
17			A	B		
18	🟩	🟩				
19					A	B
20	🟩	🟩				
21			A	B		
22	🟩	🟩				
23					A	B
24	🟩	🟩				
25			A	B		
26	🟩	🟩				
27					A	B
28	🟩	🟩				

Figure 7. Peeper sampling plan.

2.2.2.1. Peeper Sampling

Prior to retrieving the peepers, sets of bottles were prepared in the lab to simplify water sample collection for ICP, soluble reactive phosphate (SRP), alkalinity, ammonia, and dissolved sulfide analysis. Fifteen (one blank included in this total) 60-mL Nalgene sample bottles for major and trace elements analysis using an Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES) were acid washed with 5% nitric acid for 24-48 hours to remove any trace metal contamination and then rinsed with de-I water. These bottles were then filled with 20-mL of de-I water and 300-µL of concentrated nitric acid, capped, weighed, and the mass noted on the bottle. Glass “Test-n-Tube” vials for SRP analysis were weighed with the cap on and mass noted on the bottle. A set of 60-mL Nalgene sample bottles for alkalinity analysis were filled with 25-mL of de-I water, capped, weighed, and the mass was noted on the bottle. For ammonia and dissolved sulfide analysis, a set of 60-mL Nalgene sample bottles for each analysis were filled with 20-mL of de-I water, capped, weighed, and the mass was noted on the bottle. (Sulfide analysis was only performed on Peeper A since this was the only area that H_2S was detected by smell.) Sulfate was analyzed at a later date by $BaCl_2$ addition, using the remaining water from the FA samples.

Approximately 5-10 mL of water was collected using a syringe needle from the corresponding cells in the peepers according to the sampling plan, as previously described in Section 2.2.2 Peepers, and placed in the appropriate Nalgene bottles. All “FA” samples for ICP-OES analysis were filtered through a 0.2 μm PES filter. Dilution factors were calculated by keeping track of all masses before and after sampling. Field and lab data collected from the peepers can be located in Appendix D.

2.3. Analytical Methods

Analytical methods, instruments, and laboratories used for this project are listed in Table I. The practical quantification limits (PQL) for the instrumental method are also listed when applicable.

Table I. Table of analytical methods, instruments, and laboratories for each measurement.

Measurement	Instrument	Laboratory	Method	PQL-1[a]	PQL-2[a]
pH	Microelectrode	Field		N/A	N/A
ORP	Microelectrode	Field		N/A	N/A
Alkalinity	Digital titrator	MT Tech, Butte, MT	Potentiometric titration	N/A	N/A
Ammonia	HACH 2010 spectrophotometer	MT Tech, Butte, MT	HACH 8038	0.02 mg/L as N	0.1 mg/L as N
Phosphate	HACH 2600 spectrophotometer	MT Tech, Butte, MT	HACH 8048	0.01 mg/L as P	0.01 mg/L as P
Sulfate	HACH 2010 spectrophotometer	MT Tech, Butte, MT	HACH 8051	1 mg/L SO_4^{2-}	5 mg/L SO_4^{2-}
Sulfide	HACH 2010 spectrophotometer	MT Tech, Butte, MT	HACH 8131	0.01 mg/L as S	0.05 mg/L as S
Major and trace elements, speciated arsenic	ICP-OES	Author, Mercury Lab at MT Tech, Butte, MT	EPA 200.7	See Appendix	See Appendix
Trace elements, speciated arsenic	ICP-MS	MBMG, MT Tech, Butte, MT	EPA 200.8	See Appendix	See Appendix
Microwave assisted acid digestion	Microwave Digester	Author, Mercury Lab at MT Tech, Butte, MT	EPA 3015A	N/A	N/A

[a] PQL-1 is the practical quantification limit for the instrumental method; PQL-2 is the same, adjusted for five times dilution of sample prior to analysis. N/A = not applicable.

2.4. pH and Eh

The activity of hydrogen ions (pH) and the activity of electrons (Eh) of peeper pore-water samples were determined using microelectrodes (supplied by Microelectrodes, Inc.) during fieldwork. With the glove bag still encasing the peeper, the microelectrodes were pushed through the glove bag into the corresponding peeper cell and measurements were collected. Prior to field work, the pH microelectrode was calibrated with pH 4 and 7 buffers. The Eh microelectrode was immersed with Zobell's solution to determine the milli-volt (mV) offset between ORP (relative to Ag/AgCl electrode) and Eh (relative to the standard hydrogen electrode). This offset value, typically close to +220 mV, was added to all field ORP measurements to convert the data to Eh. Photographs E7 and E11 in Appendix E shows the microelectrodes taking measurements in the peeper. Unfortunately, the pH microelectrode malfunctioned after the first peeper was sampled, and consequently no pH data are reported in this thesis for Peepers 2 and 3.

2.5. Alkalinity

Alkalinity was measured at MT Tech. Each of the samples collected for alkalinity was unfiltered, unacidified, and poured into an Erlenmeyer flask and diluted as needed with de-I water to a total mass of 100 mL and then titrated to a pH of 4.5 using an indicator dye powder while a magnetic stirrer continuously stirred the sample. A HACH digital titrator with 0.16 N H_2SO_4 cartridge was used to deliver the acid titrant. Alkalinity was also determined for a blank water sample using 100 mL of de-I water. This alkalinity value was subtracted from all of the peeper samples that had been diluted up to 20x or more with de-I water prior to doing the titration. For groundwater, pond, and creek water, this step was not necessary, as 100 mL of sample was collected. Peeper cells that sampled pond water had a large error of approximately ±20%, due to a combination of high dilution factors and relatively low alkalinity values. The deeper pore water samples with higher alkalinity had a much lower error of approximately ±5%. Data can be found in Appendices C and D.

2.6. Ammonia

Water samples used for ammonia analysis had approximately 5 mL of peeper water collected in the field using a syringe needle. This water was then filtered and added to the prepared ammonia Nalgene bottles (as previously described in Section 2.2.2.1 Peeper Sampling). Upon arriving at MT Tech from the field, ammonia concentrations were measured immediately in the lab. All of the samples were re-weighed to determine the mass extracted from the peeper as well as the dilution factor. HACH Method 8038 (Nessler Method) was used to measure the ammonia concentrations. Products from this test were stored as hazardous waste. Data can be found in Appendices C and D.

2.7. Soluble Reactive Phosphate (SRP)

Water samples used for SRP analysis had approximately 5 mL of peeper water collected in the field using a syringe needle. This water was then filtered and added to the prepared Test-n-Tube (TNT) glass vials (previously described in Section 2.2.2.1 Peeper Sampling). The reagent powder packet (PhosVer 3 Phosphate Powder Pillow) was added in the field to stabilize phosphate. Soluble reactive phosphate was measured in the lab using HACH Method 8048, based on the molybdate blue test, with an approximate detection limit of 0.01 mg/L (as P). In the presence of SRP, a blue color developed. The samples were re-weighed to determine exactly the amount of water extracted from the peeper and to calculate a dilution factor. Data can be found in Appendices C and D.

2.8. Sulfate

No samples were specifically collected for sulfate analysis (e.g., by ion chromatography), as this was initially thought to be an unimportant solute. However, to perform geochemical modeling, it became necessary to obtain values for sulfate concentration, using the left-over acid-preserved samples from ICP analysis. The HACH Method 8051 was used, with the modification that $BaCl_2$ was added as a small aliquot (2.5 mL) of concentrated (10 wt %) $BaCl_2$ solution, as opposed to the usual $BaCl_2$ powder packets. Doing this saved money, and also streamlined the process. Because the spectrophotometer has a linear range of 1 to 100 mg/L, many samples had to be diluted prior to analysis. The mass of $BaCl_2$ solution was taken into account to compute dilution factors, as was the initial dilution factor that was used prior to ICP-OES analysis (e.g., of the peeper samples). Data can be found in Appendices C and D.

2.9. Dissolved Sulfide

Water samples used for dissolved sulfide analysis had approximately 6-8 mL of peeper water collected in the field using a syringe needle, filtered, and added to the prepared dissolved sulfide Nalgene bottles (previously described in Section 2.2.2.1 Peeper Sampling). HACH reagents 1 and 2 were added to the sample bottles. Dissolved sulfide analysis was completed in the lab using HACH Method 8131. The samples were re-weighed to determine exactly the amount of water extracted from the peeper and calculate a dilution factor. Peeper A was the only peeper that was tested for H_2S since the other peepers did not have a strong H_2S smell. Data can be found in Appendix D.

2.10. ICP-OES and ICP-MS

Analyses of water for major and trace elements by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) was completed by the author in the Mercury Lab at MT Tech (Butte, MT) using a Thermo-Scientific iCAP 6300 Duo ICP Spectrometer and EPA Method 200.7. Approximately 10 mL of peeper water was collected in the field using a syringe needle, filtered with a 0.2 μm pore diameter PES filter, and then added to the prepared ICP Nalgene bottles (previously described in Section 2.2.2.1 Peeper Sampling). The samples were re-weighed to determine exactly the amount of water extracted from the peeper and calculate a dilution factor. Because Peeper C had much lower arsenic concentrations as compared to the other peepers and other water samples collected, the Analytical Laboratory in the Montana Bureau of Mines and Geology in Butte, MT re-analyzed the acid-preserved samples from Peeper C on an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) using a Thermo ICP-Q and EPA Method 200.8. Data can be found in Appendices A-D.

2.11. Dissolved As Speciation

Arsenic speciation was completed in the field during sampling of Piezometers 5 to 8, and also during sampling of the Peeper C cells. The method involved attaching a disposable (single-use) cartridge filled with an alumino-silicate gel to the Luer-lock end of the sampling syringe. When the water (previously filtered) was passed through the cartridge, dissolved As(V) adsorbed onto the gel, and As(III) passed through the setup. According to the manufacturer of the cartridges (MetalSoftCenter, 2015), this method is only effective at dissolved As(V) concentrations less than 0.5 mg/L. None of the samples analyzed in this study had As(V) > 0.5 mg/L after dilution. Water samples that were processed in this way were preserved with HNO_3 and analyzed on the ICP-OES and ICP-MS along with a parallel set of samples that were not passed through the cartridge. The processed sample gave As(III) concentrations, and the unprocessed sample gave total dissolved As concentration. The concentration of dissolved As(V) was calculated by difference. Data can be found in Appendices C and D.

2.12. Geochemical Modeling

The geochemical modeling program Visual Minteq (vers. 3.0b, Gustafson, 2010) was used to compute mineral saturation indices for many of the samples collected in this study. The standard database was modified to include symplesite ($Fe_3(AsO_4)_2$), with a solubility product of 5.6E-34. Because the ICP-OES in the Mercury Lab was not set up to quantify the concentrations of dissolved K and Na, it was necessary to estimate the concentrations of these solutes to get reasonable charge balance. This was done by inputting typical values of K and Na reported in the thesis of Joshua Lee (2012) for surface water, peeper water, and deeper groundwater in Pond 2 of the WSPOU. Doing this improved the charge balance calculations, but otherwise had no effect on the computed mineral saturation indices discussed in the results.

The Eh and pH data collected for the eight piezometers were used in StabCal (Huang, 2010) to generate Eh-pH diagrams for Fe, Mn, As, and N. These diagrams can be useful to illustrate what chemical state of an element, compound, or mineral may be as a function of the pH and the Eh.

3. Results

3.1. Laboratory Experimental Results

3.1.1. Closed System Experimental Results

Field measurements of the pH collected by the Hydrolab MS-5 from the Silver Bow Creek near the inlet to WSPOU ranged from 7.17 to 8.34. Eight different samples (1-L Nalgene bottle) had the pH adjusted 2 to 3 times during the experiment. Samples (15-mL RA and FA) from pH adjustments were collected immediately and the next adjustment was performed at least 48 hours later. (The sampling log for these experiments is found in Appendix A.) Measurements were also collected prior to pH adjustment to determine any drift in pH. There were small drifts in pH noted throughout the experiment that were less than 0.7 pH unit. Measurements for the last pH adjustment performed ranged from 9.94 to as high as approximately 11.7. Specific conductance measurements for samples HB4-3, HB5-3, HB6-3, HB7-3 and HB8-3 displayed drastic increases ranging from 785 to 4556 μS/cm after the final pH increase was performed.

Streamflow was collected from the USGS website and was used to determine whether or not there was a correlation between flow and FA As concentration. Flowrates ranged from 52 to 175 cfs. The highest streamflow of 175 cfs occurred during collection of sample HB5, but the As concentration of the FA sample was only 7.6 μg/L. This arsenic concentration was third highest compared to all of the closed system initial FA samples. Sample HB2 had the highest As concentration of the FA samples with a value of 10.4 μg/L and was collected when streamflow was 140 cfs. Ironically, HB8 had the second highest As concentration of the FA samples and had the lowest flowrate during collection as compared to all of the closed system samples. See Table II for FA concentrations of As, Fe, Ca, Mn, Cu, and Zn as well as the stream flowrate, SC, and pH for the closed system experiment. Field measurements and ICP data from these experiments can be found in Appendix A.

Table II. Closed system experiment – Flowrate, pH, SC, and FA concentrations of As, Fe, Ca, Mn, Cu, & Zn.

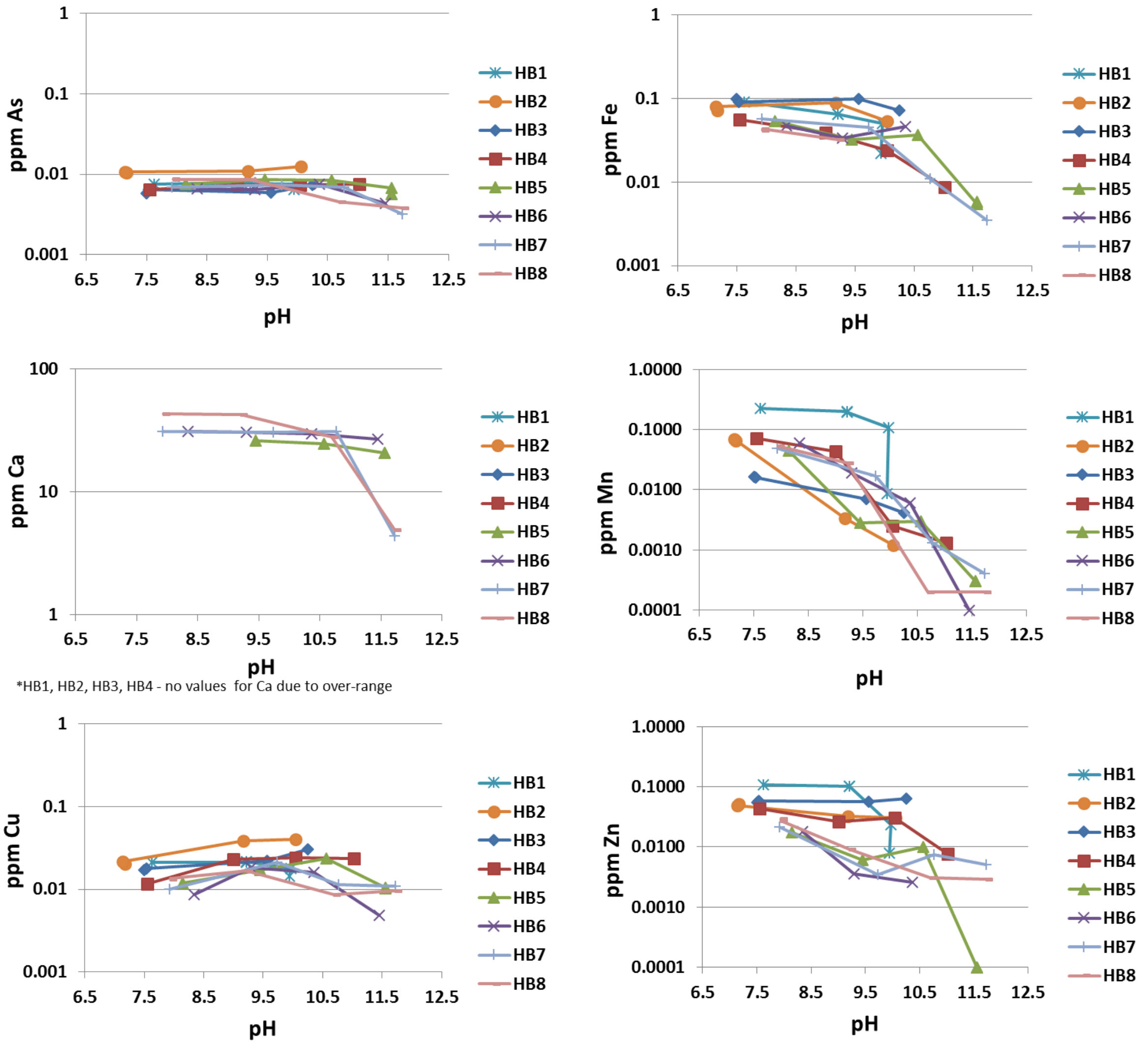
Sample ID	Stream flowrate (cfs)	pH	SC (µS/cm)	As (µg/L)	Fe (µg/L)	Ca (mg/L)	Mn (µg/L)	Cu (µg/L)	Zn (µg/L)
HB1 (4/4/14)	53	7.62	486	7.6	90.4	***	227.3	21.0	107.6
HB1_1		9.21	384	7.8	64.9	***	196.8	21.1	100.6
HB1_1DUP		9.21	384	7.7	64.8	***	195.8	21.4	101.9
HB1_2		9.97	-	7.6	49.7	***	108.4	17.7	23.3
HB1_3		9.94	506	6.5	21.9	***	8.5	14.4	8.0
HB2 (4/9/14)	140	7.17	271	10.4	71.9	***	64.6	20.1	51.1
HB2_1		7.14	279	10.6	79.6	***	69.6	21.5	48.3
HB2_2		9.17	312	11.0	89.2	***	3.4	38.6	31.9
HB2_3		10.05	414	12.6	53.0	***	1.2	40.0	30.3
HB3 (4/25/14)	119	7.50	342	5.8	97.7	***	16.6	17.2	55.6
HB3_1		7.53	116	6.5	90.9	***	15.7	18.0	57.5
HB3_2		9.56	3800	5.9	99.0	***	6.9	22.2	57.3
HB3_3		10.25	300	7.4	72.4	***	4.1	30.6	63.9
HB4 (5/13/14)	130	7.55	303	6.5	55.2	***	71.7	11.6	43.8
HB4_1		9.00	186	7.3	38.5	***	43.3	22.9	26.4
HB4_2		10.04	453	7.3	23.8	***	2.5	24.0	30.6
HB4_3		11.02	785	7.6	8.6	***	1.3	23.4	7.6
HB5 (5/27/14)	175	8.14	244	7.6	53.6	***	45.0	11.8	17.3
HB5-1		9.45	293	8.6	32.1	26.0	2.8	17.2	6.1
HB5-2		10.56	697	8.4	36.2	24.6	3.0	23.6	10.1
HB5-3		11.56	3417	6.7	5.4	20.8	b.d.	10.4	b.d.
HB5-3 DUP		11.56	3417	5.6	5.8	20.8	b.d.	10.3	b.d.
HB6 (6/10/14)	100	8.34	297	6.6	46.8	30.8	60.5	8.6	18.2
HB6-1		9.29	341	6.4	33.3	30.4	19.0	18.4	3.6
HB6-2		10.36	572	7.5	46.4	29.6	6.1	16.0	2.6
HB6-3		11.45	2006	4.3	b.d.	27.0	b.d.	4.9	b.d.
HB7 (6/23/14)	91	7.92	319	6.9	56.3	31.1	49.3	10.0	21.7
HB7-1		9.73	382	7.4	44.8	30.5	16.8	21.0	3.5
HB7-2		10.77	772	6.9	10.8	31.0	1.3	11.5	7.4
HB7-3		11.73	3496	3.2	b.d.	4.4	b.d.	11.0	5.1

(cont.) Table II. Closed system experiment - Flowrate, pH, SC, and FA concentrations of As, Fe, Ca, Mn, Cu, & Zn.

Sample ID	Stream flowrate (cfs)	pH	SC (µS/cm)	As (µg/L)	Fe (µg/L)	Ca (mg/L)	Mn (µg/L)	Cu (µg/L)	Zn (µg/L)
HB8 (7/7/14)	52	7.94	430	8.8	41.2	43.3	53.9	13.2	29.8
HB8-DUP		7.94	430	8.5	43.5	42.8	53.7	13.6	27.2
HB8-1		9.21	449	8.6	32.1	42.2	27.5	16.7	9.2
HB8-2		10.69	854	4.5	b.d.	28.2	b.d.	8.7	3.1
HB8-3		11.73	4556	3.8	b.d.	4.9	b.d.	9.7	2.9

***Over range.
b.d. - below detect
Dates in parentheses are on-site (at SBC near the inlet of Pond 3) sample collection dates.

Figure 8 displays the FA concentrations of As, Fe, Ca, Mn, Cu, and Zn versus pH. Generally, the trend noted is a decrease in metal concentration with an increase in pH. After the final pH adjustments were performed, dissolved arsenic concentrations decreased for 5 (HB1, HB5, HB6, HB7, and HB8) of the 8 inlet water samples collected; the dissolved arsenic concentrations after the final pH increase ranged from 6.5 to 3.2 µg/L with final pH values of 9.94 to 11.73. The 3 (HB2, HB3, and HB4) remaining inlet water samples that displayed an increase in dissolved arsenic concentrations had concentrations with a range of 7.4 to 12.6 µg/L with a pH range of 10.05 to 11.02. Iron concentrations generally displayed a decrease in concentration as the pH increased. Ca concentrations showed a decrease in concentration as pH increased. No values were collected for samples HB1, HB2, HB3, and HB4 since Ca was over-range. Concentrations of Mn displayed a decrease in concentration as pH increased. Cu concentrations appeared to have a slight increase when the pH is between approximately 8 to 10.5 and then the concentrations decreased with the higher pH’s. Generally, Zn concentrations displayed a decrease in concentration as pH increased.



*HB1, HB2, HB3, HB4 - no values for Ca due to over-range

Figure 8. FA concentrations of As, Fe, Ca, Mn, Cu, and Zn vs. pH in the closed system experiments.

3.1.2. Open System Experimental Results

Three mini-experiments were completed using the fish tank by adjusting the pH 2 to 3 times during each mini-experiment. Similarly to the closed system, samples (30-mL FA) from pH adjustments in the open system were collected immediately and the next adjustment was performed at least 48 hours later. (The sampling log for these experiments is found in Appendix B.) Measurements were also collected prior to pH adjustment to determine any drift in pH. Depending on the pH and length of time between adjustments, pH was observed to ‘drift’ 1 to over 2 pH units to a more neutral pH over the length of the entire experiment. Due to the nature of the fish tank set-up, the water was continuously being circulated and mixed; however, the rate of the pH change lagged somewhat due to the larger volume of water. Therefore, large amounts of NaOH or HNO_3 were consumed to adjust the pH and the pH changes were more drastic than what was expected once the reactions were complete.

