Using pore water diffusion samplers to investigate metal loading from stream sediment in Blacktail Creek and Lower Area One

A Proposal to the BNRC and Montana NRDP

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November 10, 2016

A. Project Summary

Title: Using pore water diffusion samplers to investigate metal loading from stream sediment in Blacktail Creek and Lower Area One
Sponsor: Montana NRDP
Location: lower Blacktail Creek and upper Silver Bow Creek (through slagwall canyon)
Total Dollar Amount = $59,434 (NRDP = $37,425; Montana Tech Match: $22,009)
Project Leader: Dr. Chris Gammons, Montana Tech
Begin Date: June 01, 2017 (or when funding is in place)

This is a proposal for funding for the PI and a graduate student at Montana Tech to investigate metal loading in the lower reaches of Blacktail Creek and uppermost Silver Bow Creek using pore water diffusion samplers, aka "peepers". The new data will help determine if stream sediment and/or shallow groundwater immediately underlying the stream could be a source of trace metals and nutrients to surface waters as they pass through Butte Area One.

A.1. Project Location

Figure 1 shows the approximate outline of Butte Area One and the proposed locations where our pore water diffusion samplers will be deployed. Although some sampling sites are located in Blacktail Creek upstream of Area One, the majority of the sites are within the Area One borders. The reason for including upstream sites is to gather information in the upper reaches of Blacktail Creek before it becomes contaminated from mining and the city of Butte. The exact locations of the peeper stations will depend on many factors, including the availability of a thick layer of fine sediment in the streambed. We may decide to put some peepers in additional bodies of water, such as the wetlands that border Blacktail Creek to the north and south.
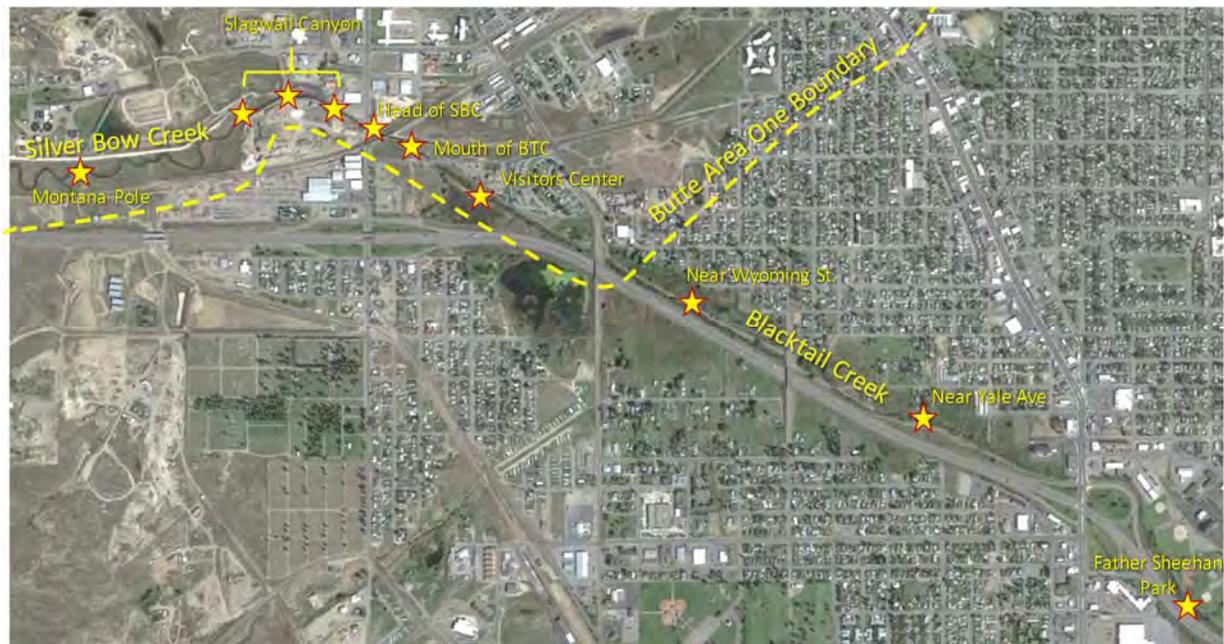

Figure 1: Google image of the confluence of lower Blacktail Creek and upper Silver Bow Creek, showing tentative locations for our peeper installations.

A.2. Background

After collecting thousands of surface water and groundwater samples from multiple agencies over four decades, there still remains controversy over where and how metal loading occurs in lower Blacktail Creek and uppermost Silver Bow Creek. Of special interest is the stream reach that extends from roughly the Kaw Avenue overpass to the mouth of the slagwall canyon downstream of Montana Street. This reach is located near the downstream end of the MSD subdrain and upstream of the LAO groundwater interception channel. There is an ongoing debate as to whether this section of the stream may be receiving contaminated groundwater that is bypassing the existing collection system. There is evidence from past synoptic sampling investigations that a measureable increase in metal loading typically occurs in this stream reach (J. Griffin, pers. commun.).

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There is also a possibility that the stream *sediment* is a source and/or sink for metals in the creeks as they pass through Area One. For example, upwelling, anoxic groundwater may precipitate Fe-oxide solids as it mixes with alkaline and oxygen-rich stream water. If so, then other dissolved trace metals (e.g., Cu, Cd, Zn) would likely adsorb onto the oxide surfaces. These solids would settle into the fine sediment that covers the streambed of the creek. During periods of high flow, this sediment could be re-suspended leading to water quality exceedences for certain COCs (e.g., Cu, Cd, Zn). During periods of low flow, bacteria in the fine sediment may re-dissolve the Fe-oxides, releasing adsorbed metals into the sediment pore water. These metals might then diffuse upwards into the water column of the creek.