The initial experiment to increase the pH values measured to be 9.54, 10.69 and 11.69; these pH increases were completed over 8 days. A second experiment decreased the pH values to 7.55, 6.55, and 2.76 over 10 days. The last experiment increased the pH values to 7.49, 8.66, and 9.75 over 5 days. Table III lists the pH, SC, and FA concentrations of As, Fe, Ca, Mn, Cu, and Zn for the open system experiments.

Table III. Open system experiments - pH, SC, and FA concentrations of As, Fe, Ca, Mn, Cu, & Zn.

Sample ID	pH	SC (µS/cm)	As (µg/L)	Fe (µg/L)	Ca (mg/L)	Mn (µg/L)	Cu (µg/L)	Zn (µg/L)
MESO-6-11-14	9.54	401	19.1	39.7	36.2	6.2	4.8	4.4
MESO-6-16-14	10.7	684	12.9	14.9	27.6	1.4	6.7	9.4
MESO-6-18-14	11.7	2441	35.0	b.d.	6.41	0.3	3.7	0.1
MESO-6-24-14	7.55	1647	149.2	267.7	5.88	11.8	90.6	28.3
Mesocosm 7-1-14	6.55	1883	154.4	334.2	9.05	14.2	104.4	37.3
Mesocosm 7-3-14	2.76	2545	143.7	338.9	13.4	73.3	122.3	157.7
Mesocosm7-7-14 pH7	7.49	2388	80.6	117.2	42.3	53.8	81.8	29.6
Mesocosm 7-7-14 4:15	8.66	2406	55.9	120.3	43.3	36.6	81.5	14.3
Mesocosm 7-11-14	9.75	2606	76.9	134.9	48.5	1.6	84.1	22.0

b.d. - below detect

Figure 9 displays the concentrations of As, Fe, Ca, Mn, Cu, and Zn for the fish tank experiments. Generally, the highest concentrations were observed when the pH was decreased from 7.55 to 2.76. The highest concentration observed for Ca was noted during the second pH increase from 7.49 to 9.75. Lab measurements and ICP data from these experiments can be found in Appendix B.

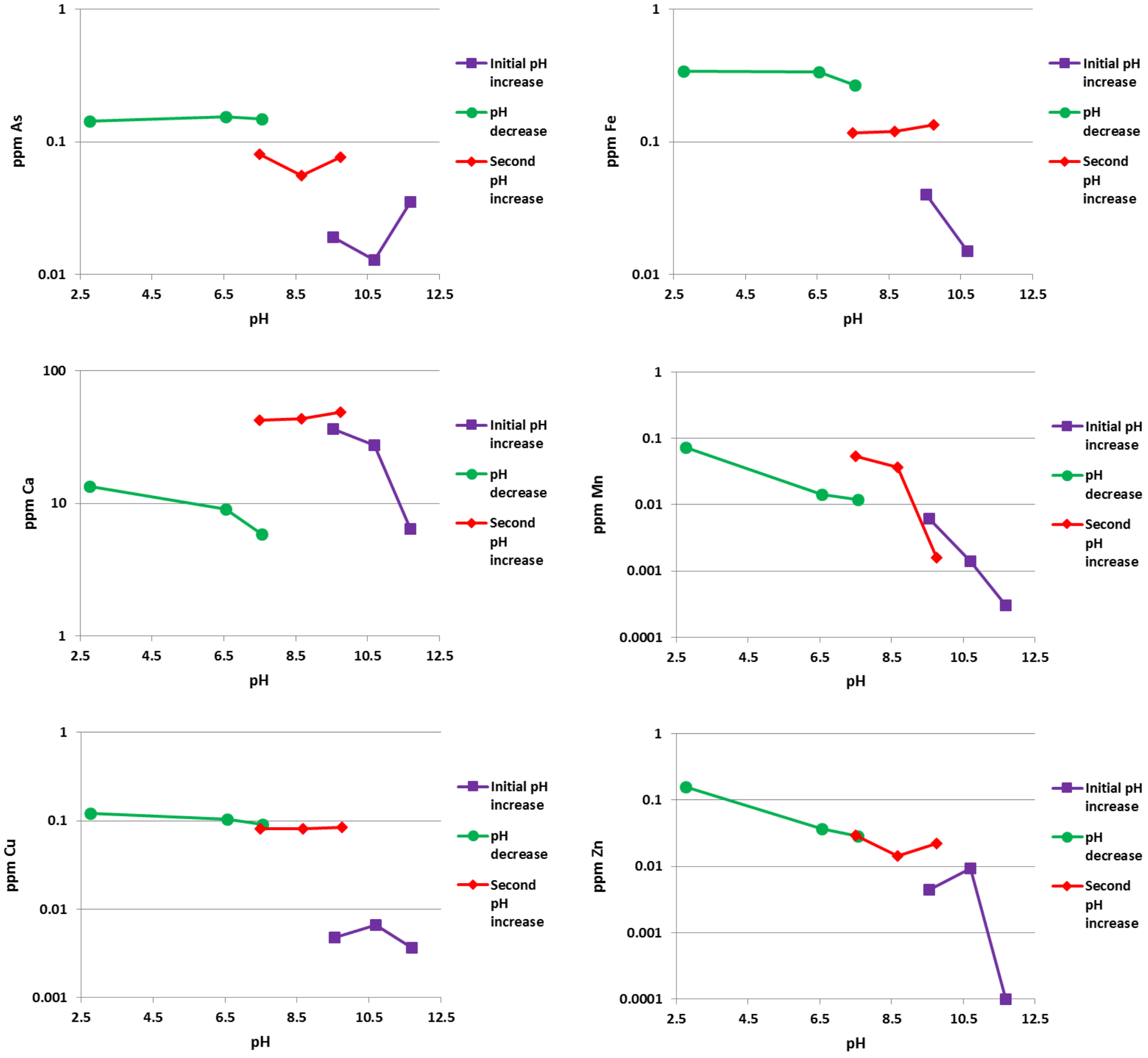


Figure 9. Concentrations of As, Fe, Ca, Mn, Cu, and Zinc vs. pH in the open system experiments.

3.2. Field Results

3.2.1. Vertical gradients in hydraulic head

Eight piezometers were installed in the southern half of Pond 3 during August (PZ1-4) and November 2014 (PZ5-8). Table IV displays the dates the piezometers were installed, depth into sediment, static water level inside the pipe from the top of the casing (TOC-SWI), static water level of the pond from the top of the casing (TOC-Pond), and the vertical gradients. The vertical gradients were determined by subtracting the TOC-SWI from the TOC-Pond and dividing by the length of the piezometer submerged into the pond sediment and the piezometer screen. All of the piezometers showed a negative gradient meaning that the water had a downward gradient.

Table IV. SWL results for piezometers collected from Pond 3 on 8/1/14 and 11/8/14.

Piezometer	Date Installed	Depth into sediment (ft)	TOC-SWI (ft)	TOC-Pond (ft)	dh/dl vertical	Vertical Gradients
PZ-1	8/5/2014	4.0	1.59	1.53	-0.012	Down
PZ-2	8/5/2014	5.3	*7.32	1.52	-	-
PZ-3	8/5/2014	5.0	1.44	1.39	-0.013	Down
PZ-4	8/5/2014	4.4	2.71	2.70	-0.002	Down
PZ-5	10/18/2014	5.5	3.33	3.11	-0.063	Down
PZ-6	10/18/2014	7.5	5.20	4.38	-0.126	Down
PZ-7	10/18/2014	8.0	3.83	2.52	-0.219	Down
PZ-8	10/18/2014	9.0	5.14	3.00	-0.201	Down

PZ 1-5 are PVC pipes 10 ft long; PZ 6 and 7 are PVC pipes 15 ft long; and PZ 8 is PVC pipe 20 ft long.
*Vacuum created inside piezometer; true measurement not collected

3.2.2. Piezometer Hydro-geochemistry

The piezometers revealed several interesting trends between the groundwater and the water directly collected from Pond 3. As seen in Table V, the pH measured in the groundwater from each of the piezometers ranged from 8.2 to 6.96 and was generally lower than the pond water itself that had values of 9.11 and 8.2 for pH near PZ1-4 and PZ5-8, respectively. Complete field and laboratory data for each of the piezometers can be found in Appendix C.

Table V. Piezometer Results for pH, SC, As, Fe, and Mn

Piezometer	Date	Depth into sediment (ft)	pH (s.u.)	SC (µS/cm)	As (µg/L)	Fe (mg/L)	Mn (mg/L)
PZ-1	8/5/2014	4.0	8.20	1321	28.0	0.13	1.07
PZ-2	8/5/2014	5.3	7.71	2700	99.0	BD	1.55
PZ-3	8/5/2014	5.0	7.84	2997	28.0	0.94	2.57
PZ-4	8/5/2014	4.4	7.23	3034	333	29.8	12.4
**Pond 3 AVG. at PZ1-4*			*9.11*	*487*	*22.7*	*0.048*	*0.072*
PZ-5	11/8/2014	5.50	7.72	2468	169	*0.464*	*1.92*
PZ-6	11/8/2014	7.50	6.96	2871	639	60.8	3.52
PZ-7	11/8/2014	8.00	7.81	2049	19.9	0.949	2.32
PZ-8	11/8/2014	9.00	7.38	3050	403	2.48	1.57
**Pond 3 AVG. at PZ5-8*			*8.20*	*477*	*8.14*	*0.017*	*0.776*

PZ 1-5 are PVC pipes 10 ft long; PZ 6 and 7 are PVC pipes 15 ft long; and PZ 8 is PVC pipe 20 ft long.
*Pond water samples collected near corresponding piezometers.

Specific conductivity had an inverse relationship as compared to the pH; the specific conductivity is shown to be consistently much higher in the groundwater with values of 1321 to 3050 µS/cm versus the pond that recorded 487 and 477 µS/cm near PZ1-4 and PZ5-8, respectively. The lowest specific conductivity was collected at PZ1, which was installed into the shallowest depth of sediment. Conversely, PZ8 had the highest specific conductivity and was the piezometer installed at the deepest depth into the pond sediment.

Groundwater collected from the piezometers displayed higher concentrations of arsenic, iron, and manganese as compared to the water collected from Pond 3. Piezometers 1 to 4, which paralleled the southern shore of Pond 3, had arsenic concentrations ranging from 28 to 333 µg/L, iron concentrations from b.d. to 29.8 mg/L, and manganese concentrations from 1.07 to 12.4 mg/L. Piezometers 5 to 8, which extend from the south shore in a northerly direction towards the center of the pond, had arsenic concentrations ranging from 20 to 640 µg/L, iron concentrations from 0.46 to 60.8 mg/L, and manganese concentrations from 1.57 to 3.52 mg/L.

Further assessment of the piezometer water data can be completed by using Figures 10, 11 and 12. Figure 10 compares the pH, specific conductivity, and alkalinity for each of the piezometers as well as the samples collected from the pond. As previously mentioned, the pH was higher in the pond water as compared to the groundwater and the specific conductivity was much higher in the groundwater as compared to the pond water. The alkalinity values range from 36 to 392 mg/L as $CaCO_3$ for the groundwater samples and no real pattern is defined. PZ4 and PZ8 had the highest alkalinity values of 392 mg/L as $CaCO_3$ and the corresponding pH values are slightly lower than the average pH but are still in the neutral range. (The only pond water sample measured for alkalinity was collected near PZ2.)

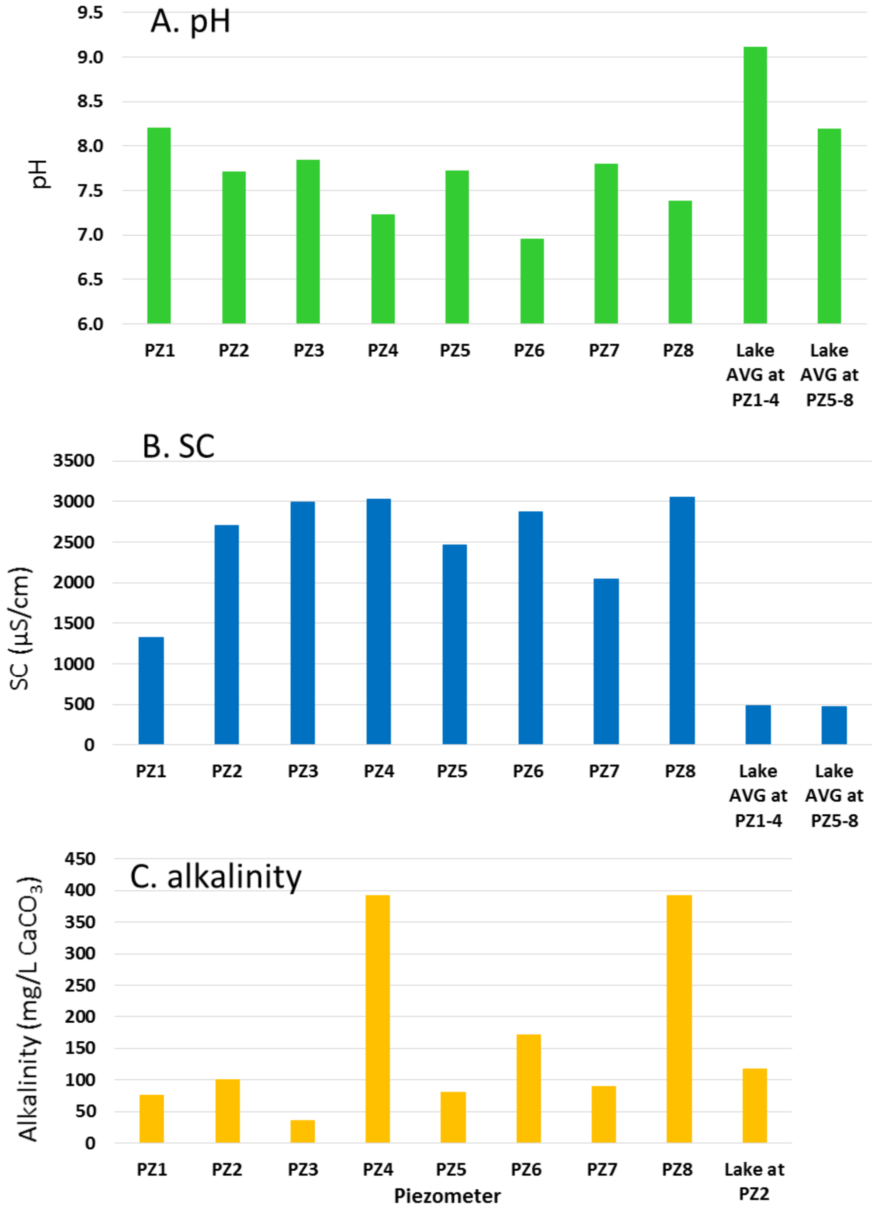


Figure 10. Piezometer pH, specific conductivity, and alkalinity.

Figure 11 compares the arsenic, iron, and manganese concentrations for each piezometer. Arsenic, iron, and manganese concentrations vary among the piezometers without a pattern related to position or depth in the pond, or to other solute concentrations; the exception to this may be PZ6 which had the highest arsenic and iron concentrations and the second highest manganese concentration.

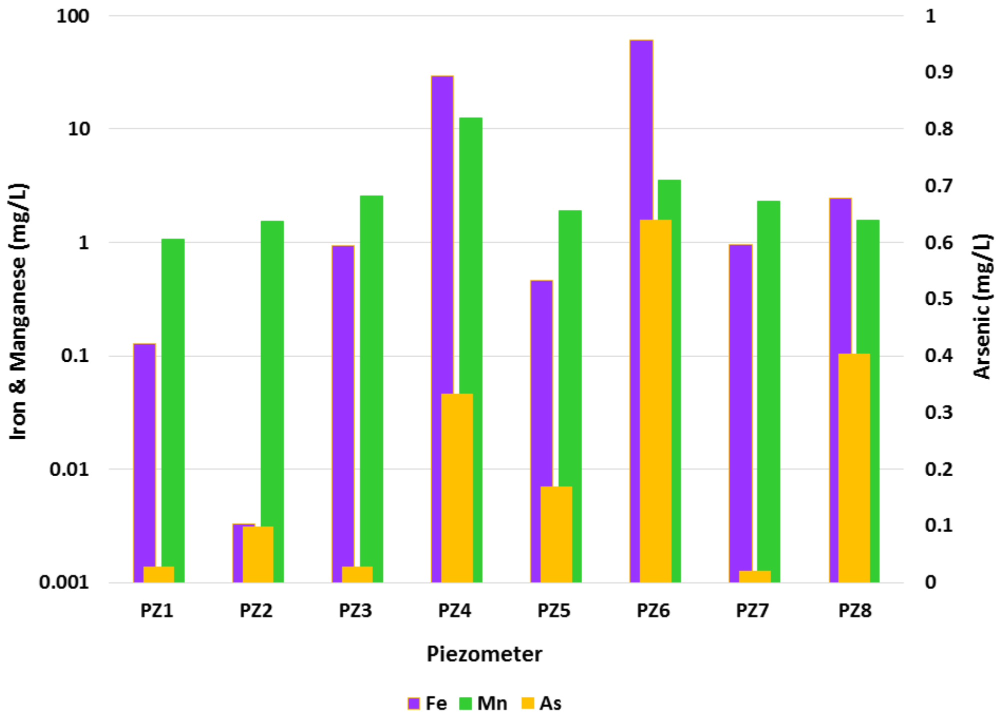


Figure 11. Arsenic, iron, and manganese concentrations for each piezometer.

Figure 12 displays the correlations between arsenic and iron concentrations (Figures 12A and 12D) as well as the correlation between manganese and arsenic concentrations (Figures 12B and 12E) and iron and manganese concentrations (Figures 12C and 12F). Because PZ1-4 were installed at shallower depths and in a westerly to easterly direction, these were separated from PZ5-8 results. Again, PZ5-8 were installed at deeper depths and in a northerly and southerly direction. Figures 12A, 12B, and 12C show a strong correlation between these elements in PZ1-4 and Figure 12F shows also a somewhat strong correlation between iron and manganese in PZ5-8.

Figure 12D displays a slight correlation between arsenic and iron and Figure 12E displays not much of a correlation at all between manganese and iron in PZ5-8.

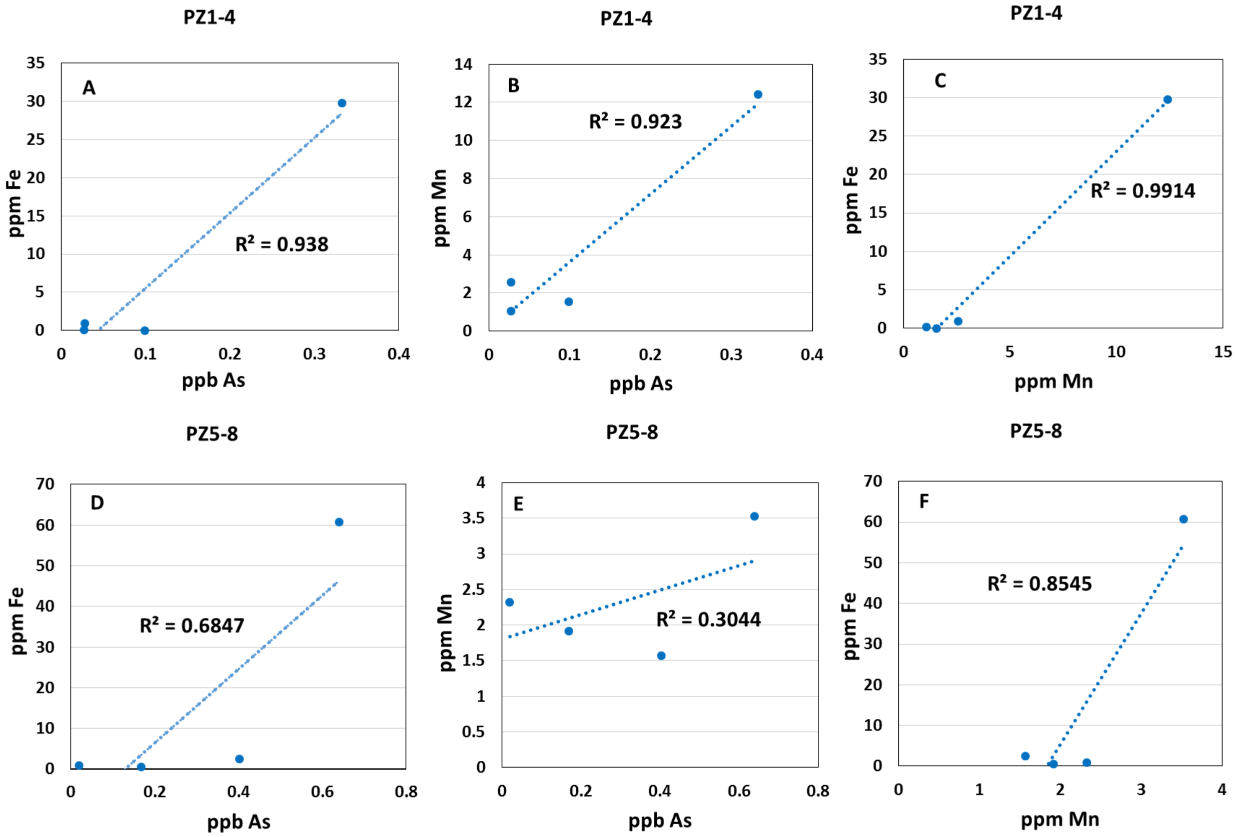


Figure 12. Correlation between arsenic, iron, and manganese concentrations in piezometer samples.

Figure 13 compares the phosphate, ammonium, and sulfate concentrations for each piezometer. Higher concentrations of sulfate and NH_4^+-N are displayed in the groundwater as compared to the pond water. Phosphate concentrations were similar between the groundwater and the average concentration collected from the pond. PZ3 had the highest concentrations for each of these analytes with 946 mg/L SO_4^{2-}, 46 mg/L NH_4^+-N, and 1.36 mg/L PO_4^{3-}. PZ8 had the next highest levels of phosphate and NH_4^+-N with 0.3 mg/L and 31.5 mg/L, respectively. Sulfate concentrations were higher in PZ2, PZ3, and PZ4 than the other piezometers and were installed at the more shallow depths of 4.4 to 5.3 feet into the pond sediment. PZ7 had the lowest concentrations of sulfate and phosphate with 374 mg/L and 0.08 mg/L, respectively.

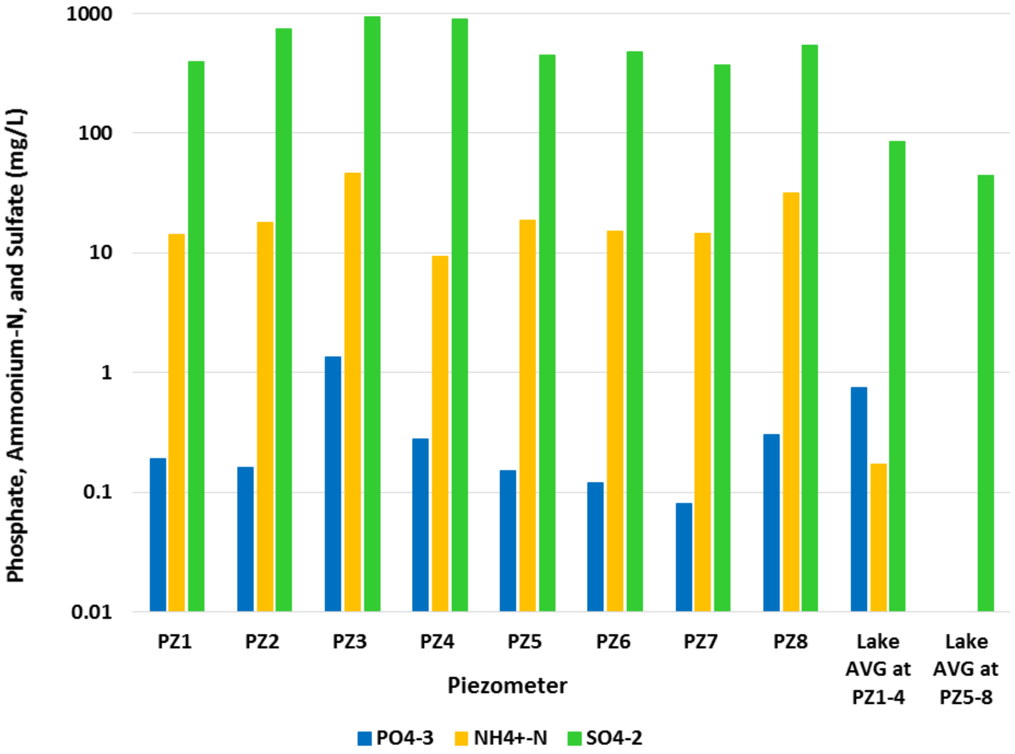


Figure 13. Phosphate, ammonium, and sulfate concentrations for each piezometer.

3.2.3. Peepers

Three peepers were installed in the southern portion of Pond 3. Table VI lists the locations and dates of deployment and sampling. Complete field and laboratory data for each of the peepers can be found in Appendix D.

Table VI. Peeper locations and dates of deployment and sampling.

Peeper	Location	Deployed	Sampled
A	Near PZ2	7/18/2014	8/5/2014
B	Near PZ3	8/1/2014	8/14/2014
C	Near PZ5	11/6/2014	12/6/2014

3.2.3.1. pH and Eh

The pH was measured for only Peeper A because the pH mini-probe was not functioning during fieldwork when Peepers B and C were collected. Values for pH ranged from 7.16 (approximately 6 cm below SWI) to 9.31 (approximately 4 cm above SWI) for Peeper A. These pH values correlate to the values collected from the groundwater in the piezometers. Also, the high pH values collected from Peeper A cells located above the SWI are within a similar range of the pond water samples.

Eh was measured from Peeper A and B. (The Eh mini-probe was not functioning during fieldwork when Peeper C was collected.) The Eh chart displays a sharp decrease in Eh values from +359 to +259 to +38 mV (0 to 4 to 6 centimeters below SWI) for Peeper A and +176 to +96 mV (0 to 4 cm below SWI) for Peeper B. See Figure 14 below.

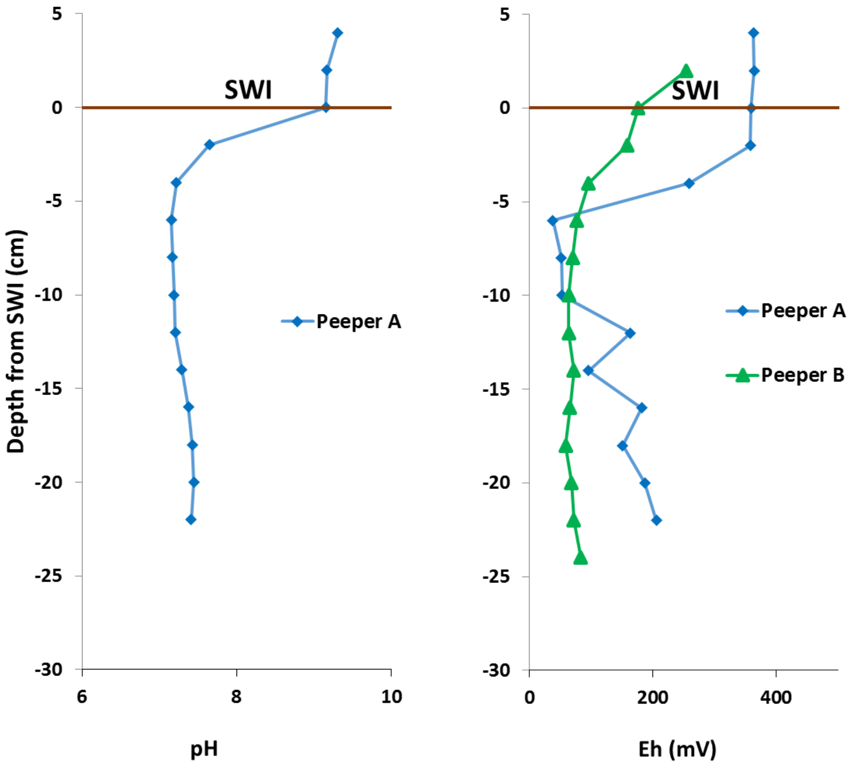


Figure 14. Peepers A and B depth profiles for pH and Eh.

3.2.3.2. Arsenic, iron, and manganese concentrations

Peeper A showed a simultaneous increase in dissolved arsenic and iron concentrations at a depth of 5 to 10 cm below SWI (Figure 15), the same depth as a drop in Eh (Figure 14). Peeper B shows a slight pattern between the arsenic and iron concentrations, but not nearly as evident as in Peeper A. Peeper C had surprisingly low concentrations of arsenic and seemed to peak in concentration 1 cm below the SWI and then decreased as depth increased; however, Peeper C had similar ranges of iron concentrations as Peepers A and B. Peeper A had the highest arsenic and iron concentrations for all 3 peepers and ranged from 23 to 528 µg/L and below detect to 23.6 mg/L, respectively. Peeper B had mid-range arsenic concentrations of 30 to 486 µg/L and the lowest iron concentrations ranging below detect to 4.4 mg/L. Peeper C had the lowest arsenic concentrations ranging from 8 to 39 µg/L and mid-range iron concentrations of 1.46 to 12.3 mg/L.

Manganese concentrations followed similar trends as arsenic and iron for Peepers A and B. Peeper A had a range from below detect (4 cm above SWI) to 8.71 mg/L (8 cm below SWI). Peeper B had a range from below detect (2 cm above SWI) to 4.95 mg/L (16 cm below SWI). Peeper C demonstrated an overall decrease in manganese concentration as depth increased below the SWI except where the concentration increased around 13 to 17 cm below SWI with concentrations of 7.17 to 6.73 mg/L, respectively. The highest manganese concentration for Peeper C was 9.95 mg/L and was actually 1 cm above SWI; the lowest concentration for Peeper C was 3.0 mg/L and was 25 cm below SWI.

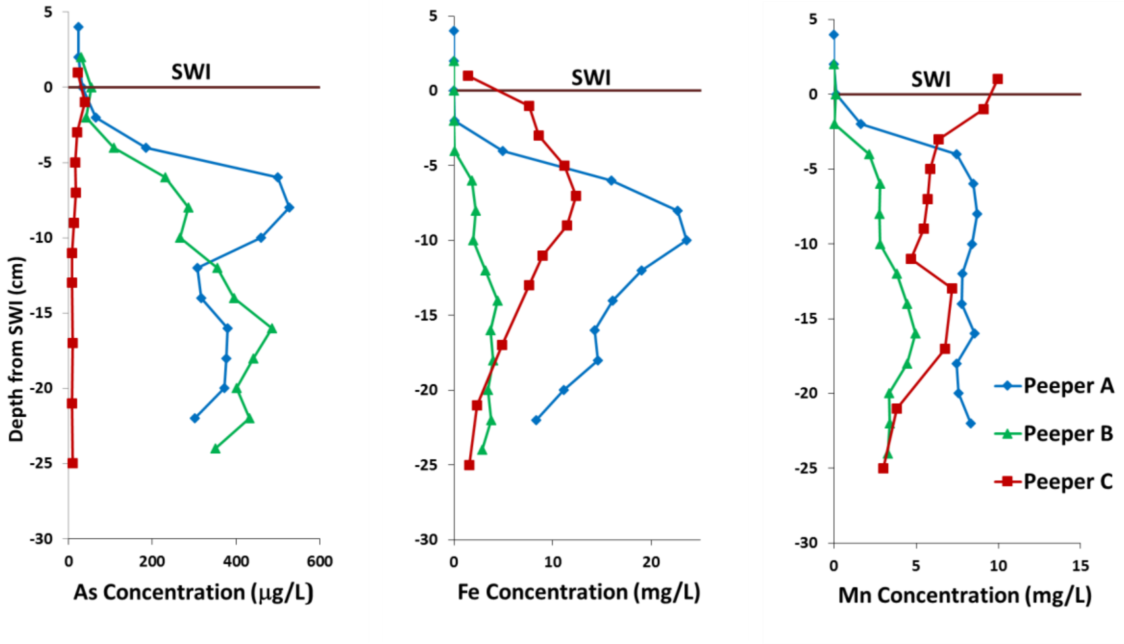


Figure 15. Arsenic, iron, and manganese concentrations from Peepers A, B, and C.

3.2.3.3. Sulfate, sulfide, phosphate and ammonium concentrations

Sulfate, sulfide, phosphate and ammonium concentrations are displayed in Figure 16. Peepers A and C demonstrate that a reduction zone of sulfate to hydrogen sulfide (and then oxidized back to sulfate) exists at similar depths as with the reduction zone previously noted for arsenic, iron, and manganese. The sulfate concentration in Peeper B dropped steeply in the top 10 cm of sediment and remained at a very low concentration as depth increased. Concentrations for sulfate ranged from 6.4 mg/L (8-10 cm below SWI) to 218 mg/L (22 cm below SWI), below detect (10-22 cm below SWI) to 119 mg/L (2 cm above SWI), and below detect (5-9 cm below detect) to 254 mg/L (21 cm below SWI) for Peepers A, B, and C, respectively. Sulfate concentrations were much lower in the sediment pore-water versus the groundwater (by factors ranging from 3.8 to 8) and had similar values as to what was measured in the pond.

Peeper A was the only peeper to have concentrations of hydrogen sulfide measured since the water in the other peepers did not have a rotten egg smell. Hydrogen sulfide concentrations ranged from below detect (1 to 5 cm above SWI) to 54.5 μg/L (11 cm below SWI) for Peeper A.

Soluble reactive phosphate concentrations generally increased with depth below SWI for all three peepers. Peeper A had the highest concentrations of phosphate ranging from 0.6 mg/L PO_4^{3-} (5 cm above SWI) to 5.77 mg/L PO_4^{3-} (19 cm below SWI). Peeper B had mid-range phosphate concentrations ranging from 0.52 mg/L PO_4^{3-} (3 cm above SWI) to 4.48 mg/L PO_4^{3-} (5 cm below SWI). Peeper C had the lowest phosphate concentrations ranging from 0.33 mg/L PO_4^{3-} (2 cm above SWI) to 3.51 mg/L PO_4^{3-} (22 cm below SWI). The lowest levels of phosphate measured in the peepers are similar to concentrations measured in the pond. The highest levels of phosphate greatly exceed the pond values, and also exceed the concentrations measured in the groundwater by 2.5 to 4 times.

Ammonium concentrations also increased with increase in depth below the SWI. Peeper A had the highest concentrations of ammonium ranging from 0.35 mg/L N (3 cm above SWI) to 16.7 mg/L N (21 cm below SWI). Peeper B had mid-range ammonium concentrations ranging from below detect (1 cm below SWI) to 11.3 mg/L N (21 cm below SWI). Peeper C had generally the lowest ammonium concentrations ranging from 1.84 mg/L N (2 cm above SWI) to 2.83 mg/L N (18 cm below SWI). The sediment pore water had concentrations higher than the pond water by at least a factor of 2. Conversely, as seen with the phosphate concentrations, the sediment pore-water had ammonium concentrations closer to the lowest concentration measured in the groundwater (9.3 mg/L N). (The maximum ammonium concentration for the piezometers was measured at 46 mg/L N.)

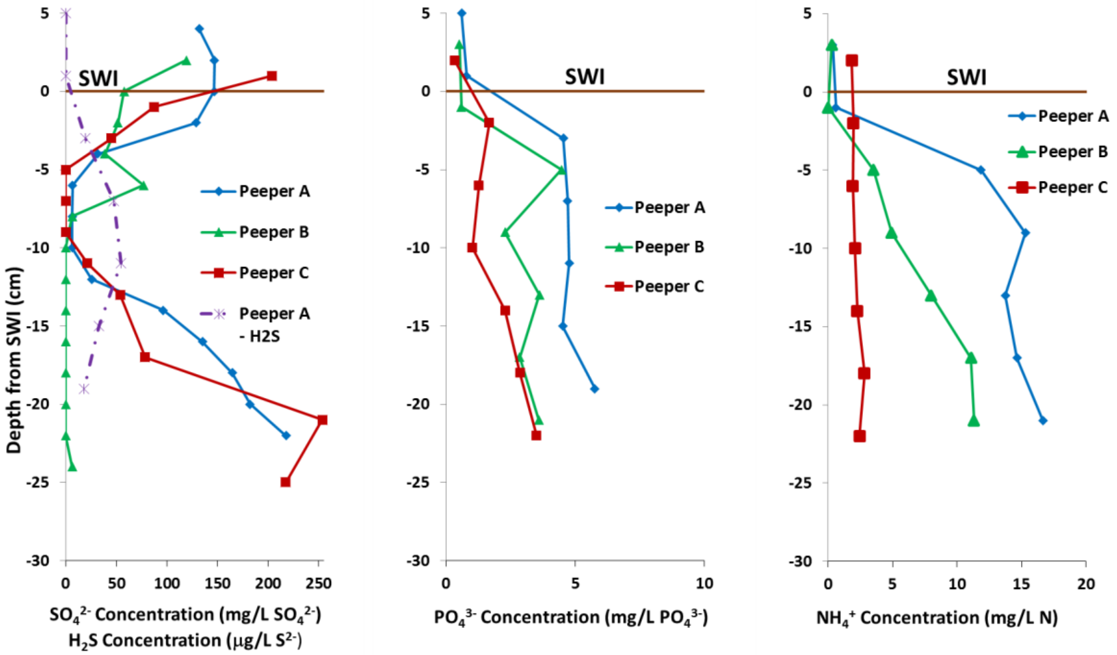


Figure 16. Sulfate, sulfide, phosphate, and ammonium concentrations from Peepers, A, B, and C.

3.2.4. Arsenic Speciation

Arsenic speciation was performed on water collected from four piezometers (PZ5-8) and one peeper (Peeper C) to determine whether the dominant valence state of arsenic is arsenite (III) or arsenate (V).

Figure 17 exhibits the arsenic speciation for the groundwater collected from PZ5-8 as dominantly arsenite with very low concentrations of arsenate. Arsenite would be the expected dominant valence state for this groundwater since this groundwater is in a reduced state versus an oxidized state.

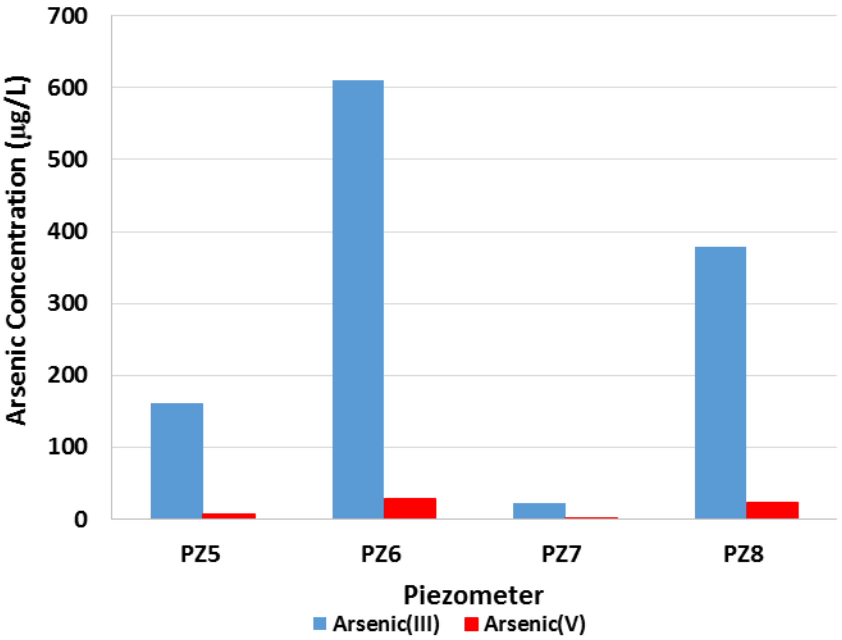


Figure 17. Arsenic speciation for Piezometers 5-8.

Figure 18 summarizes the results for arsenic speciation for Peeper C. Peeper C was deployed near PZ5 in late November 2014 prior to the pond freezing and then was retrieved early December 2014 after the pond had at least 8 inches of ice on top.

As noted in Figure 18, arsenate was the dominant valence state in the peeper cells located above the SWI in the pond water and arsenite was the dominant valence state in the sediment pore-water. As mentioned in the peeper section, the highest concentration of total arsenic occurred 1 cm below the SWI with 39.4 µg/L. The switch in dominant valence state of As at a depth of 5 to 8 cm below SWI is not expected, therefore, an explanation is unavailable at this time.

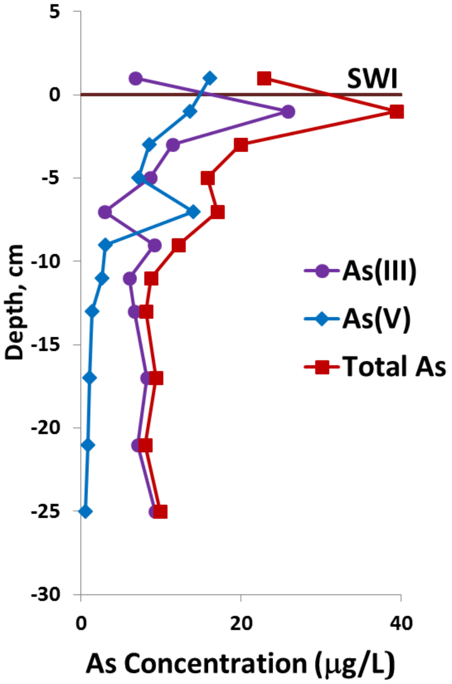


Figure 18. Arsenic speciation for Peeper C.

4. Discussion

4.1. Arsenic Total Recoverable and Total Suspended Solids

Table VII summarizes the As concentrations measured in filtered (FA) and raw (RA) samples collected from Silver Bow Creek at the inlet to WSPOU. The RA samples were acidified with 1% HNO_3, but were not microwave-digested, and therefore are not true total recoverable (TR) concentrations. Also shown are the concentrations of total suspended solids (TSS) measured gravimetrically, and the As concentration of the TSS determined by microwave digestion of the filter papers and solids. The values in italics in the second to last column show the computed “total-recoverable” As concentrations in the influent SBC samples, based on a combination of the As-FA measurements and the “As in TSS” measurements. In general, the As-TR measurements are about twice the value of the As-FA measurements, indicating that about half of the As entering the ponds is dissolved, and about half exists as suspended particles. The fact that the As-TR values are higher than the As-RA values indicates that some (about half) of the particulate As was not dissolved upon acidification with 1% HNO_3.

Table VII. Arsenic concentrations of Silver Bow Creek at inlet to Warm Springs Ponds.

Date	**ID**	**flow cfs**	**water mass g**	**TSS mass g**	**TSS mg/L**	**As-FA mg/L**	**As-RA mg/L**	***As-TR mg/L***	**As in TSS mg/kg**
4/4/2014	HB1	53	235.5	0.0024	10.1	0.008	0.010	*0.014*	646
4/9/2014	HB2	140	262.4	0.0285	108.7	0.010	0.017	*0.023*	117
4/25/2014	HB3	119	202.4	0.0029	14.1	0.006	0.009	*0.014*	589
5/13/2014	HB4	130	207.8	0.0013	6.3	0.007	0.008	*0.014*	1196
5/27/2014	HB5	175	234.5	0.0086	36.6	0.008	0.011	*0.015*	191
6/10/2014	HB6	100	229.1	0.0020	8.6	0.007	0.007	*0.013*	750
6/23/2014	HB7	91	261	0.0031	11.7	0.007	0.008	*0.013*	538
7/7/2014	HB8	52	258.8	0.0022	8.5	0.009	0.008	*0.015*	743

Another interesting point to make from Table VII is that the As concentration in the suspended solids is highly variable, ranging from 117 to 1196 mg/kg, with an average concentration of 596 mg/kg. Figure 19 shows a clear negative correlation between the As content of the TSS and the TSS concentration. In other words, when the inlet water was flowing high and turbid, the As content of the TSS was lower. This could have been caused by a lot of organic debris and sand with very low As content suspended in the creek at these high-flow times which would have diluted the As content of the suspended solid.

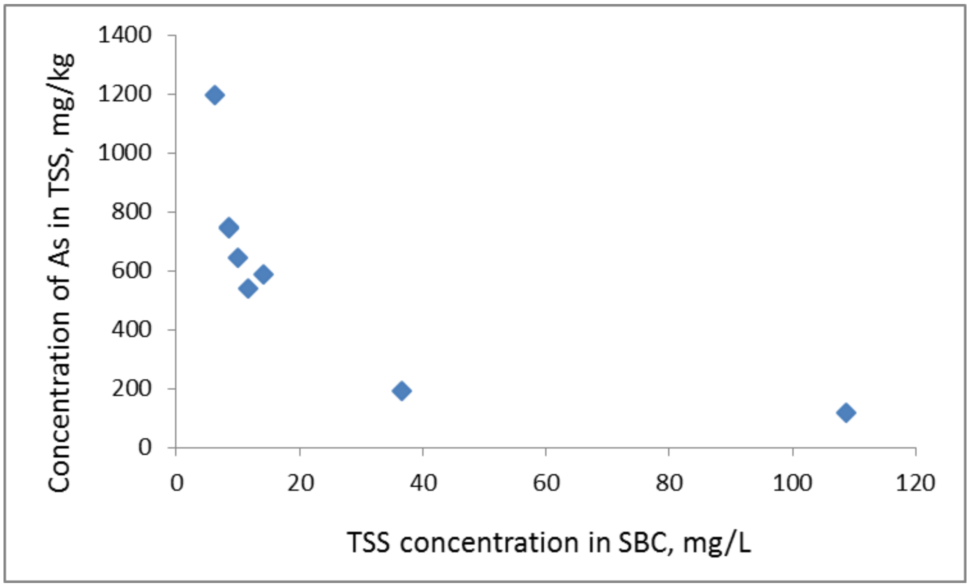


Figure 19. Correlation between As concentration in suspended solids and TSS concentration in Silver Bow Creek.

The previous discussion is important because it shows that the creek water that was used in the closed-system experiments had both dissolved and suspended arsenic for all dates of sampling. Importantly, adjustment of the pH of these waters from ambient stream values (typically 7.5 to 8.5) to values as high as 11.5 in the experiments did not mobilize As from the suspended sediment into the dissolved phase. If it had, then dissolved As concentrations in the experiments would have increased, potentially by as much as a factor of two. If anything, dissolved As concentrations went down after raising the pH. This shows that pH changes alone, either by lime addition or by natural photosynthesis, cannot be the major cause for the observed increases in dissolved arsenic as water passes through the WSPOU.

4.2. Laboratory Experiments

Laboratory experiments explored the effects of pH adjustments to the SBC WPSOU inlet water as well as to a mixture of Pond 3 water and benthic sediment. These experiments also allowed the different systems to be compared and contrasted. The closed system allowed more pH control compared to the open system. The open system was left open to the air and the fish tank circulation pump was continuously operating allowing the system to re-equilibrate with the air and the pH to return to more of a neutral range. The reason that the pH drifted back down is that CO_2 in air diffuses into the water, reacting with dissolved OH^-, as shown in the following equation:

$$CO_2 + OH^- \rightarrow HCO_3^-$$

Arsenic concentrations were fairly low in the unfiltered SBC WSPOU inlet water collected in the Spring of 2014. Simple pH adjustment showed very little increase in dissolved As concentrations.

Higher As concentrations were measured from the water and benthic sediment from Pond 3, so increases in As concentrations appeared more noticeably. However, the As was generally liberated when the pH was decreased below a pH of 8. Both laboratory experiments used for this thesis project help to debunk the idea that arsenic was becoming mobilized from the increase in pH alone.

4.3. Field Results

4.3.1. Vertical gradients in hydraulic head of shallow groundwater

It may be reasoned that groundwater could possibly be a contributing source to the increase of the arsenic concentrations in the Warm Springs Ponds. However, all of the piezometers installed into the south side of Pond 3 in this study had negative vertical gradients (Table IV), meaning that the flow of groundwater is out of the pond and into the sediment. The five piezometers that extend into the pond from the southern shore (PZ3, PZ5, PZ6, PZ7, PZ8) show a general steepening in the downward gradient to the north. Figure 20 demonstrates this vertical gradient in the southern portion of Pond 3. It is expected that the downward gradients in Pond 3 will steepen towards the north, as the dams and dikes are maintaining a pond elevation that is quite a bit higher than the valley floor. Lee (2012) also concluded that influent groundwater was a minor source of dissolved arsenic in Pond 2 and the West Wet Closure. Also, it should be mentioned that just because the vertical gradients are directed downwards doesn't mean that the ponds are leaking large amounts of water to the subsurface. This is because the hydraulic conductivity of the pond sediment is extremely low, being rich in mud and compacted organic matter.

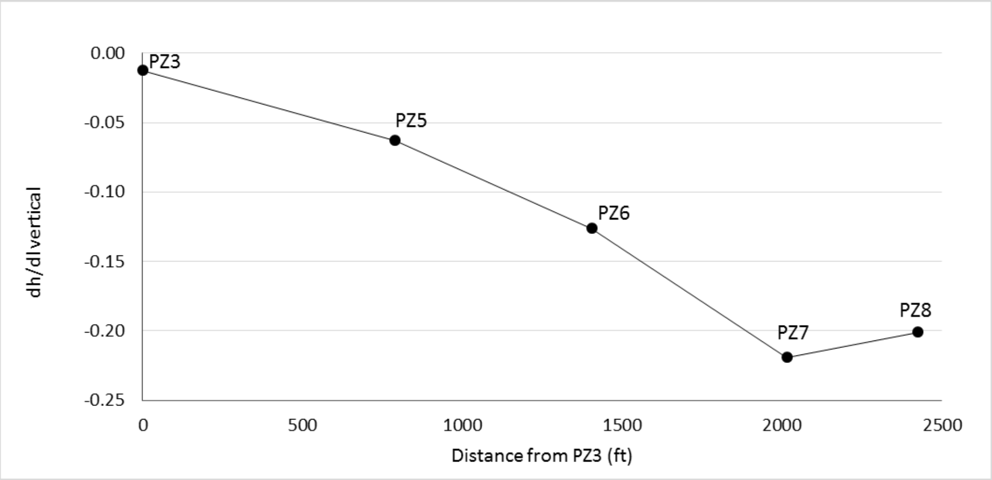


Figure 20. Vertical gradient in the southern portion of WSPOU - Pond 3.

4.3.2. General controls on groundwater chemistry

4.3.2.1. Variability of pH and Eh

In general, the pH of the shallow groundwater beneath Pond 3 was lower than the pH of the pond itself. The difference in pH between the pond and the groundwater can be explained by a couple different reasons. One reason is the decay of organic carbon within the pond sediment that causes an increased partial pressure of CO_2 which then causes a decrease in pH. The overall reaction can be written as follows:

$$CH_2O(s) + O_2 \rightarrow CO_2 + H_2O \qquad \text{(a)}$$

where $CH_2O(s)$ refers to organic carbon. Another reason for the pH variance is that the pH in the pond is kept at a pH greater than 9 and is increased either with the addition of lime (during fall, winter, and early spring) or by plant photosynthesis (during summer) to assist with the settling of heavy metals.

At the same time that reaction (a), above, lowers the pH by producing CO_2, the Eh of the groundwater is lowered by consumption of O_2. When all dissolved O_2 is gone, bacteria use other electron acceptors for respiration, such as nitrate, manganese, and iron. The reduction of nitrate, Mn-oxides, and Fe-oxides results in an increase in dissolved NH_4^+, Mn^{2+}, and Fe^{2+}, as shown by the following reactions:

$$NO_3^- + 2CH_2O + 2H^+ \rightarrow NH_4^+ + 2CO_2 + H_2O \qquad \text{(b)}$$

$$2MnO_2(s) + CH_2O + 4H^+ \rightarrow 2Mn^{2+} + CO_2 + 3H_2O \qquad \text{(c)}$$

$$4Fe(OH)_3(s) + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_2O \qquad \text{(d)}$$

These reactions consume protons and produce CO_2, which causes a further drop in pH of the groundwater. As shown in Figure 13 of Section 3.2, all of the piezometer samples had elevated concentrations of ammonium ion. However, the concentrations of dissolved Fe^{2+} and Mn^{2+} in the same samples were highly variable (Table V). This variation may reflect differences in the amount of biodegradable organic carbon from one site to the next, or may reflect differences in the amount of reducible Fe-oxide and Mn-oxide in the sediment.

4.3.3. Peepers

4.3.3.1. pH and Eh

Peeper results provided more information as to the most likely cause behind the increase in arsenic concentrations in the Warm Springs Ponds. The pH was measured for Peeper A, however, there is a slight uncertainty in the accuracy of the pH values. This is because the pH was measured shortly after the peeper was retrieved, but this small amount of time between retrieval and collecting measurements may have allowed the degassing of CO_2 causing a slight increase in pH. With this being said, it is believed by the author that the general trend of the pH decreasing as the depth increases below SWI shown for the Peeper A data (Fig. 14) is probably close to being correct. As previously mentioned, the decay of organic carbon within the pond sediment causes the partial pressure of CO_2 to increase, therefore, causing a decrease in pH. This relationship seen in the peepers between pH and As concentration follows the trend displayed for both the lab experiments and groundwater data; the pH decreased while the arsenic concentration increased in the peepers.

4.3.3.2. Redox reactions

Iron and manganese are redox-sensitive metals that potentially affect arsenic concentrations. Fe- and Mn-oxides are known to be strong adsorbents for arsenic and other trace metals, and reductive dissolution of Fe- and Mn-oxides may release any arsenic that is adsorbed onto these solids back into solution. In its oxidized state, arsenic (V) reacts with water to form an oxyanion ($HAsO_4^{2-}$) which strongly adsorbs to the surface of positively-charged hydrous ferric oxide (Drever, 1997; Langmuir, 1997). These relationships were taken into account when determining the cause of the increase in arsenic concentration.

The iron and arsenic adsorption relationship was well evident in the depth profile of Peeper A. Both concentrations displayed an increase at a similar depth range of approximately 5 to 10 cm below SWI (Fig. 15). This is due to the reductive dissolution of iron-oxides (reaction d). Once the iron is in a dissolved state, any arsenic that was adsorbed onto the Fe-oxides is also released to solution, where it can diffuse upwards into the pond water. Figure 16 shows a similar relationship where dissolved phosphate concentrations increase at 5 to 10 cm below SWI. Phosphate dissolves into water as a mix of $H_2PO_4^-$ and HPO_4^{2-}, depending on pH, and so it also adsorbs strongly onto Fe-oxides (Drever, 1997; Langmuir, 1997). When the Fe-oxides dissolve, both arsenate and phosphate are released to solution. Some phosphate can also be released by the decay of plant and algal matter as it is buried.

Similar to iron, the manganese depth profile for Peeper A demonstrated an increase approximately 5 cm below SWI (Fig. 15). These data suggest a reductive dissolution of manganese oxy-hydroxide minerals in the sediment pore-water (reaction c) as well as the previously mentioned reductive dissolution of iron oxy-hydroxide minerals (Martin and Pedersen, 2002). With respect to manganese, it is worth noting that the Butte mineral deposits were highly enriched in Mn-minerals, such as rhodochrosite and rhodonite. After milling and blasting, exposure to air and water causes these minerals to oxidize to black Mn-oxide. Thus, the sediment washed down SBC had a relatively high Mn-oxide content, especially in the early days prior to stream reclamation.

Compared to Peepers A and B, which were installed along the southern shore of Pond 3, Peeper C, installed near PZ5, had much lower concentrations of arsenic (see Fig. 15). The reason for this difference is not known, but may have had something to do with the time of year that the peepers were deployed. Peeper C was installed in November and retrieved in December, through the ice. The other two peepers were installed and sampled in the summer. The low concentrations of arsenic in Peeper C are especially odd considering that PZ5 did not have particularly low As concentration compared to the other piezometers (Fig. 11).

The decrease in sulfate concentration and the increase in hydrogen sulfide (Fig. 16) occurred because of the reducing conditions within the sediment pore water. This reaction is most likely assisted by sulfate reducing bacteria, as follows:

$$SO_4^{2-} + 2C(org) + 2H_2O \rightarrow H_2S + 2HCO_3^-. \qquad (e)$$

Similarly to the reduction of iron and manganese (reactions c and d), bacteria use sulfate as an electron acceptor to oxidize (respire) organic carbon, producing hydrogen sulfide and bicarbonate ion. If reactions (d) and (e) happen at the same time, there is an increase in Fe^{2+}, H_2S, HCO_3^-, and dissolved As concentrations. This provides opportunity for the dissolved Fe to be captured as Fe-sulfide (FeS or FeS_2) where H_2S is present in abundance, or as siderite ($FeCO_3$) where HCO_3^- is present in abundance. Because As forms no insoluble carbonate or sulfide minerals, dissolved As remains in solution and travels its own way.

4.3.4. Arsenic Speciation

Arsenic is usually found in the oxidized (V or arsenate) valence state in waters that contain dissolved oxygen, but can be reduced to arsenite (III) in anaerobic environments such as the pond sediment of the WSPOU. Due to the slow kinetics of arsenic redox reactions, both valence states are often observed together in the environment (TAMU, 2014). Oxidation states are important because they affect how arsenic adsorbs to minerals, dissolves or precipitates from solution, as well as the level of toxicity to plants and animals. Several publications (TAMU, 2014; LaGrega, Buckingham, and Evans, 1994) demonstrate that As(III) is both more toxic and more highly soluble compared to As(V). Therefore, it is important to determine the relative amounts of As(V) and As(III) in an environmental study.

In Section 3.2.4, it was shown that dissolved As was mainly present as As(III) in peeper cells at depths exceeding 5 cm below the SWI, and was almost entirely present as As(III) in the shallow groundwater of the piezometers. In contrast, results from the top peeper cells, which were situated above the SWI, showed As(V) > As(III). In general, the arsenic speciation results of this study make geochemical sense. Furthermore, the redox behavior of As in the WSPOU system is similar to what has been observed in other lakes impacted by mining processes. Arsenic speciation displayed in other lakes show a dominance in As(V) in the lake water and a dominance of As(III) in the sediment pore-water (e.g., Martin and Pedersen, 2002).

4.4. Eh-pH Diagrams

Figure 21 shows an Eh-pH diagram for the Fe-C-S system, drawn using the program Stabcal (Huang, 2010). The “x” and “o” symbols plot field data for the groundwater piezometers and pond samples, respectively. The diagram was drawn for total S, C, and Fe concentrations of 200, 20, and 1 mg/L, respectively. These values were close to the average values from all of the piezometers. The stability fields of crystalline Fe-bearing solids were suppressed to better show possible equilibrium between the groundwaters and ferrihydrite ($Fe(OH)_3$), siderite ($FeCO_3$), and amorphous FeS. The results show that all of the waters are close to saturation or supersaturated with ferrihydrite. In addition, a couple samples are close to equilibrium with siderite. Overall, it is likely that the redox state of the groundwaters is buffered near the solid $Fe(OH)_3$/aqueous Fe^{2+} boundary.

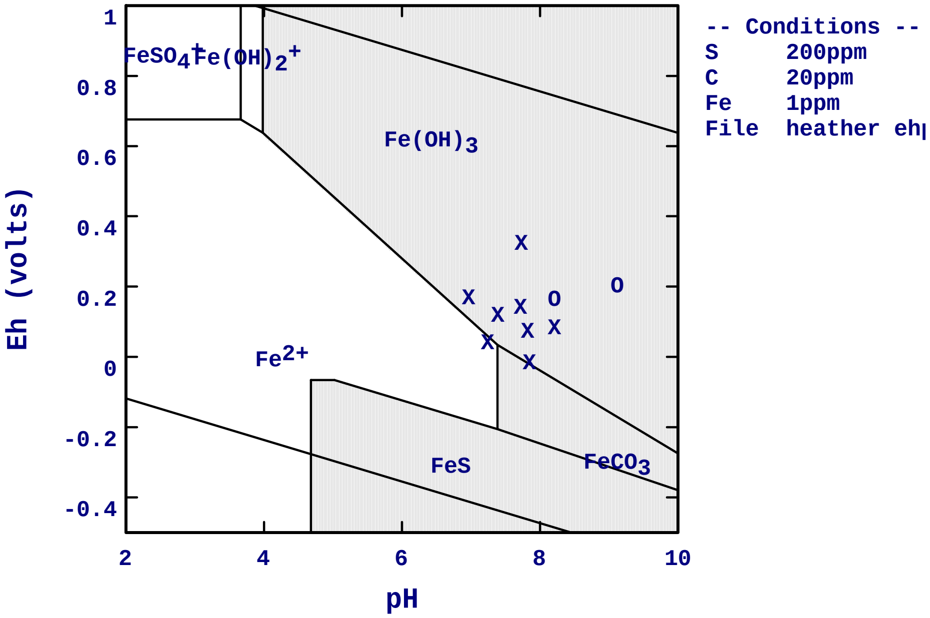


Figure 21. Eh-pH diagram for the Fe-C-S system. "X" symbols are groundwater piezometer samples; "O" symbols are pond water samples. Shaded regions show stability fields of solids.

Figure 22 shows a similar Eh-pH diagram for the Mn-C-S system, assuming a Mn concentration of 4 mg/L (average of piezometer values). According to the results, all of the water samples are near equilibrium or supersaturated with rhodochrosite ($MnCO_3$), and 1 or 2 samples have Eh poised near the $MnCO_3$/Mn-oxide boundary. These results are consistent with Visual Minteq saturation indices (Section 4.5) that also predict the groundwaters are saturated or supersaturated with $MnCO_3$.

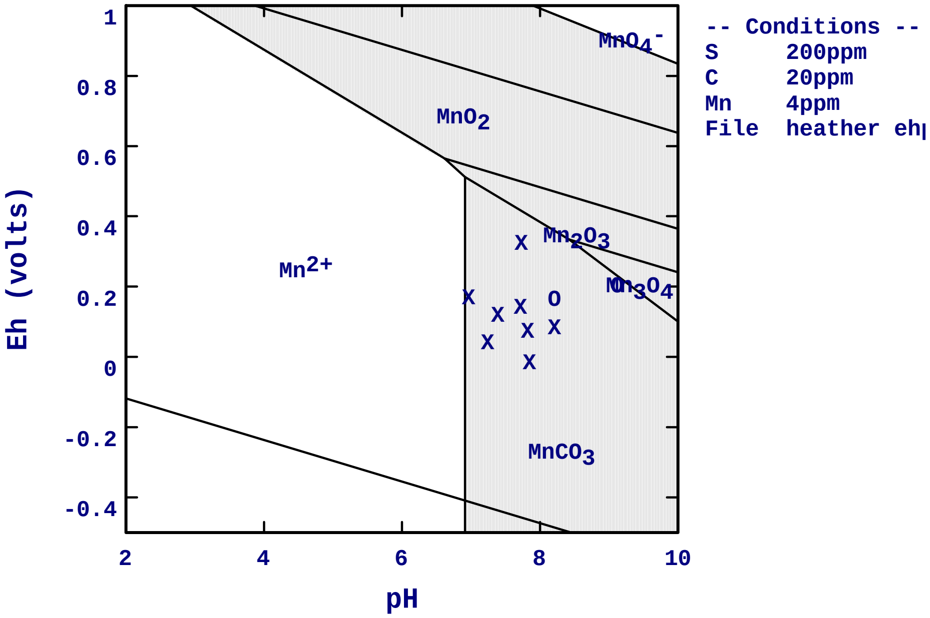


Figure 22. Eh-pH diagram for the Mn-C-S system. "X" symbols are groundwater piezometer samples; "O" symbols are pond water samples. Shaded regions show stability fields of solids.

Figure 23 shows a similar Eh-pH diagram for the As-C-S system, assuming a dissolved As concentration of 0.1 mg/L. According to the results, all of the water samples plot in the stability field of dissolved As(V), or $HAsO_4^{2-}$, with a few samples near the dissolved As(V)/As(III) boundary. This result is not in agreement with the field speciation results, which showed that almost all of the dissolved As in the PZ samples was present as As(III). The cause of this disagreement is not known, but could be one of three things: 1) maybe the field ORP values were off-calibration (normally the MS-5 is calibrated in the lab to read true Eh); 2) maybe the cartridges used to speciate As(V) from As(III) were not working; and 3) maybe the waters were not in redox equilibrium. If the cartridges are to blame, then there could have been other solutes dissolved in the water samples that loaded up the cartridge resin, allowing the dissolved As(V) to pass through the filters. The third possibility, redox disequilibrium, is considered the most likely explanation to explain the difference between modeled and measured redox states of arsenic. It is common for different redox couples (e.g., Fe^{2+}/Fe^{3+}, As^{3+}/As^{5+}) in a single water sample to be out of equilibrium with each other (Drever, 1997; Langmuir, 1997).

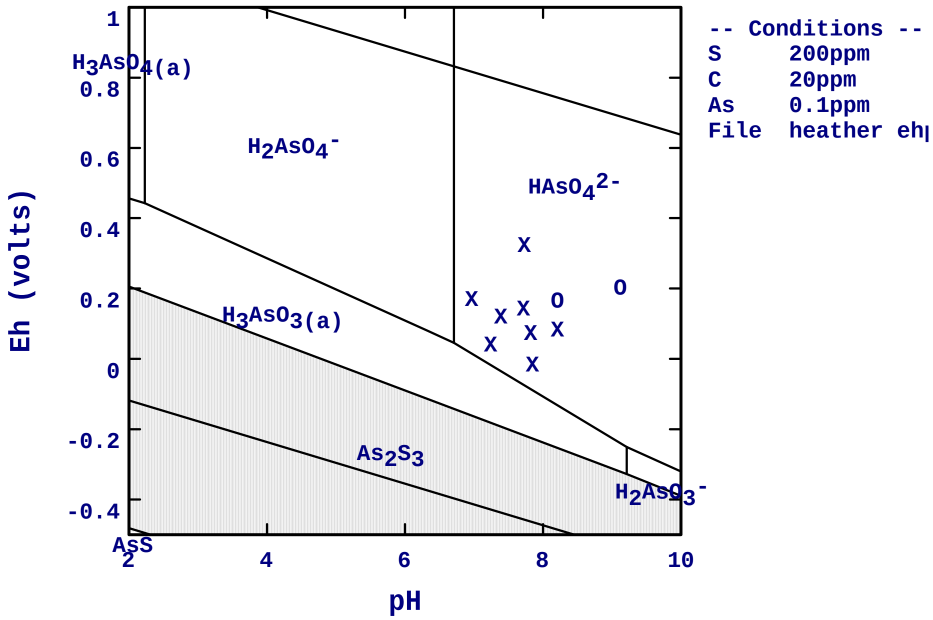


Figure 23. Eh-pH diagram for the As-C-S system. "X" symbols are groundwater piezometer samples; "O" symbols are pond water samples. Shaded regions show stability fields of solids.

Finally, Figure 24 shows an Eh-pH diagram for the dissolved N species. As expected, most of the groundwater samples plot in the stability field of the ammonium ion, NH_4^+. The two pond samples straddle the boundary between ammonium and nitrite (NO_2^-), and it is possible that this reaction is helping to buffer redox in the pond. The Warm Springs Ponds receive large loads of nitrogen from Silver Bow Creek, so this is a possibility.

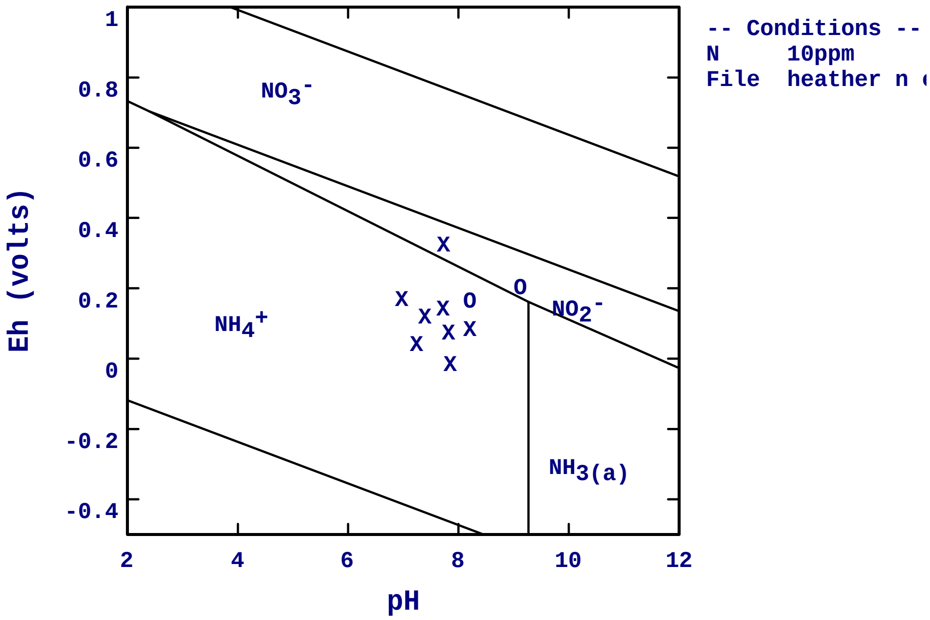


Figure 24. Eh-pH diagram for the N system. "X" symbols are groundwater piezometer samples; "O" symbols are pond water samples. Shaded regions show stability fields of solids.

4.5. Geochemical Modeling

Geochemical modeling was performed using Visual Minteq (vers. 3.1, Gustafson, 2014) to assist in determining possible minerals the groundwater and sediment pore water may be coming in contact with and impacting the geochemistry. One way to determine this is by calculating the mineral's saturation index (S.I.). The mineral's S.I. is calculated by taking the ion activity quotient (Q) and dividing it by the equilibrium constant (K_{eq}) and then taking the log of this quotient. Once this S.I. value has been calculated, it quantifies which minerals may be precipitating, dissolving, or close-to-equilibrium within a water sample. S.I. values that are positive are believed to be super-saturated and should precipitate out of the water. Negative S.I. values indicate that the solution is under-saturated with the mineral of interest, and that it should dissolve if present. For the purposes of this section, S.I. values within 0.3 units of zero are believed to be near equilibrium. In this type of modeling, it is understood that a mineral's S.I. value only tells us what *should* happen in an environmental system. Equilibrium models do not take kinetics (rates of reactions) into account.

Figure 25 summarizes the S.I.'s for several minerals of interest for the groundwater at the WSPOU collected from PZ1-8. These include the carbonate minerals calcite, dolomite, siderite, and rhodochrosite; gypsum which is a calcium sulfate bearing mineral; hydroxyapatite which is a calcium phosphate bearing mineral; arsenolite (As_2O_3), symplesite ($Fe_3(AsO_4)_2$), calcium arsenate ($Ca_3(AsO_4)_2$▪$4H_2O(s)$), and manganese arsenate ($Mn_3(AsO_4)_2$▪$8H_2O(s)$) which are arsenic bearing minerals; and $Fe(OH)_2$(am) and ferrihydrite ($Fe(OH)_3$) which are iron(II) and iron(III) hydroxide minerals, respectively. The yellowish rectangle on the graph shows S.I. values that are within 0.3 units of zero, i.e., near-equilibrium. Generally, all of the minerals listed within the carbonate system as well as gypsum are predicted to be in equilibrium or close to equilibrium with the groundwater. Hydroxyapatite is shown to be super-saturated. Arsenolite, an As(III) valence mineral, is indicating a very under-saturated S.I. while symplesite, calcium arsenate, and manganese arsenate, all As(V) valence minerals, are all shown to be under-saturated but closer to equilibrium than arsenolite. (PZ4 and PZ6 are displayed to be slightly saturated or within equilibrium with symplesite.) This is quite interesting because the arsenic speciation had determined the dominant valence state of dissolved arsenic in the groundwater was As(III); however, a mineral that is of one elemental valence state (i.e. As(V)) may possibly be in contact with water that has the dissolved species with a different valence state (i.e. As(III)). $Fe(OH)_2$(am) is predicted to be quite under-saturated and in dissolved form and ferrihydrite is predicted to be super-saturated and precipitating.

Input data included temperature, pH, alkalinity, As, Ca, Fe, Mg, Mn, Sr, Zn, PO_4^{3-}, NH_4^+-N, and sulfate. The As and Fe concentrations were added as both As(III) and As(V) and Fe(II) and Fe(III). The charge balances calculated by VM were quite high ranging from 13 to 51% with an excess of cations. PZ4 had a charge balance of -10.7% showing an excess of anions. These charge balances may have been more extreme than what is realistic because of limited analytical data input into the program. However, this program provides some insight on possible minerals within the WSPOU sediment.

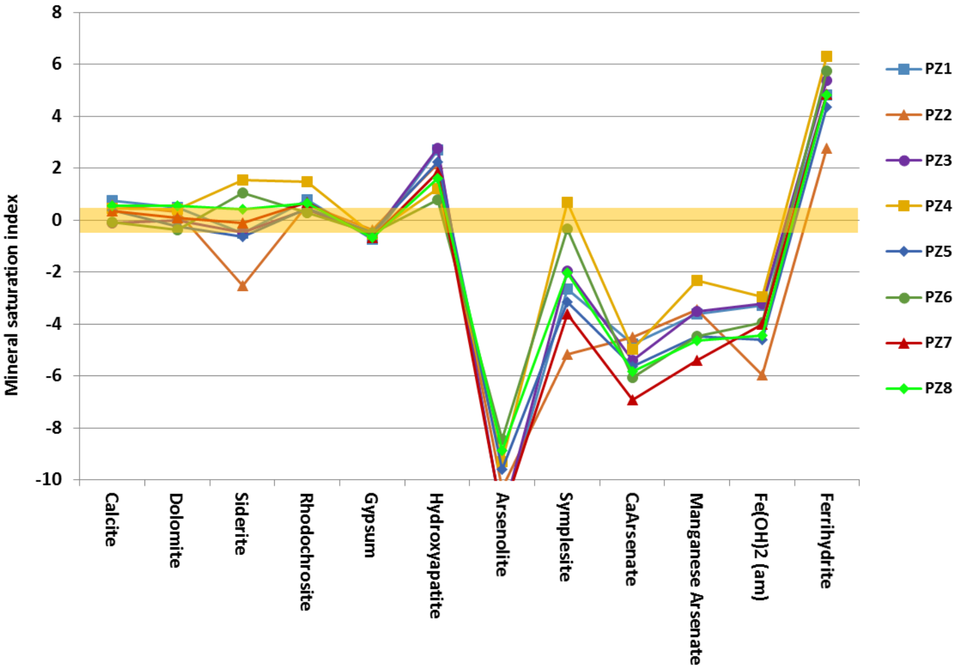


Figure 25. VM geochemical model of the mineral saturation indices for PZ1-8.

Figure 26 shows the S.I. values for the minerals of interest for the sediment pore water at the WSPOU collected from Peeper A. Similar minerals as those used for the groundwater were studied with the addition of scorodite ($FeAsO_4{:}2H_2O(s)$) which was provided by VM after the water quality data for Peeper A were input and the program was executed. The charge balances ranged from -6.7 to -18.8% (depths 4 cm above SWI to 2 cm below SWI) with an excess of anions; charge balances also ranged from 2.31 to 11.2% (depth 4 to 22 cm below SWI) with an excess of cations.

These results are fairly similar to the groundwater results. The carbonate minerals are generally displaying higher S.I.'s, meaning these minerals are most likely precipitating out of the water. Gypsum is slightly to moderately under-saturated, so it would be dissolving when in contact with the water. The arsenic and iron minerals, once again, are demonstrating similar trends as those observed in the groundwater. When looking closely at the graph, the peeper rows that are displaying S.I. values near or above zero for symplesite were actually located deepest in the sediment pore water. Previous data on arsenic speciation determined that As(III) should be the more dominant valence state for the deeper cells located within the sediment pore water. This being the case, it is considered unlikely that symplesite would be present in the Pond 3 sediment.

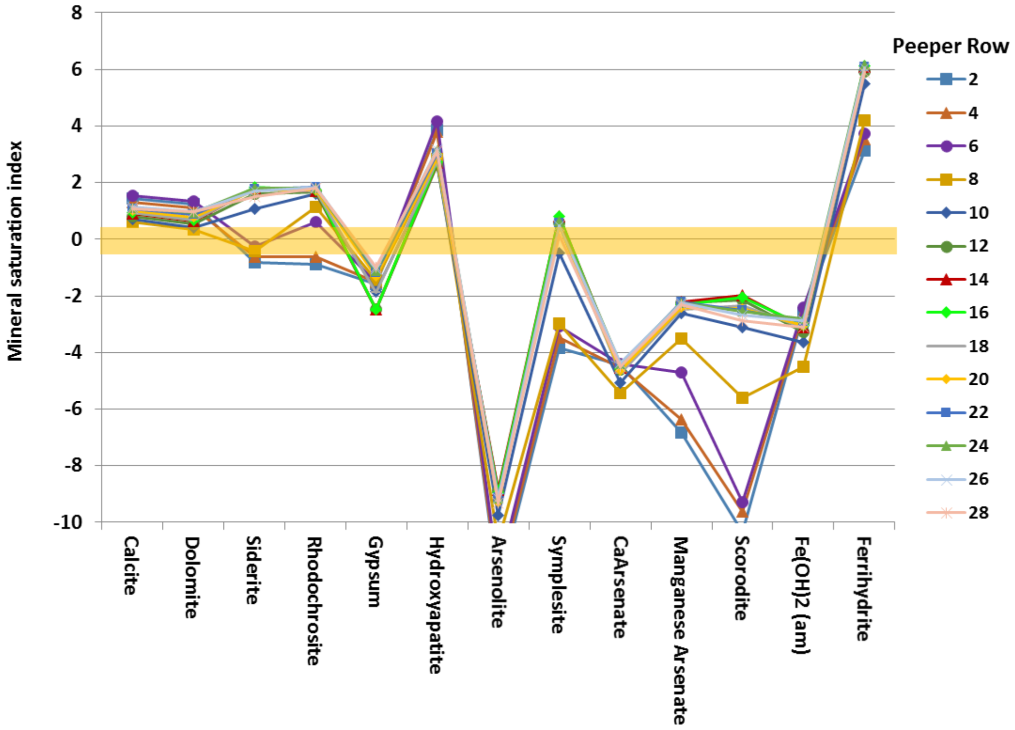


Figure 26. VM geochemical model of the mineral SI's for Peeper A.

Figure 27 represents the depth profile for Peeper A versus the mineral SI’s. It is observed that the carbonate minerals are fairly close to equilibrium throughout the depth profile, especially calcite, dolomite, and siderite. Rhodochrosite appears to be under-saturated within the pond water and then once below the SWI it begins to precipitate within the sediment pore-waters. Gypsum appears to be under-saturated throughout the depth profile while hydroxyapatite appears to be super-saturated. Arsenolite, the As(III) mineral, is extremely under-saturated in the depth profile. Symplesite is shown to be under-saturated in the pond water, but then equilibrates with the sediment pore-water approximately 4 cm below the SWI. Calcium arsenate, scorodite, and manganese arsenate display under-saturated SI’s which agrees with the sediment pore-water speciation data. The $Fe(OH)_2$(am) is also under-saturated and in the dissolved form. Ferrihydrite is super-saturated and precipitating which agrees with reaction (d) in Section 4.3.2.1.

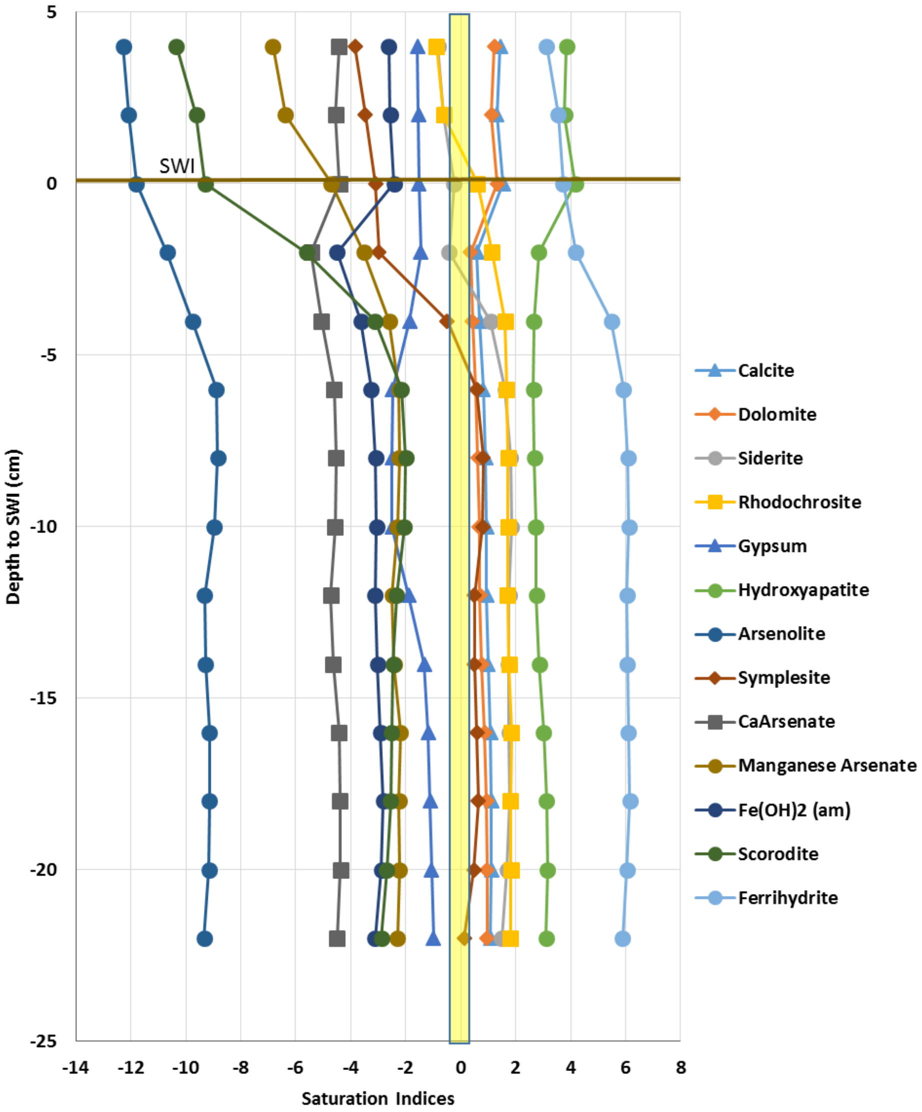


Figure 27. VM geochemical model of the depth profile for the mineral SI's for Peeper A.

5. Conclusions and Recommendations

5.1. Conclusions

The focus of this project was to continue studying the geochemistry in the Warm Springs Ponds, more specifically, to explore the mechanism of the arsenic increase in Pond 3. Lab experiments and field work were performed to determine possible answers. The main conclusions are listed below:

- The FA and calculated TR arsenic concentrations for the SBC inlet water samples determined that approximately half of the arsenic concentration entering into the WSPOU was dissolved and the other half existed as suspended particulates. Also, because the TR values were higher than the RA values, it is estimated that approximately half of the particulate As was not dissolved upon acidification with 1% HNO_3.
- SBC inlet water demonstrated very low concentrations of dissolved arsenic entering the ponds and very little change in concentration as pH was adjusted. The range of dissolved arsenic for the inlet water was 5.8 to 10.4 μg/L with a pH range of 7.17 to 8.34. After the final pH adjustments were performed, dissolved arsenic concentrations decreased for 5 (HB1, HB5, HB6, HB7, and HB8) of the 8 inlet water samples collected; the dissolved arsenic concentrations after the final pH increase ranged from 6.5 to 3.2 μg/L with final pH values of 9.94 to 11.73. The 3 (HB2, HB3, and HB4) remaining inlet water samples that displayed an increase in dissolved arsenic concentrations had concentrations with a range of 7.4 to 12.6 μg/L with a pH range of 10.05 to 11.02.

- Water and benthic sediment collected from Pond 3 did have higher concentrations of As and adjusting the pH to a lower pH did seem to cause the concentration to increase, however, this experiment demonstrated that an increase in pH did not increase the arsenic concentration. The concentration of dissolved arsenic during the initial pH increase (pH range of 9.54 to 11.69), the pH decrease (pH range of 7.55 to 2.76), and the second pH increase (pH range of 7.49 to 9.75) ranged from 12.9 to 35 µg/L, 143.7 to 154.4 µg/L, and 55.9 to 80.6 µg/L, respectively. Both the closed and open systems indicate that an increase of pH alone is not causing the dissolved arsenic concentration to increase.
- Experiments with pH adjustment were complicated by CO_2 re-equilibrating within the open system but less so in the closed system. An open system, such as the WSPOU, will re-equilibrate with CO_2 (either degas or dissolve within the water) from the atmosphere causing the pH to travel back to a neutral range no matter what the pH is adjusted to and the closed system, such as a sealed bottle, will not be able to re-equilibrate because no interaction between CO_2 is occurring.
- Groundwater sampled 4 to 9 ft below SWI had concentrations of As between 28 to 333 µg/L for PZ1-4 and 19.9 to 639 µg/L for PZ5-8. However, the WSPOU complex is perched above the surrounding land with a downward vertical gradient indicating it is a losing pond. Therefore, it is unlikely that influent groundwater would increase the arsenic concentration in the pond water. The downward vertical gradients ranged from 0.0002 to 0.219 (dh/dl). PZ4 had the least downward vertical gradient and the third highest As concentration (333 µg/L)

while PZ7 had the highest vertical gradient and the lowest As concentration (19.9 µg/L) as compared to the other piezometers.

- Measurements for pH determined that the groundwater had lower pH values (ranging from 7.23 to 8.2) as compared to the pond pH values (ranging from 8.0 to 9.89) most likely due to the microbial decay of organic carbon which then causes the partial pressure of CO_2 to increase causing the pH to decrease.
- Sediment pore water in Peeper A showed a decrease in pH with a value of 7.16 approximately 6 cm below SWI due to the process of microbial decay of organic carbon as seen in the groundwater. As and Fe concentrations at the SWI were 33 µg/L and 0.01 mg/L and increased to 528 µg/L and 22.7 mg/L approximately 5 to 10 cm below SWI in Peeper A, respectively, and appear to be strongly correlated. The cause of this increase is the reductive dissolution of iron-oxides. These iron-oxides have dissolved in the anoxic pore water due to the microbial decay of organic carbon. Therefore, this is causing arsenic to desorb from the iron and diffuse out of the sediment pore water and traveling upwards increasing the concentration in the effluent water.
- An inverse correlation between sulfate and hydrogen sulfide concentrations for Peeper A demonstrated microbial assistance of sulfate reducing to hydrogen sulfide within the sediment pore water. The reduction of sulfate produces H_2S and HCO_3^- which then may be capturing the Fe that is released during the reductive dissolution and forming Fe-sulfide or siderite in the sediment.
- Using the aluminosilicate resin cartridge to perform As speciation in the field was quite easy and quick. Arsenic speciation determined that the groundwater was

dominated by As(III) valence state and the sediment pore water was also dominated by As(III) valence state while the peeper cells located within the pond indicated that As(V) was the dominant valence state.

5.2. Recommendations

A large amount of data was collected on the southern portion of Pond 3, however, with Pond 3 being the largest pond within the WSPOU complex more exploration and data collection similar to what was performed in this thesis is highly recommended. The following are recommendations for the WSPOU as well as future work ideas:

- As it has been shown throughout this thesis that pH alone is not increasing the As concentration, the continued use of lime is recommended to keep the pH above 9 to help settle dissolved heavy metals (Cd, Cu, Mn, Pb, and Zn) from influent water.
- As the remediation efforts continue along SBC, the concentrations of arsenic in Silver Bow Creek entering the ponds should decrease; however, this thesis has shown that the main source of arsenic release in WSPOU is the pond sediment. Therefore, the concentrations of arsenic in the effluent water may not decrease for some time. The addition of a reactor located at the WSPOU effluent to decrease arsenic concentrations may be of future value.
- Water samples were analyzed for a broad spectrum of analytes, however, it would be helpful to analyze for Cl^-, NO_3^-, Na^+, K^+ to provide information on these chemical constituents in the water. Plus, in the event geochemical modeling is

performed, the model will be better representative of the water and hopefully have a better charge balance.

- A wide array of data was collected from Pond 3 of the WSPOU, however, no sediment core samples were collected. This would be valuable information to help determine actual minerals that may be causing other geochemical reactions within the sediment. (Geochemical modeling was performed, but this tool provides a list of what should be in the sediment and/or water, not what is really there.)
- Preparation of a more thorough and extensive sampling plan may benefit from reviewing historic aerial photos of Pond 3 prior to it being built in the 1950's. Photos may show the pre-existing flowpath into the WSPOU complex where tailings and heavy metals were deposited and provide possible desired sampling locations.
- Sediment pore water samplers ("peepers") were quite insightful on the release mechanism of arsenic into Pond 3. The use of additional peepers throughout more of the pond would be useful to provide more geochemistry data within the sediment pore water.
- Piezometers were placed on the southern end of Pond 3; additional piezometers throughout more of the pond would assist with the continued studies of the groundwater geochemistry as well as the vertical gradients at the WSPOU.

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Appendix A: “Closed System” Data – Bottled Site Water

Table A1. Lab and ICP-OES TSS (determined from sediment on filters - microwave digested) data from Silver Bow Creek near Pond 3 inlet. All data in mg/L.

Sample	pH	SC (µS/cm)	As	Be	Ca	Cd	Co	Cr	Cu	Fe
HB1-I-MD	7.62	486	0.031	0.005	215	0.003	0.014	0.092	0.05	7.0
HB2-I-MD	7.17	271	0.067	0.009	223	0.006	0.021	0.140	0.30	29.0
HB3-I-MD	7.50	342	0.034	0.009	222	0.003	0.013	0.106	0.05	7.9
HB4-I-MD	7.55	303	0.031	0.009	218	0.003	0.013	0.102	0.02	6.7
HB5-I-MD	8.14	244	0.033	0.005	218	0.004	0.014	0.094	0.10	10.3
HB5-I-DUP-MD	8.14	244	0.034	0.005	217	0.004	0.014	0.095	0.10	10.4
HB5-F-MD	11.56	3417	0.040	0.006	226	0.005	0.015	0.098	0.19	12.2
HB5-F-DUP-MD	11.56	3417	0.040	0.006	224	0.005	0.015	0.097	0.19	12.5
HB6-I-MD	8.34	297	0.030	0.005	221	0.003	0.014	0.090	0.04	7.6
HB6-F-MD	11.45	2006	0.061	0.005	224	0.005	0.014	0.095	0.29	11.1
HB7-I-MD	7.92	319	0.033	0.005	224	0.003	0.014	0.092	0.05	8.4
HB7-F-MD	11.73	3496	0.068	0.006	***	0.005	0.016	0.110	0.36	13.0
HB8-I-MD	7.94	430	0.033	0.008	218	0.003	0.013	0.096	0.05	7.7
HB8-F-MD	11.73	4556	0.090	0.005	***	0.006	0.014	0.094	0.38	10.6

Sample	pH	SC (µS/cm)	Li	Mg	Mn	Mo	Pb	Sr	Ti	Zn
HB1-I-MD	7.62	486	0.128	32.3	0.678	0.005	0.036	0.39	5.45	3.27
HB2-I-MD	7.17	271	0.198	38.1	1.274	0.005	0.119	0.50	5.98	4.93
HB3-I-MD	7.50	342	0.155	33.2	0.408	0.005	0.044	0.44	5.21	4.64
HB4-I-MD	7.55	303	0.144	32.1	0.182	b.d.	0.039	0.41	5.07	3.55
HB5-I-MD	8.14	244	0.131	31.9	0.426	b.d.	0.054	0.41	5.34	3.42
HB5-I-DUP-MD	8.14	244	0.131	32.0	0.426	0.005	0.054	0.41	5.31	3.44
HB5-F-MD	11.56	3417	0.145	44.4	0.461	0.005	0.070	0.47	5.47	5.13
HB5-F-DUP-MD	11.56	3417	0.144	44.1	0.455	0.005	0.071	0.47	5.42	5.11
HB6-I-MD	8.34	297	0.158	31.2	0.185	0.005	0.045	0.44	5.35	5.65
HB6-F-MD	11.45	2006	0.162	80.5	0.599	0.006	0.064	0.48	5.31	6.64
HB7-I-MD	7.92	319	0.131	31.4	0.207	0.005	0.046	0.42	5.24	4.27
HB7-F-MD	11.73	3496	0.193	75.6	0.489	0.006	0.075	1.37	5.93	7.57
HB8-I-MD	7.94	430	0.157	30.2	0.208	0.005	0.045	0.44	4.83	5.48
HB8-F-MD	11.73	4556	0.169	106.6	0.487	0.005	0.073	0.98	5.29	6.07

Ni, Sb, Se, Tl, and V below detection limits.

*** - Over-range

b.d. – below detect

Table A2. Lab and ICP-OES FA data from Silver Bow Creek near Pond 3 inlet - closed system pH adjustment experiments. All data in mg/L.

Sample ID	pH	SC (µS/cm)	As	Cu	Fe	Li	Mg	Mn	Sr	Zn
Filtered Acidified										
HB1 FA	7.62	486	0.008	0.021	0.09	0.046	8.0	0.227	0.29	0.108
HB1_1 FA	9.21	384	0.008	0.021	0.06	0.048	8.3	0.197	0.30	0.101
HB1_1DUP FA	9.21	384	0.008	0.021	0.06	0.049	8.5	0.196	0.30	0.102
HB1_2 FA	9.97	-	0.008	0.018	0.05	0.049	8.2	0.108	0.29	0.023
HB1_3 FA	9.94	506	0.007	0.014	0.02	0.049	7.8	0.009	0.16	0.008
HB2 FA	7.17	271	0.010	0.020	0.07	0.021	5.1	0.065	0.17	0.051
HB2_1 FA	7.14	279	0.011	0.022	0.08	0.022	5.4	0.070	0.17	0.048
HB2_2 FA	9.17	312	0.011	0.039	0.09	0.022	5.3	0.003	0.17	0.032
HB2_3 FA	10.05	414	0.013	0.040	0.05	0.023	5.2	0.001	0.16	0.030
HB3 FA	7.50	342	0.006	0.017	0.10	0.027	6.2	0.017	0.21	0.056
HB3_1 FA	7.53	116	0.007	0.018	0.09	0.028	6.6	0.016	0.22	0.058
HB3_2 FA	9.56	3800	0.006	0.022	0.10	0.029	6.5	0.007	0.21	0.057
HB3_3 FA	10.25	300	0.007	0.031	0.07	0.030	6.4	0.004	0.21	0.064
HB4 FA	7.55	303	0.007	0.012	0.06	0.019	5.7	0.072	0.19	0.044
HB4_1 FA	9.00	186	0.007	0.023	0.04	0.020	6.0	0.043	0.19	0.026
HB4_2 FA	10.04	453	0.007	0.024	0.02	0.022	5.9	0.003	0.19	0.031
HB4_3 FA	11.02	785	0.008	0.023	0.01	0.022	5.2	0.001	0.18	0.008

Be, Cd, Co, Cr, Mo, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

Calcium - Over range.

(cont.)Table A2. Lab and ICP-OES FA data from Silver Bow Creek near Pond 3 inlet - closed system pH adjustment experiments. All data in mg/L.

Sample ID	pH	SC (µS/cm)	As	Ca	Cu	Fe	Li	Mg	Mn	Sr	Zn
HB5 FA	8.14	244	0.008	***	0.012	0.05	0.012	4.8	0.045	0.14	0.017
HB5-1 FA	9.45	293	0.009	26.0	0.017	0.03	0.011	5.9	0.003	0.13	0.006
HB5-2 FA	10.6	697	0.008	24.6	0.024	0.04	0.011	5.1	0.003	0.13	0.010
HB5-3 FA	11.6	3417	0.007	20.8	0.010	0.01	0.012	0.2	b.d.	0.11	b.d.
HB5-3 DUP FA	11.6	3417	0.006	20.8	0.010	0.01	0.012	0.2	b.d.	0.11	b.d.
HB6 FA	8.34	297	0.007	30.8	0.009	0.05	0.014	7.2	0.061	0.16	0.018
HB6-1 FA	9.29	341	0.006	30.4	0.018	0.03	0.015	7.4	0.019	0.16	0.004
HB6-2 FA	10.4	572	0.008	29.6	0.016	0.05	0.016	7.0	0.006	0.15	0.003
HB6-3 FA	11.5	2006	0.004	27.0	0.005	b.d.	0.016	0.7	b.d.	0.14	b.d.
HB7 FA	7.92	319	0.007	31.1	0.010	0.06	0.017	7.5	0.049	0.18	0.022
HB7-1 FA	9.73	382	0.007	30.5	0.021	0.04	0.017	7.8	0.017	0.17	0.004
HB7-2 FA	10.8	772	0.007	31.0	0.012	0.01	0.019	21.3	0.001	0.17	0.007
HB7-3 FA	11.7	3496	0.003	4.36	0.011	b.d.	0.019	0.8	b.d.	0.06	0.005
HB8 FA	7.94	430	0.009	43.3	0.013	0.04	0.030	29.3	0.054	0.24	0.030
HB8 FA-DUP	7.94	430	0.009	42.8	0.014	0.04	0.031	29.3	0.054	0.24	0.027
HB8-1 FA	9.21	449	0.009	42.2	0.017	0.03	0.030	31.1	0.028	0.24	0.009
HB8-2 FA	10.7	854	0.005	28.2	0.009	b.d.	0.031	10.3	b.d.	0.17	0.003
HB8-3 FA	11.7	4556	0.004	4.92	0.010	b.d.	0.031	0.3	b.d.	0.06	0.003

Be, Cd, Co, Cr, Mo, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

***Over range.

b.d. - below detect

Table A3. Lab and ICP-OES RA data from Silver Bow Creek near Pond 3 inlet - closed system pH adjustment experiments. All data in mg/L.

Sample ID	pH	SC (µS/cm)	As	Ca	Cu	Fe	Li	Mg	Mn	Sr	Zn
Raw Acidified											
HB1 RA	7.62	486	0.010	***	0.036	0.40	0.047	8.7	0.245	0.31	0.329
HB2 RA	7.17	271	0.017	***	0.067	0.97	0.021	5.7	0.191	0.18	0.160
HB3 RA	7.50	342	0.009	***	0.030	0.38	0.027	6.8	0.117	0.22	0.115
HB4 RA	7.55	303	0.008	***	0.023	0.30	0.019	6.1	0.109	0.20	0.220
HB5 RA	8.14	244	0.011	***	0.026	0.34	0.012	5.2	0.090	0.15	0.136
HB5-1 RA	9.45	293	0.010	25.6	0.044	0.46	0.011	5.7	0.086	0.14	0.110
HB5-2 RA	10.6	697	0.009	24.6	0.041	0.44	0.012	5.2	0.086	0.13	0.050
HB5-3 RA	11.6	3417	0.008	21.4	0.040	0.36	0.012	3.7	0.076	0.11	0.048
HB5-3 DUP RA	11.6	3417	0.009	21.9	0.050	0.58	0.012	4.7	0.120	0.11	0.060
HB6 RA	8.34	297	0.007	30.4	0.015	0.22	0.015	6.9	0.084	0.16	0.032
HB6-1 RA	9.29	341	0.008	29.5	0.029	0.18	0.015	7.1	0.059	0.16	0.019
HB6-2 RA	10.4	572	0.007	28.8	0.029	0.15	0.016	6.8	0.050	0.15	0.021
HB6-3 RA	11.5	2006	0.006	26.3	0.025	0.12	0.016	5.0	0.045	0.14	0.022
HB7 RA	7.92	319	0.008	31.3	0.017	0.22	0.017	7.5	0.081	0.18	0.050
HB7-1 RA	9.73	382	0.008	29.5	0.038	0.17	0.017	7.6	0.054	0.17	0.025
HB7-2 RA	10.8	772	0.007	32.5	0.048	0.22	0.022	20.9	0.043	0.18	0.119
HB7-3 RA	11.7	3496	0.007	27.1	0.042	0.21	0.022	13.7	0.043	0.15	0.042
HB8 RA	7.94	430	0.008	43.3	0.022	0.14	0.034	27.6	0.073	0.25	0.045
HB8 DUP RA	7.94	430	0.009	43.3	0.021	0.14	0.033	27.6	0.073	0.25	0.049
HB8-1 RA	9.21	449	0.009	42.4	0.029	0.18	0.034	29.0	0.063	0.25	0.033
HB8-2 RA	10.7	854	0.009	32.6	0.037	0.16	0.035	25.4	0.044	0.20	0.029
HB8-3 RA	11.7	4556	0.008	15.8	0.039	0.13	0.034	20.1	0.040	0.11	0.036

Be, Cd, Co, Cr, Mo, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

***Over range.

Table A4. Lab and ICP-OES MD data from Silver Bow Creek near Pond 3 inlet - closed system pH adjustment experiments. All data in mg/L.

Sample ID	pH	SC (µS/cm)	As	Ca	Cu	Fe	Li	Mg	Mn	Mo	Sr	Ti	Zn
Microwave Digested Samples													
HB1- MD	7.62	486	0.008	61.7	0.044	0.61	0.041	12.4	0.299	0.007	0.319	0.02	0.205
HB1-1-MD	9.21	384	0.006	64.3	0.043	0.48	0.040	12.6	0.299	0.007	0.334	0.01	0.282
HB1-2-MD	9.97	-	0.007	63.9	0.043	0.48	0.041	12.4	0.290	0.007	0.332	0.01	0.214
HB1-3-MD	9.94	506	0.005	55.0	0.044	0.47	0.042	11.9	0.287	0.006	0.298	0.02	0.222
HB2-MD	7.17	271	0.015	34.8	0.091	3.67	0.023	7.1	0.260	0.005	0.199	0.17	0.176
HB2-1-MD	7.14	279	0.015	37.7	0.108	3.57	0.023	7.5	0.309	0.006	0.212	0.16	0.250
HB2-2-MD	9.17	312	0.013	35.8	0.117	3.20	0.022	6.9	0.261	0.005	0.200	0.14	0.181
HB2-3-MD	10.1	414	0.013	35.3	0.117	3.14	0.023	6.7	0.254	0.005	0.199	0.14	0.207
HB3-MD	7.50	342	0.007	43.6	0.039	0.79	0.026	7.9	0.151	0.005	0.231	0.03	0.138
HB3-1-MD	7.53	116	0.004	48.6	0.049	0.79	0.026	8.4	0.148	0.005	0.254	0.02	0.198
HB3-1-DUP-MD	7.53	116	0.005	48.3	0.049	0.79	0.027	8.3	0.149	0.006	0.254	0.02	0.197
HB3-2-MD	9.56	3800	0.007	43.9	0.054	0.77	0.026	7.5	0.158	0.007	0.229	0.03	0.175
HB3-3-MD	10.3	300	0.005	42.5	0.067	0.77	0.027	7.1	0.161	0.005	0.220	0.03	0.141
HB4-MD	7.55	303	0.006	40.5	0.032	0.72	0.020	6.7	0.144	b.d.	0.205	0.03	0.110
HB4-1-MD	9.00	186	0.004	41.9	0.063	0.72	0.019	6.7	0.148	b.d.	0.209	0.03	0.171
HB4-2-MD	10.0	453	0.005	41.7	0.062	0.71	0.020	6.7	0.136	b.d.	0.210	0.03	0.115
HB4-3-MD	11.0	785	0.006	39.8	0.063	0.73	0.020	6.2	0.133	b.d.	0.196	0.03	0.134

Be, Cd, Co, Cr, Ni, Pb, Sb, Se, Tl, and V below detection limits.

b.d. - below detect

(cont.)Table A4. Lab and ICP-OES MD data from Silver Bow Creek near Pond 3 inlet - closed system pH adjustment experiments. All data in mg/L.

Sample ID	pH	SC (µS/cm)	As	Ca	Cu	Fe	Li	Mg	Mn	Mo	Sr	Ti	Zn
HB5-MD	8.14	244	0.011	36.3	0.041	1.05	0.013	5.5	0.120	0.003	0.157	0.05	0.076
HB5-1-MD	9.45	293	0.000	35.5	0.071	0.78	0.011	5.3	0.100	0.005	0.152	0.04	0.286
HB5-2-MD	10.6	697	0.005	45.3	0.158	1.14	0.015	6.6	0.137	0.007	0.193	0.05	0.283
HB5-3-MD	11.6	3417	0.007	32.6	0.060	0.70	0.014	3.9	0.097	0.003	0.135	0.03	0.110
HB5-3-DUP-MD	11.6	3417	0.007	33.3	0.077	1.24	0.015	4.9	0.155	0.003	0.138	0.06	0.116
HB6-MD	8.34	297	0.007	40.1	0.025	0.32	0.016	6.0	0.097	0.003	0.177	0.01	0.055
HB6-1-MD	9.29	341	0.006	41.3	0.047	0.30	0.016	6.4	0.072	0.003	0.180	0.01	0.138
HB6-2-MD	10.4	572	0.002	41.0	0.046	0.28	0.017	6.2	0.062	0.004	0.175	0.01	0.059
HB6-3-MD	11.5	2006	0.003	42.4	0.046	0.28	0.020	5.1	0.065	0.004	0.181	0.01	0.078
HB7-MD	7.92	319	0.007	42.1	0.028	0.46	0.019	6.5	0.098	0.003	0.198	0.02	0.061
HB7-1-MD	9.73	382	0.004	44.3	0.058	0.42	0.020	7.3	0.074	0.004	0.206	0.02	0.120
HB7-2-MD	10.8	772	0.005	38.9	0.036	0.33	0.019	5.9	0.048	0.004	0.180	0.01	0.084
HB7-3-MD	11.7	3496	0.006	34.7	0.054	0.36	0.022	4.0	0.053	0.004	0.158	0.02	0.077
HB8-MD	7.94	430	0.007	53.6	0.073	0.21	0.030	8.3	0.087	0.005	0.260	0.01	0.130
HB8-1-MD	9.21	449	0.007	54.5	0.037	0.29	0.030	8.7	0.077	0.005	0.266	0.01	0.091
HB8-1-DUP-MD	9.21	449	0.008	54.5	0.037	0.29	0.030	8.7	0.077	0.005	0.267	0.01	0.090
HB8-2-MD	10.7	854	0.007	41.0	0.041	0.28	0.032	7.4	0.053	0.006	0.212	0.01	0.069
HB8-3-MD	11.7	4556	0.008	22.0	0.053	0.28	0.036	6.7	0.054	0.005	0.130	0.01	0.091

Be, Cd, Co, Cr, Ni, Pb, Sb, Se, Tl, and V below detection limits.

b.d. - below detect

Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	**Time**	**Location**	**Sample ID**	**Approx. Stream flowrate (cfs)**	**Temp (°C)**	**pH (s.u.)**	**SC (µS/cm)**	**Eh (mV)**	**DO (%)**	**Sample Volumes Collected**	**Comments**
HB1 Sample											
4/4/14	11:07 AM	WSPOU - Inlet	HB1	53	4.7	7.62	486	413	99.4	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	Windy, slightly overcast. About 45 °F.
4/7/14	9:00 AM	Lab			20.7	7.67	501		102		HB1 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
	12:00 PM	Lab	HB1-1			*9.21	384			One 15-mL RA, one 15-mL FA	Used 0.5 M NaOH (added less than 1 mL) to raise pH. Collected RA and FA. HB1 sealed with parafilm and placed on stir plate.
4/9/14	9:40 AM	Lab			20.4	9.01	550		90.2		Measurements collected only.
		Lab	HB1-2			*9.97				One 15-mL RA, one 15-mL FA	Used 0.5 M NaOH to raise pH. Collected RA and FA. HB1 sealed w/ parafilm and placed on stir plate.
4/11/14	3:15 PM	Lab	HB1-3		21.35	9.94	506	328	74.5-99.3	One 15-mL RA, one 15-mL FA	Calibrated hydrolab. Calibration failed when using pH 10 buffer, so contacted Dr. Steve Parker and George Williams for help. Dr. Parker replaced electrolyte in reference probe (potassium chloride and DI water). ***Not sure if pH was increased-not in notes.*** Collected RA and FA.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp . (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
HB2 Sample											
4/9/14	4:10 PM	WSPOU - Inlet	HB2	140	9.23	7.17	271	346	94	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	Windy, warm day. Construction activities going-on during sampling. Water very turbid.
4/16/14	9:20 AM	Lab	HB2								Delay of experiment start due to finishing HB1 experiment. HB2 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
	11:56 AM	Lab	HB2-1		20.15	7.14	279	389	92.4	One 15-mL RA, one 15-mL FA	Acid added in lab, samples collected in field. No pH adjustment made.
		Lab	HB2-2			*9.17	312			One 15-mL RA, one 15-mL FA	Used 0.5 M NaOH (added 1 mL) to raise pH. Collected RA and FA. HB2 sealed w/ parafilm and placed on stir plate.
4/23/14	3:05 PM	Lab	HB2		21.45	8.56	324	318	76.1		pH may have decreased because of the increased amount of time between last time and this time or the Parafilm may not have been a tight seal allowing CO_2 to equilibrate with the water.
		Lab	HB2-3			*10.05	414	261		One 15-mL RA, one 15-mL FA	Used 0.5 M NaOH (added 2 mL) to raise pH. Collected RA and FA. HB2 sealed with parafilm and placed back on stir plate.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp. (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
5/5/14	3:15 PM	Lab	HB2		21.89	9.68	402	274	80.4		Took measurements prior to dumping 1-L HB2 sample. Slight pH drift noted.
HB3 Sample											
4/25/14	10:10 AM	WSPOU - Inlet	HB3	119	6.14	7.5	342	377	99.9	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	Beautiful day, overcast, slight breeze. 42 °F. No construction activities.
5/5/14	3:15 PM	Lab	HB3		14.02	7.53	116	388	81.1		HB3 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
	4:05 PM	Lab	HB3-1							One 15-mL RA, one 15-mL FA	Collected RA and FA. HB3 sealed with parafilm and placed on stir plate.
5/6/14	1:55 PM	Lab	HB3		21.41	8.02	4600	286	86.9		Measurements collected only.
		Lab	HB3-2			*9.56	3800			One 15-mL RA, one 15-mL FA	Added 1.5 mL of 0.5 M NaOH to increase pH. Collected RA and FA. HB3 sealed w/ parafilm and placed on stir plate.
5/13/14	10:00 AM	Lab	HB3		20.57	9.3	400	218	86.9		Measurements collected only.
		Lab	HB3-3			*10.25	300			One 15-mL RA, one 15-mL FA	Added 1.0 mL of 0.5 M NaOH to increase pH. Collected RA and FA. HB3 dumped.
HB4 Sample											
5/13/14	11:10 AM	WSPOU - Inlet	HB4	130	6.99	7.55	303	318	106.2	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	53°F. Sunny, nice day, few clouds in the sky, gentle breeze, no construction activities.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp . (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
	12:00 PM	Lab	HB4								HB4 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
5/15/14	10:25 AM	Lab	HB4		20.36	7.83	175	353	96.6		Measurements collected only.
		Lab	HB4-1			*9.0	186			One 15-mL RA, one 15-mL FA	Added 1.0 mL of 0.5 M NaOH to increase pH. Collected RA and FA. HB4 sealed with parafilm and placed on stir plate.
5/20/14	10:40 AM	Lab	HB4		22.49	8.66	356	221	87.1		Slight pH drift noted.
		Lab	HB4-2			*10.04	453			One 15-mL RA, one 15-mL FA	Added 2.25 mL of 0.5 M NaOH to increase pH. Collected RA and FA. HB4 sealed with parafilm and placed back on stir plate.
5/22/14	3:50 PM	Lab	HB4		22.29	10.06	451	302	88.8		Measurements collected only.
		Lab	HB4-3			*11.02	785			One 15-mL RA, one 15-mL FA	Added 3 mL of 0.5 M NaOH to increase pH. Collected RA and FA. HB4 sealed with parafilm and placed back on stir plate.
HB5 Sample											
5/27/14	12:49 PM	WSPOU - Inlet	HB5	175	10.96	8.14	244	310	81.8	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	64 °F, sunny but cloudy. No construction activities nearby. Water brownish color. Dr. Gammons did mention later that day that construction activities were happening upstream and they may play role with water quality.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp. (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
6/3/14	2:30 PM	Lab	HB5								HB5 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
6/9/14	8:25 AM	Lab	HB5		21.6	7.62	252	338	87.9		Measurements collected only.
		Lab	HB5-1			*9.45	293			One 15-mL RA, one 15-mL FA	Added 1 mL of 0.5 M NaOH. Collected RA and FA. HB5 sealed with parafilm and placed on stir plate.
6/11/14	10:25 AM	Lab	HB5		21.69	8.97	320	206	99.4		pH drift noted.
		Lab	HB5-2			*10.56	697			One 15-mL RA, one 15-mL FA	Added 3.5 mL of 0.5 M NaOH. Collected RA and FA. HB5 sealed with parafilm and placed on stir plate.
6/16/14	10:15 AM	Lab	HB		22.03	10.41	609	150	98.5		Measurements collected only.
		Lab	HB5-3			*11.56	3417			One 30-mL RA, one 30-mL FA	Added 17 mL of 0.5 M NaOH. Collected RA and FA. HB5 dumped.
HB6 Sample											
6/10/14	1:00 PM	WSPOU - Inlet	HB6	100	13.92	8.34	297	269	118.9	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	69°F, some construction activities upstream. S. Reedy assisted with field work.
6/16/14	10:30 AM	Lab	HB6								HB6 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
6/17/14	3:05 PM	Lab	HB6		21.56	8.13	308	268	101.5		Measurements collected only.
		Lab	HB6-1			*9.29	341			One 30-mL RA, one 30-mL FA	Added 1 mL of 0.5 M NaOH. Collected RA and FA. HB6 sealed w/parafilm and placed on stir plate.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp. (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
6/19/14	3:00 PM	Lab	HB6		21.08	9.13	346	250	98.9		Measurements collected only.
		Lab	HB6-2			*10.36	572			One 30-mL RA, one 30-mL FA	Added 1.75 mL of 0.5 M NaOH. Collected RA and FA. HB6 sealed w/parafilm and placed on stir plate.
6/21/14	4:00 PM	Lab	HB6		21.17	10.23	-	213	100.4		SC was not functioning, therefore, no reading was collected.
6/23/14	4:48 PM	Lab	HB6		21.79	10.41	538	327	-		DO meter was not function, therefore, no reading was collected.
		Lab	HB6-3			*11.45	2006			One 30-mL RA, one 30-mL FA	Added 4.5 mL of 0.5 M NaOH. Collected RA and FA. HB6 dumped.
HB7 Sample											
6/23/14	12:40 PM	WSPOU - Inlet	HB7	91	14.32	7.92	319	384	-	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	70°F, warm breezy day. Previous days had rainfall. Creek is slightly turbid. DO meter was not function, therefore, no reading was collected.
	4:48 PM	Lab	HB7		14.67	7.99	316	557	-		HB7 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp. DO meter was not function, therefore, no reading was collected.
6/24/14	12:25 PM	Lab	HB7		21.92	8.42	327	446	-		DO meter was not function, therefore, no reading was collected.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp. (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
		Lab	HB7-1			*9.73	382		-	One 30-mL RA, one 30-mL FA	Added 1 mL of 0.5 M NaOH. Collected RA and FA. HB7 sealed w/parafilm and placed on stir plate. DO meter was not function, therefore, no reading was collected.
7/1/14	12:20 PM	Lab	HB7		22.36	9.43	383	364	-		DO meter was not function, therefore, no reading was collected.
		Lab	HB7-2			*10.77	772		-	One 30-mL RA, one 30-mL FA	Added 3.25 mL of 0.5 M NaOH. Collected RA and FA. HB7 sealed w/parafilm and placed on stir plate. DO meter was not function, therefore, no reading was collected.
7/3/14	11:15 PM	Lab	HB7		22.13	10.53	583	306	-		DO meter was not function, therefore, no reading was collected.
			HB7-3			*11.73	3496			One 30-mL RA, one 30-mL FA	Added 15 mL of 0.5 M NaOH. Collected RA and FA. HB7 dumped.
HB8 Sample											
7/7/14	11:30 AM	WSPOU - Inlet	HB8	52	18.98	7.94	430	315	-	Two 1-L (both RU), two 60-mL (1-RA & 1-FA)	76°F, sunny, some clouds and light breeze. Creek has receeded quite a bit. No construction activities seen nearby. DO meter was not function, therefore, no reading was collected.

(cont.)Table A5 . Sampling and experimental log for SBC near Pond 3 inlet water - closed system.

Date	Time	Location	Sample ID	Approx. Stream flowrate (cfs)	Temp. (°C)	pH (s.u.)	SC (µS/cm)	Eh (mV)	DO (%)	Sample Volumes Collected	Comments
	12:20 PM	Lab	HB8								HB8 sealed w/Parafilm and placed on stir plate to raise water temp. to ambient temp.
	3:50 PM	Lab	HB8		25.18	8.19	439	302	-		DO meter was not functioning, therefore, no reading was collected.
		Lab	HB8-1			*9.21	449			One 30-mL RA, one 30-mL FA	Added 1 mL of 0.5 M NaOH. Collected RA and FA. HB8 sealed w/parafilm and placed on stir plate.
7/9/14	11:10 AM	Lab	HB8		22.72	9.02	471	238	-		DO meter was not function, therefore, no reading was collected.
		Lab	HB8-2			*10.69	854			One 30-mL RA, one 30-mL FA	Added 5.5 mL of 0.5 M NaOH. Collected RA and FA. HB8 sealed w/parafilm and placed on stir plate.
7/11/14	7:30 AM	Lab	HB8		20.39	10.47	732	196	-		DO meter was not function, therefore, no reading was collected.
		Lab	HB8-3			*11.73	4556			One 30-mL RA, one 30-mL FA	Added 25.5 mL of 0.5 M NaOH. Collected RA and FA. HB8 dumped.

-All samples collected were preserved w/1% HNO_3 and refrigerated.
-Approximate stream flow rates were gathered from USGS website using SBC @ Opportunity, MT Site#:12323600.
*pH value after adjustment made

Appendix B: “Open System” Data – Fish tank

Table B1. Lab and ICP-OES FA data from water and sediment from Pond 3 - open system pH adjustment experiments. All data in mg/L.

Sample ID	pH	SC (µS/cm)	As	Ca	Cr	Cu	Fe	Li	Mg	Mn	Mo	Sr	Zn
MESO-6-11-14	9.54	401	0.019	36.2	b.d.	0.005	0.04	0.020	8.0	0.006	0.004	0.19	0.004
MESO-6-16-14	10.7	684	0.013	27.6	b.d.	0.007	0.01	0.022	8.0	0.001	0.006	0.16	0.009
MESO-6-18-14	11.7	2441	0.035	6.41	b.d.	0.004	b.d.	0.020	0.6	0.000	0.007	0.05	0.000
MESO-6-24-14	7.55	1647	0.149	5.88	0.023	0.091	0.27	0.016	2.8	0.012	0.010	0.03	0.028
Mesocosm 7-1-14	6.55	1883	0.154	9.05	0.034	0.104	0.33	0.024	10.3	0.014	0.013	0.06	0.037
Mesocosm 7-3-14	2.76	2545	0.144	13.4	0.022	0.122	0.34	0.026	12.6	0.073	0.011	0.08	0.158
Mesocosm7-7-14 pH7	7.49	2388	0.081	42.3	0.013	0.082	0.12	0.030	19.2	0.054	0.012	0.19	0.030
Mesocosm 7-7-14 4:15	8.66	2406	0.056	43.3	0.014	0.082	0.12	0.030	19.1	0.037	0.008	0.19	0.014
Mesocosm 7-11-14	9.75	2606	0.077	48.5	0.019	0.084	0.13	0.033	20.6	0.002	0.013	0.21	0.022

Be, Cd, Co, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

b.d. - below detect

Table B2. Mesocosm sample data.

Sample ID / Date Collected	Time	Temp. (°C)	pH	ORP (mV)	DO (%)	SC (µS/cm)	Sample Volume Collected	Comments
Initial pH increase								
Fish tank 6-11-14	11:10 AM	20.2	8.48	468	89.9	369	N/A	Measurements collected only
MESO-30ML 6-11-14	11:10 AM	20.2	*9.54	375	87.8	401	30-mL FA	23 mL 0.5 M NaOH added
Fish tank 6-13-14	9:10 AM	20.9	8.42	569	88.1	408	N/A	Measurements collected only. Note drift in pH.
Fish tank 6-16-14	11:40 AM	20.4	8.40	564	88.4	432	N/A	Measurements collected only
MESO-30ML 6-16-14	11:40 AM		*10.7			684	30-mL FA	90 mL 0.5 M NaOH added. Cloudiness in water due to NaOH.
Fish tank 6-17-14	3:40 PM	19.9	9.58	391	89.0	530	N/A	Measurements collected only
Fish tank 6-18-14	10:40 AM	19.4	9.08	477	89.9	532	N/A	Measurements collected only
MESO-30ML 6-18-14	10:40 AM	19.5	*11.7	229	89.7	2441	30-mL FA	283 mL 0.5 M NaOH added. Cloudiness remains in water.
Fish tank 6-19-14	8:00 AM	19.5	11.1		90.0	1886	N/A	Measurements collected only
Fish tank 6-23-14	5:55 PM	21.5	9.78	392	-	1514	N/A	Measurements collected only. DO meter not functioning, measurements not taken.
pH decrease								
Fish tank 6-24-14	2:40 PM	22.1	9.65	294	-	1510	N/A	Measurements collected only. DO meter not functioning, measurements not taken.

(cont.) Table B2. Mesocosm sample data.

Sample ID / Date Collected	Time	Temp. (°C)	pH	ORP (mV)	DO (%)	SC (µS/cm)	Sample Volume Collected	Comments
MESO-30ML 6-24-14	2:40 PM		*7.55			1647	30-mL FA	3 mL conc. HNO_3 added
Fish tank 6-25-14	12:45 PM	21.6	8.80	372	93.7	1675	N/A	Measurements collected only. Note drift in pH.
Fish tank 7-1-14	11:35 AM	20.4	8.93	318	86.4	1782	N/A	Measurements collected only
Mesocosm 7-1-14			*6.55			1883	30-mL FA	3.5 mL conc. HNO_3 added.
Fish tank 7-3-14	12:15 PM	22.3	8.67	337	98.7	1933	N/A	Measurements collected only. Note drift in pH.
Mesocosm 7-3-14			*2.76			2545	30-mL FA	6 mL conc. HNO_3 added.
Second pH increase								
Mesocosm 7-7-14 pH7	7:35 AM	22.0	7.49	344	96.1	2388	30-mL FA	Nothing added. Note drift in pH.
Fish tank 7-7-14	4:30 PM	23.7	7.66	335	-	2399	N/A	Measurements collected only. DO meter not functioning, measurements not taken.
Mesocosm 7-7-14			*8.66			2406	30-mL FA	4.5 mL conc. HNO_3 added.
Fish tank 7-11-14	3:00 PM	23.6	7.84	380	-	2543	N/A	Measurements collected only. DO meter not functioning, measurements not taken. Note drift in pH.
Mesocosm 7-11-14			*9.75			2606	30-mL FA	23.5 mL conc. HNO_3 added.

-All samples perserved w/1% HNO_3 and refrigerated.
-MESO-30ML and Mesocosm samples analyzed w/ICP-OES.
*pH value after adjustment made

Appendix C: Piezometer Data

Table C1. Field and lab parameters for samples collected in Pond 3.

Pond Sample near listed PZ	Date Collected	Temp (°C)	Field pH (s.u.)	SC (µS/cm)	Eh (mV)
PZ1	8/5/2014	21.0	9.89	414	174
PZ2	8/5/2014	18.9	8.83	498	167
PZ3	8/5/2014	19.5	9.14	519	150
PZ4	8/5/2014	17.6	8.80	504	357
PZ3	8/14/2014	18.9	8.88	502	339
August AVG.		**19.2**	**9.11**	**487**	**237**
PZ7	11/1/2014	6.54	8.39	469	208
PZ8	11/8/2014	5.11	8.00	485	192
November AVG.		**5.83**	**8.20**	**477**	**200**
PZ5	12/6/2014	-	-	-	-

Table C2. Field parameters at PZ1-8. (PZ1-4 collected 8-5-14 and PZ5-8 collected 11-8-14.)

Sample ID	GPS Location		Depth in sediment (ft)	Temp (°C)	Field pH (s.u.)	SC (µS/cm)	Eh (mV)	Alkalinity (mg/L as $CaCO_3$)	PO_{4-} PO_{4-} (mg/L)	NH_4^+-N (mg/L)	SO_4^{2-} as SO_4^{2-} (mg/L)
PZ1	46°8'27"N	112°46'47"W	4.0	20.8	8.20	1321	118	76	0.19	14.1	396
PZ2	46°8'33"N	112°47'02"W	4.4	20.4	7.71	2700	177	101	0.16	17.8	748
PZ3	46°8'36"N	112°47'12"W	5.0	21.5	7.84	2997	18	36	1.36	46.0	946
PZ4	46°8'37"N	112°47'20"W	5.3	*20.7**	7.23	3034	75	392	0.28	9.30	902
PZ5	46°8'38"N	112°47'01"W	5.5	5.32	7.72	2468	358	80	0.15	18.8	451
PZ6	46°8'44"N	112°47'02"W	7.5	6.42	6.96	2871	203	172	0.12	15.3	484
PZ7	46°8'50"N	112°47'02"W	8.0	6.44	7.80	2049	108	89	0.08	14.5	374
PZ8	46°8'54"N	112°47'02"W	9.0	7.83	7.38	3050	154	392	0.3	31.5	539

**Temperature interpolated.*

Table C3. ICP-OES data (corrected for dilution) from PZ1-8. (PZ1-4 collected 8-5-14 and PZ5-8 collected 11-8-14.) All units in mg/L.

Sample ID	**As**	**Ca**	**Fe**	**Li**	**Mg**	**Mn**	**Mo**	**Sr**	**V**	**Zn**
PZ 1	0.028	212	0.13	0.086	31.8	1.07	0.026	0.84	0.01	0.003
PZ2	0.099	389	0.00	0.091	55.9	1.55	0.040	1.44	0.03	0.006
PZ3	0.028	197	0.94	0.066	142	2.57	0.016	0.76	0.10	0.008
PZ4	0.316	234	32.8	0.063	106	10.7	0.006	0.89	0.08	0.049
PZ4-DUP	0.350	324	26.7	0.070	167	14.1	b.d.	1.21	0.13	0.055
Numbers extrapolated from data (Ca vs. Sr)										
Arsenic(total) Data										
PZ5	0.169	436	0.46	0.076	23.2	1.92	0.047	2.30	b.d.	0.013
PZ6	0.639	420	60.8	0.116	96.5	3.52	0.018	2.58	0.02	0.065
PZ7	0.022	288	1.06	0.098	66.5	2.31	0.020	1.53	0.01	0.008
PZ7-DUP-F	0.018	292	0.84	0.097	67.4	2.34	0.018	1.54	0.01	0.004
PZ8	0.403	306	2.48	0.078	274	1.57	b.d.	2.03	0.17	0.017
Arsenic(III) Data										
PZ5-FA3	0.161	448	0.46	0.075	23.5	1.91	0.040	2.40	b.d.	0.015
PZ6-FA3	0.610	419	60.1	0.122	98.3	3.67	0.018	2.73	b.d.	0.075
PZ7-FA3	0.022	287	0.97	0.095	65.9	2.31	0.019	1.61	b.d.	0.009
PZ8-FA3	0.379	296	2.31	0.074	259	1.54	b.d.	2.07	0.13	0.015
PZ8-FA3-DUP-F	0.445	293	2.08	0.078	253	1.48	b.d.	2.05	0.12	0.015

Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Ti, and Tl below detection limits.

b.d. - below detect

Appendix D: Peeper Data

Table D1. Peeper A cell parameters collected in the field and at Montana Tech. Corrected for dilution. Removed 8-5-14 near PZ2.

Cell Location	below SWI* (cm)	pH (s.u.)	Eh SHE (mV)	SO_4^{2-} (SO_4^{2-} mg/L)	H_2S (S µg/L)	PO_{4-} (PO_{4-} mg/L)	NH_4^+ (N mg/L)	Alkalinity (mg/L as $CaCO_3$)
Pond at PZ2	direct sample	8.83		116		0.94	0.17	117
P1	5				B.D.	0.60		
P2	4	9.31	363	132				
P3	3						0.35	77.5
P4	2	9.17	364	147				
P5	1				B.D.	0.79		
P6	0	9.16	359	147				
P7	-1						0.60	220
P8	-2	7.65	358	129				
P9	-3				19.5	4.54		
P10	-4	7.22	259	31.8				
P11	-5						11.9	720
P12	-6	7.16	38	6.7				
P13	-7				47.7	4.71		
P14	-8	7.17	52	6.4				
P15	-9						15.3	900
P16	-10	7.19	53	6.4				
P17	-11				54.5	4.78		
P18	-12	7.21	164	25.6				
P19	-13						13.7	849
P20	-14	7.29	96	96.5				
P21	-15				32.7	4.52		
P22	-16	7.38	182	135				
P23	-17						14.6	823
P24	-18	7.43	151	165				
P25	-19				18.3	5.77		
P26	-20	7.45	187	182				
P27	-21						16.7	770
P28	-22	7.41	206	218				

SHE – standard hydrogen electrode

SWI* - positive values are above sediment water interface, negative values are below SWI.

Table D2. ICP-OES data (corrected for dilution) from Peeper A. Removed 8-5-14 near PZ2. All data in mg/L.

Sample ID	below SWI* (cm)	As	Ca	Cd	Cu	Fe	Li	Mg	Mn	Mo	Sr	Zn
Pond at PZ2	Direct sample	0.022	59.3	b.d.	0.015	0.07	0.040	9.3	0.129	0.006	0.241	0.009
P2	4	0.023	55.4	b.d.	0.025	0.00	0.035	10.4	0.005	0.006	0.251	b.d.
P4	2	0.024	55.5	b.d.	0.029	0.01	0.035	10.4	0.009	0.006	0.253	0.001
P6	0	0.033	62.1	b.d.	0.029	0.01	0.036	11.2	0.140	0.007	0.279	0.007
P8	-2	0.065	87.6	b.d.	0.020	0.09	0.044	14.6	1.62	0.007	0.374	0.013
P10	-4	0.185	186	b.d.	0.012	4.92	0.077	27.3	7.47	0.007	0.765	0.003
P12	-6	0.499	240	0.007	0.011	16.0	0.085	34.5	8.46	0.008	0.991	0.013
P14	-8	0.528	266	0.007	0.011	22.7	0.087	37.2	8.71	0.008	1.072	0.020
P16	-10	0.460	271	0.006	0.011	23.6	0.087	39.0	8.38	0.009	1.056	0.012
P18	-12	0.307	267	0.004	0.013	19.0	0.088	41.0	7.82	0.010	0.992	0.004
P18-DUP	-12	0.308	268	0.004	0.014	19.0	0.088	40.4	7.74	0.010	0.989	0.004
P20	-14	0.317	267	0.005	0.016	16.1	0.094	44.8	7.76	0.015	0.962	0.007
P22	-16	0.381	278	0.006	0.017	14.3	0.099	52.8	8.55	0.015	0.973	0.012
P24	-18	0.377	276	0.006	0.016	14.6	0.107	60.9	7.47	0.015	0.988	0.004
P26	-20	0.373	281	0.006	0.019	11.2	0.113	68.8	7.57	0.012	1.020	0.013
P28	-22	0.301	291	0.005	0.019	8.36	0.122	84.0	8.32	0.010	1.094	0.018

Be, Co, Cr, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

SWI* - positive values are above sediment water interface, negative values are below SWI.
b.d. - below detect

Table D3. Peeper B cell parameters collected in the field and at Montana Tech. Corrected for dilution. Removed 8-14-14 near PZ3.

Cell Location	below SWI* (cm)	pH (s.u.)	Eh, SHE (mV)	SO_4^{2-} (SO_4^{2-} mg/L)	PO_{4-} (PO_{4-} mg/L)	NH_4^+ (N mg/L)	Alkalinity (mg/L as $CaCO_3$)
Pond at PZ3	direct sample	8.88		55.0	0.57		
1	3	*			0.52	0.28	
2	2	*	254	119.13			
3	1	*					97.6
4	0	*	176	57.51			
5	-1	*			0.58	0.00	
6	-2	*	158	51.45			
7	-3	*					246.3
8	-4	*	96	38.58			
9	-5	*			4.48	3.53	
10	-6	*	77	76.93			
11	-7	*					258.1
12	-8	*	70	6.41			
13	-9	*			2.28	4.93	
14	-10	*	64	0.00			
15	-11	*					323.1
16	-12	*	64	0.00			
17	-13	*			3.62	7.99	
18	-14	*	72	0.00			
19	-15	*					458.1
20	-16	*	66	0.00			
21	-17	*			2.85	11.08	
22	-18	*	59	0.00			
23	-19	*					465.3
24	-20	*	68	0.00			
25	-21	*			3.58	11.30	
26	-22	*	72	0.00			
27	-23	*					515.6
28	-24	*	83	6.51			

* Mini-probe not functioning, so pH was not collected for Peeper B.

SWI* - positive values are above sediment water interface, negative values are below SWI

SHE – standard hydrogen electrode

Table D4. ICP-OES data (corrected for dilution) from Peeper B. Removed 8-14-14 near PZ3. All data in mg/L.

Sample ID	below SWI* (cm)	As	Ca	Cu	Fe	Li	Mg	Mn	Mo	Sr
Pond at PZ3	Direct sample	0.023	62.9	0.013	0.04	0.048	12.7	0.04	0.005	0.376
Pond at PZ3-DUP	Direct sample	0.023	62.9	0.013	0.04	0.046	13.0	0.04	0.005	0.360
PB-2	2	0.030	67.9	0.015	0.00	0.039	14.4	0.01	0.006	0.366
PB-4	0	0.055	70.8	0.018	0.02	0.039	14.8	0.11	0.006	0.385
PB-6	-2	0.042	65.4	0.013	0.00	0.034	13.3	0.04	0.006	0.337
PB-8	-4	0.108	73.4	0.009	0.08	0.036	13.5	2.13	b.d.	0.389
PB-10	-6	0.232	75.4	0.009	1.85	0.039	13.3	2.80	b.d.	0.411
PB-12	-8	0.286	78.0	0.009	2.24	0.041	13.9	2.76	b.d.	0.455
PB-14	-10	0.266	85.9	0.009	1.92	0.041	15.7	2.80	0.008	0.478
PB-16	-12	0.355	109	0.008	3.17	0.049	21.1	3.84	0.015	0.616
PB-18	-14	0.395	125	0.009	4.40	0.055	25.4	4.44	0.020	0.726
PB-18-DUP	-14	0.395	125	0.011	4.33	0.054	25.2	4.39	0.020	0.711
PB-20	-16	0.486	132	0.010	3.71	0.059	29.4	4.95	0.023	0.787
PB-22	-18	0.442	128	0.010	4.00	0.062	30.6	4.44	0.024	0.781
PB-24	-20	0.401	119	0.010	3.45	0.062	31.6	3.36	0.020	0.736
PB-26	-22	0.431	110	0.010	3.80	0.063	32.1	3.38	0.013	0.692
PB-28	-24	0.351	105	0.011	2.88	0.065	36.0	3.29	0.008	0.658

Be, Cd, Co, Cr, Ni, Pb, Sb, Se, Ti, Tl , V and Zn below detection limits.

SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

Table D5. Peeper C cell parameters collected in the field and at Montana Tech. Corrected for dilution. Removed 12-6-14 near PZ5.

Cell Location	below SWI* (cm)*	Field pH (s.u.)	SO_4^{2-} (SO_4^{2-} mg/L)	PO_{4-} (PO_{4-} mg/L)	NH_4^+ (N mg/L)	Alkalinity (mg/L as $CaCO_3$)
Pond at PZ8 (Collected 11-8-14)	direct sample	8.00				
Pond at PZ5	direct sample		44.0			
P3-1	2			0.33	1.84	
P3-2	1		204.0			
P3-3	0	6.34				317.2
P3-4	-1		87.4			
P3-5	-2			1.67	1.97	
P3-6	-3		45.1			
P3-7	-4	6.45				377.5
P3-8	-5		0.0			
P3-9	-6			1.27	1.92	
P3-10	-7		0.0			
P3-11	-8	6.48				465.3
P3-12	-9		0.0			
P3-13	-10			1.01	2.09	
P3-14	-11		21.4			
P3-15	-12	6.58				504.5
P3-16	-13		53.8			
P3-17	-14			2.28	2.27	
P3-18	-15					
P3-19	-16	6.76				576.4
P3-20	-17		78.6			
P3-21	-18			2.86	2.83	
P3-22	-19					
P3-23	-20	6.83				419.9
P3-24	-21		253.6			
P3-25	-22			3.51	2.43	
P3-26	-23					
P3-27	-24	6.9				406.4
P3-28	-25		217.4			

SWI* - positive values are above sediment water interface, negative values are below SWI

* Mini-probe not functioning, so Eh was not collected for Peeper C

Table D6. As(III) ICP-OES data (corrected for dilution) from Peeper C. Removed 12-6-14 near PZ5. All data in mg/L.

Sample ID	below SWI* (cm)	As	Ca	Cr	Cu	Fe	Li	Mg	Mn	Mo	Sr	Zn
Pond at PZ5 As(III)	Direct sample	0.002	68.9	b.d.	0.007	b.d.	0.049	16.8	0.93	b.d.	0.436	0.045
P3-2-As III	1	b.d.	133	0.013	b.d.	1.16	0.047	25.4	9.55	b.d	0.965	0.027
P3-4-As III	-1	0.023	113	0.014	b.d.	5.63	0.039	27.5	9.39	0.005	0.852	0.017
P3-6-As III	-3	0.004	127	0.020	b.d.	8.02	0.039	29.3	6.85	b.d	0.971	0.023
P3-8-As III	-5	0.004	124	0.016	b.d.	8.40	0.041	33.0	5.98	b.d	0.956	0.008
P3-10-As III	-7	0.007	123	0.015	b.d.	8.88	0.045	37.7	5.88	b.d	0.995	0.009
P3-10-DUP As III	-7	0.005	121	0.017	b.d.	8.88	0.045	37.2	5.88	b.d	0.994	0.009
P3-12-As III	-9	b.d.	121	0.017	0.006	8.60	0.048	45.3	5.58	b.d	0.903	0.006
P3-14-As III	-11	0.007	119	0.016	0.008	7.73	0.048	53.4	4.95	b.d	0.916	0.010
P3-16-As III	-13	0.003	111	0.016	b.d.	6.22	0.048	65.4	7.48	b.d	0.909	0.004
P3-28-18-As III	-15	b.d.	106	0.014	b.d.	4.39	0.049	74.3	6.71	b.d	0.806	0.009
P3-18-As III	-15	0.009	159	0.018	0.197	5.89	0.068	79.8	7.04	0.008	1.455	0.292
P3-20-As III	-17	0.007	99.8	0.015	b.d.	4.15	0.047	87.1	6.99	0.005	0.789	0.012
P3-22-As III	-19	b.d.	94.7	0.012	b.d.	3.60	0.048	100	5.61	b.d	0.764	0.011
P3-24-As III	-21	0.005	82.0	0.012	b.d.	1.96	0.050	110	3.90	b.d	0.665	0.008
P3-26-As III	-23	b.d.	69.9	0.010	b.d.	1.38	0.056	125	3.17	b.d	0.538	0.006
P3-28-As III	-25	0.012	86.0	0.011	b.d.	1.50	0.060	135	3.10	0.006	0.636	0.010

Be, Cd, Co, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

Table D7. Arsenic(total) ICP-OES data (corrected for dilution) from Peeper C. Removed 12-6-14 near PZ5. All data in mg/L.

Sample ID	below SWI* (cm)	As	Ca	Cr	Fe	Li	Mg	Mn	Mo	Sr	Zn
Pond at PZ5 As(Total)	Direct sample	0.008	63.5	b.d.	0.02	0.040	12.2	0.70	b.d.	0.380	0.048
P3-2 Total	1	0.012	94.7	0.011	1.50	0.053	25.5	9.89	0.009	0.602	0.017
P3-4 Total	-1	0.036	81.9	0.015	8.39	0.041	27.0	9.61	0.009	0.571	0.003
P3-6 Total	-3	0.021	80.8	0.015	9.88	0.042	29.2	7.10	0.009	0.574	0.004
P3-8 Total	-5	0.017	82.6	0.017	12.3	0.048	33.1	6.23	0.008	0.604	b.d.
P3-10 Total	-7	0.011	84.8	0.017	13.4	0.050	37.9	6.07	0.007	0.628	0.002
P3-12 Total	-9	0.011	85.6	0.017	12.5	0.051	45.7	5.75	0.006	0.638	b.d.
P3-14 Total	-11	0.009	84.4	0.013	10.2	0.052	55.3	5.05	0.006	0.623	b.d.
P3-16 Total	-13	0.010	78.4	0.014	8.36	0.052	65.8	7.61	0.007	0.607	b.d.
P3-16 DUP Total	-13	0.007	79.2	0.014	8.37	0.052	66.4	7.66	0.007	0.608	b.d.
P3-18 Total	-15	0.008	71.7	0.009	5.81	0.053	76.7	6.87	0.006	0.562	b.d.
P3-20 Total	-17	0.007	64.9	0.011	5.45	0.052	90.8	7.15	0.006	0.528	b.d.
P3-22 Total	-19	0.003	57.8	0.009	4.53	0.052	102	5.63	0.008	0.475	b.d.
P3-24 Total	-21	0.007	46.4	0.011	2.53	0.054	113	3.92	0.007	0.381	b.d.
P3-26 Total	-23	0.007	41.8	0.008	1.90	0.060	129	3.21	0.006	0.331	b.d.
P3-28 Total	-25	0.005	45.3	0.009	1.77	0.063	137	3.14	0.007	0.328	b.d.

Be, Cd, Co, Cu, Ni, Pb, Sb, Se, Ti, Tl, and V below detection limits.

SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

Table D8. ICP-MS data (corrected for dilution) from Peeper C. Removed 12-6-14 near PZ5. Confirmation analysis performed by the Montana Bureau of Mines and Geology. All data in µg/L unless noted underneath element.

Sample ID	**below SWI* (cm)**	**Al**	**As**	**B**	**Ba**	***Ca***	**Co**	**Cu**	***Fe***	**Ga**	***K***	**Li**
		µg/L	µg/L	µg/L	µg/L	*mg/L*	µg/L	µg/L	*mg/L*	µg/L	*mg/L*	µg/L
PQL		0.5	0.2	0.2			0.5	1	0.005			
Arsenic(III) Samples												
Pond (III) at PZ5	Direct sample	182	2.10	36.5	37.3	33.6	0.732	8.75	0.006	1.58	0.358	22.1
P3-2 (III)	1	2106	6.77	50.4	96.0	66.8	1.57	13.0	0.846	4.23	0.391	22.8
P3-4 (III)	-1	1826	25.8	38.8	111	58.8	1.08	7.52	4.45	5.03	0.458	19.3
P3-6 (III)	-3	2711	11.4	41.5	112	62.9	1.32	17.1	6.13	4.98	0.452	19.4
P3-8 (III)	-5	4107	8.61	42.0	117	65.1	b.d.	8.88	6.64	5.32	0.399	20.8
P3-10 (III)	-7	1218	2.99	26.2	36.5	18.7	b.d.	b.d.	1.96	1.72	0.128	b.d.
P3-12 (III)	-9	2995	9.14	59.2	130	65.5	b.d.	19.4	6.97	5.80	0.579	25.1
P3-14 (III)	-11	1603	6.04	64.4	106	62.0	0.853	19.5	5.99	4.63	0.564	23.3
P3-16 (III)	-13	2567	6.72	75.1	122	54.6	b.d.	11.6	4.71	5.56	0.604	24.3
P3-20 (III)	-17	1698	8.27	98.7	133	50.3	b.d.	13.1	3.23	5.76	0.782	24.0
P3-24 (III)	-21	2394	7.08	135	99.3	43.6	b.d.	8.34	1.57	4.49	0.897	27.2
P3-28 (III)	-25	2364	9.30	162	98.2	43.5	b.d.	12.5	1.16	4.40	1.09	32.4

Denotes units in mg/L.

SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

(cont.) Table D8. ICP-MS data (corrected for dilution) from Peeper C. Removed 12-6-14 near PZ5. Confirmation analysis performed by the Montana Bureau of Mines and Geology. All data in µg/L unless noted underneath element.

Sample ID	**below SWI* (cm)**	***Mn*** *mg/L*	**Mo** µg/L	**Ni** µg/L	**P** µg/L	**Rb** µg/L	**Sr** µg/L	**Ti** µg/L	**Zn** µg/L	**W** µg/L	**U** µg/L
PQL		0.002	0.5	0.5	5	0.5			1	0.2	0.2
Arsenic(III) Samples											
Pond (III) at PZ5	Direct sample	0.763	2.62	1.08	5.34	6.33	379	44.5	54.7	0.666	0.654
P3-2 (III)	1	7.66	b.d.	2.86	9.47	13.8	861	88.1	34.1	b.d.	b.d.
P3-4 (III)	-1	7.84	2.90	b.d.	126	12.2	765	72.6	18.8	1.30	b.d.
P3-6 (III)	-3	5.56	b.d.	b.d.	66.7	13.5	847	82.4	30.4	b.d.	b.d.
P3-8 (III)	-5	5.03	b.d.	b.d.	46.6	13.5	876	84.2	14.9	b.d.	b.d.
P3-10 (III)	-7	1.41	b.d.	b.d.	b.d.	3.31	223	19.1	4.90	b.d.	b.d.
P3-12 (III)	-9	4.81	b.d.	b.d.	74.2	14.3	831	78.3	13.7	b.d.	b.d.
P3-14 (III)	-11	4.01	b.d.	b.d.	61.1	14.0	815	73.1	17.7	b.d.	b.d.
P3-16 (III)	-13	5.90	b.d.	b.d.	76.0	13.8	776	75.4	12.2	b.d.	b.d.
P3-20 (III)	-17	5.71	b.d.	b.d.	77.3	18.2	687	72.6	19.0	1.23	b.d.
P3-24 (III)	-21	3.31	2.44	b.d.	20.2	19.0	589	68.9	16.7	1.65	b.d.
P3-28 (III)	-25	2.59	3.56	b.d.	55.6	22.7	567	72.2	18.4	3.03	b.d.

Denotes units in mg/L.

SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

Table D9. ICP-MS data (corrected for dilution) from Peeper C. Removed 12-6-14 near PZ5. Confirmation analysis performed by the Montana Bureau of Mines and Geology. All data in µg/L unless noted underneath element.

Sample ID	**below SWI* (cm)**	**Al**	**As**	**B**	**Ba**	***Ca***	**Co**	**Cu**	***Fe***	**Ga**	***K***	**Li**
		µg/L	µg/L	µg/L	µg/L	*mg/L*	µg/L	µg/L	*mg/L*	µg/L	*mg/L*	µg/L
PQL		0.5	0.2	0.2			0.5	1	0.005			
Arsenic (total) Samples												
Pond at PZ5	Direct sample	5.16	8.14	42.7	41.7	35.2	0.781	6.69	0.015	1.82	0.452	27.4
P3-2	1	8.45	22.8	75.3	127	61.2	1.37	b.d.	1.46	5.50	0.880	42.2
P3-4	-1	2.71	39.4	49.8	137	49.3	0.871	b.d.	7.63	6.16	0.801	30.3
P3-6	-3	6.09	19.9	50.5	128	45.8	b.d.	b.d.	8.59	5.92	0.752	30.9
P3-8	-5	b.d.	15.8	55.1	150	49.3	b.d.	b.d.	11.2	6.71	0.792	34.7
P3-10	-7	4.72	17.0	59.0	161	50.7	b.d.	b.d.	12.3	7.30	0.802	35.5
P3-12	-9	b.d.	12.2	70.5	152	50.5	b.d.	b.d.	11.5	6.98	0.855	35.8
P3-14	-11	2.06	8.73	77.8	126	47.7	b.d.	b.d.	9.01	5.78	0.925	35.0
P3-16	-13	b.d.	8.15	93.4	155	46.2	b.d.	b.d.	7.62	7.14	1.07	35.7
P3-20	-17	b.d.	9.37	122	163	37.8	b.d.	b.d.	4.90	7.42	1.29	36.5
P3-24	-21	4.56	8.00	156	115	28.2	b.d.	b.d.	2.35	5.27	1.44	39.5
P3-28	-25	b.d.	9.85	193	112	27.4	b.d.	b.d.	1.59	4.90	1.55	44.3

Denotes units in mg/L.

SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

(cont.)Table D9. ICP-MS data (corrected for dilution) from Peeper C. Removed 12-6-14 near PZ5. Confirmation analysis performed by the Montana Bureau of Mines and Geology. All data in µg/L unless noted underneath element.

Sample ID	**below SWI* (cm)**	***Mn*** *mg/L*	**Mo** µg/L	**Ni** µg/L	**P** µg/L	**Rb** µg/L	**Sr** µg/L	**Ti** µg/L	**Zn** µg/L	**W** µg/L	**U** µg/L
PQL		0.002	0.5	0.5	5	0.5			1	0.2	0.2
Arsenic (total) Samples											
Pond at PZ5	Direct sample	0.857	4.81	1.17	78.4	3.94	337	44.3	65.2	1.59	7.09
P3-2	1	9.95	9.50	3.97	173	6.12	548	77.6	27.6	7.85	13.9
P3-4	-1	9.10	8.84	b.d.	660	5.59	504	61.9	11.3	5.82	6.42
P3-6	-3	6.37	8.09	b.d.	236	5.38	482	51.1	15.6	3.08	3.44
P3-8	-5	5.83	6.94	b.d.	327	5.19	510	58.2	b.d.	2.60	2.03
P3-10	-7	5.72	5.95	b.d.	316	5.49	542	57.9	11.1	2.59	1.34
P3-12	-9	5.46	5.41	b.d.	353	6.06	562	63.3	b.d.	2.62	1.37
P3-14	-11	4.67	5.87	b.d.	265	6.61	527	59.8	7.65	2.76	1.97
P3-16	-13	7.17	5.80	b.d.	471	8.21	527	56.6	b.d.	5.56	2.97
P3-20	-17	6.73	6.24	b.d.	849	10.2	461	50.5	9.70	10.6	5.30
P3-24	-21	3.83	5.86	b.d.	861	11.8	333	32.5	10.3	9.30	6.55
P3-28	-25	3.00	6.70	b.d.	1262	13.8	286	37.1	b.d.	8.90	4.02

Denotes units in mg/L.

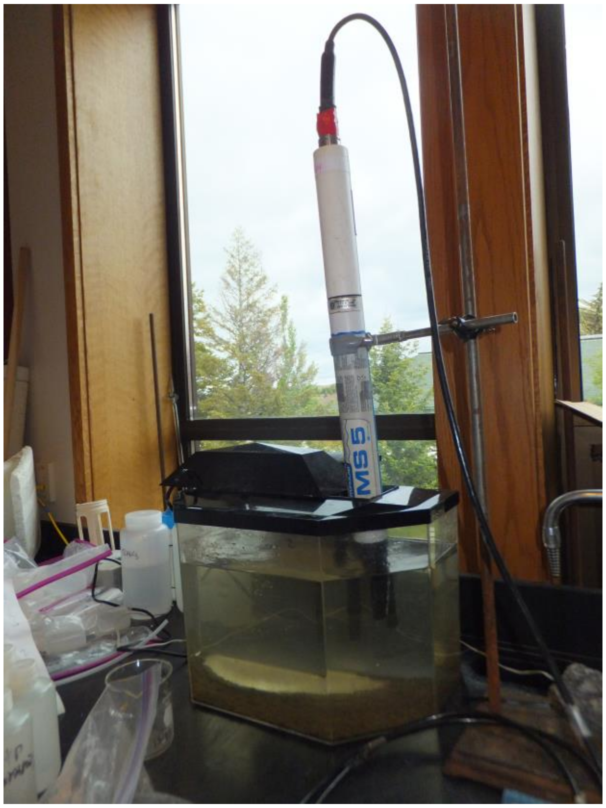
SWI* - positive values are above sediment water interface, negative values are below SWI

b.d. - below detect

Appendix E: Photographs

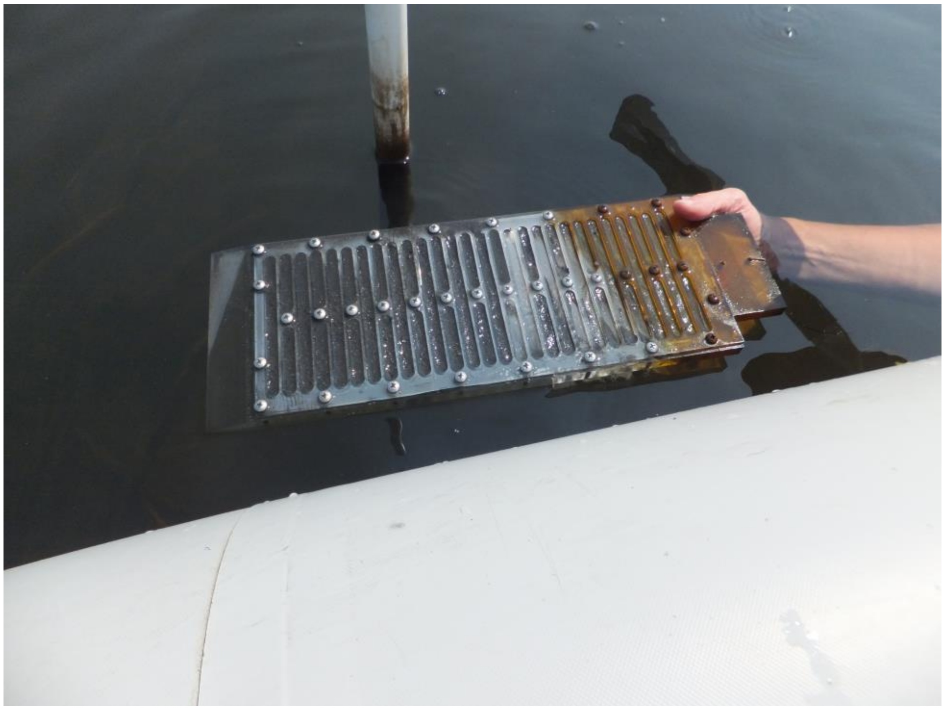
E1. Sampling area at Silver Bow Creek near the inlet to WSPOU. 5/18/2014

E2. Hydrolab MS-5 collecting field measurements in SBC near the inlet to WSPOU. 5/18/2014



E3. Fish tank set-up with Hydrolab MS-5 collecting measurements. 6/24/2014

E4. ICP-OES set-up in the Environmental Engineering Department's mercury laboratory. 7/31/2014



E5. Peeper A retrieval near PZ2 in WSPOU Pond 3. 8/5/2014

E6. Peeper A in glove bag with argon gas continuously flowing. 8/5/2014

E7. Mini-probes for pH and ORP inserted into Peeper A through glove bag. 8/5/14

E8. Heather Boese holding Peeper B in glove bag with argon gas continuously flowing. Piezometers can be seen in the background in Pond 3. 8/14/2014

E9. Collecting samples with a syringe needle from Peeper B through the glove bag. 8/14/2014

E10. Filtering water samplings into prepared sample bottles from Peeper B. 8/14/2014

E11. Mini-probe inserted into Peeper B through glove bag. 8/14/2014

E12. Arsenic speciation performed in the field with a cartridge, with aluminosilicate resin, placed on the end of a syringe. 11/8/2014

E13. PZ5 in Pond 3 – Peeper C installed near this PZ. 11/8/2014

E14. Retrieval of Peeper C. 12/6/2014

E15. Peeper C in glove bag with argon continuously flowing. 12/6/2014

E16. H. Boese heading to field workbench with Peeper C in glove bag. 12/6/2014

SIGNATURE PAGE

This is to certify that the thesis prepared by Heather E. Boese entitled "Arsenic Geochemistry in Warm Springs Ponds: New Field and Experimental Results" has been examined and approved for acceptance by the Department of Environmental Engineering, Montana Tech of The University of Montana, on this 5th day of May, 2015.

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