The proposed study aims to examine geochemical gradients in the stream sediment of Butte Area One. We will use pore-water diffusion samplers (aka "peepers") to collect vertical profiles of closely-spaced water samples across the sediment-water interface.   Figure 2 shows a schematic of what a peeper looks like, following the original design of Hesslein (1976). It is basically two slabs of plastic that are screwed together with an intervening nylon membrane. The back piece of plastic has 28 horizontal rows of sample chambers, spaced vertically 1 cm apart, and each with a volume of 5 mL or 12 mL. Before deployment, the peeper cells are filled with de-oxygenated and deionized water. The peepers are inserted vertically, by hand, into the sediment, with 2 or 3 rows of samples projecting above the sediment-water interface. Dissolved solutes in the pore water of the sediment diffuse across the nylon membrane into the sample cells until the composition of the water inside the cells is the same as the composition of the pore water.   After equilibrium is attained (2-3 weeks depending on temperature), the peeper is removed from the sediment, placed in a glovebag, and the cells are sampled. The result is a closely-spaced vertical profile for a wide range in chemical parameters.
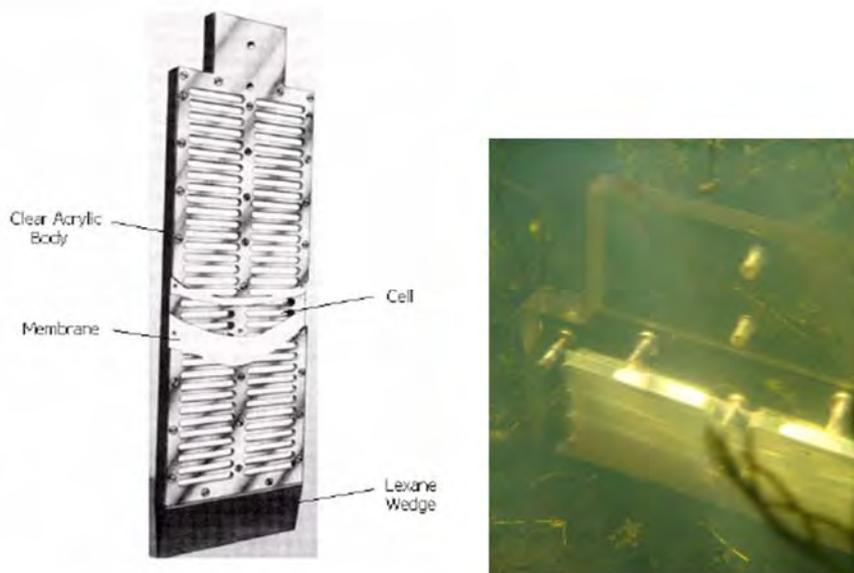

Figure 2. Left: schematic of a peeper sampler. The peeper is about 1.5 feet long from top to bottom.   Right: photo of a peeper during deployment into the sediment of Warm Springs Ponds.

B. Project Goals and Objectives

The main goal of this project is to characterize vertical gradients in chemistry of shallow groundwater across the sediment-water interface in lower Blacktail Creek and uppermost Silver Bow Creek (Figure 1). Conventional groundwater sampling collects water from a location that is well below this interface, typically 3 to 20 feet below the streambed. However, our own recent experience with pore water diffusion samplers (peepers) shows that very sharp chemical gradients can occur at a cm-scale in fine sediment at the bottom of a lake or river. These gradients can drive chemical diffusion of dissolved solutes from the sediment into the stream, or vice versa. Lower Blacktail Creek is largely "silted up" from sediment washed into the stream. Any groundwater entering the stream must first pass through this fine sediment.   It is important to learn more about the geochemical reactions that are taking place in this boundary zone, and peepers are the best field sampling tool to use.   It is also important to characterize the chemistry and mineralogy of the sediment at the same locations where the peeper samplers are deployed.

The two main project objectives are as follows:

1) Learn more about the chemistry of sediment pore-water in streams in Butte Area One:
We will deploy 12-15 peepers at locations summarized in Figure 1. Some locations will be revisited to test for reproducibility of the results. The samples will be analyzed for a full suite of geochemical parameters, including pH, Eh, major and trace metals, anions, alkalinity, hydrogen sulfide, and nutrients (nitrate, nitrite, ammonium, phosphate).

An example of the type of data that can be collected using peepers is shown in Figure 3. These data were collected in a recent study by C. Gammons and his graduate students of sediment pore water chemistry in Warm Springs Ponds (Lee, 2012).   The vertical scale is cell depth, measured in cm. In most cases the top 2-3 rows of samples are positioned above the sediment-water interface (SWI), and therefore have the same chemistry as the surface water. One can see sharp gradients across the SWI which can be used to estimate diffusive fluxes of solutes, such as arsenic, from the sediment into the ponds.

2) Characterize the chemistry and mineralogy of the sediment at each peeper station
We will collect stream sediment samples at each of the peeper stations for chemical and mineralogical analysis. We will use sequential extraction methods to speciate metals in the sediment with respect to the mineralogical form that the metal is most closely associated with (e.g., "readily exchangeable", "carbonate minerals", "amorphous Fe-oxides", "crystalline Fe oxides", "organics and residuals"). In some cases, we will examine the sediment by SEM, Raman, and XRD to determine the mineral form of selected metals of interest.

By combining the results of objectives 1 and 2, we will construct a conceptual hydro-geochemical model for how shallow groundwater and surface water interact in the stream reach of interest. Depending on the results, it may be possible to quantify the flux of metals from the sediment into the water column using simple "Fick's Law" diffusion equations.
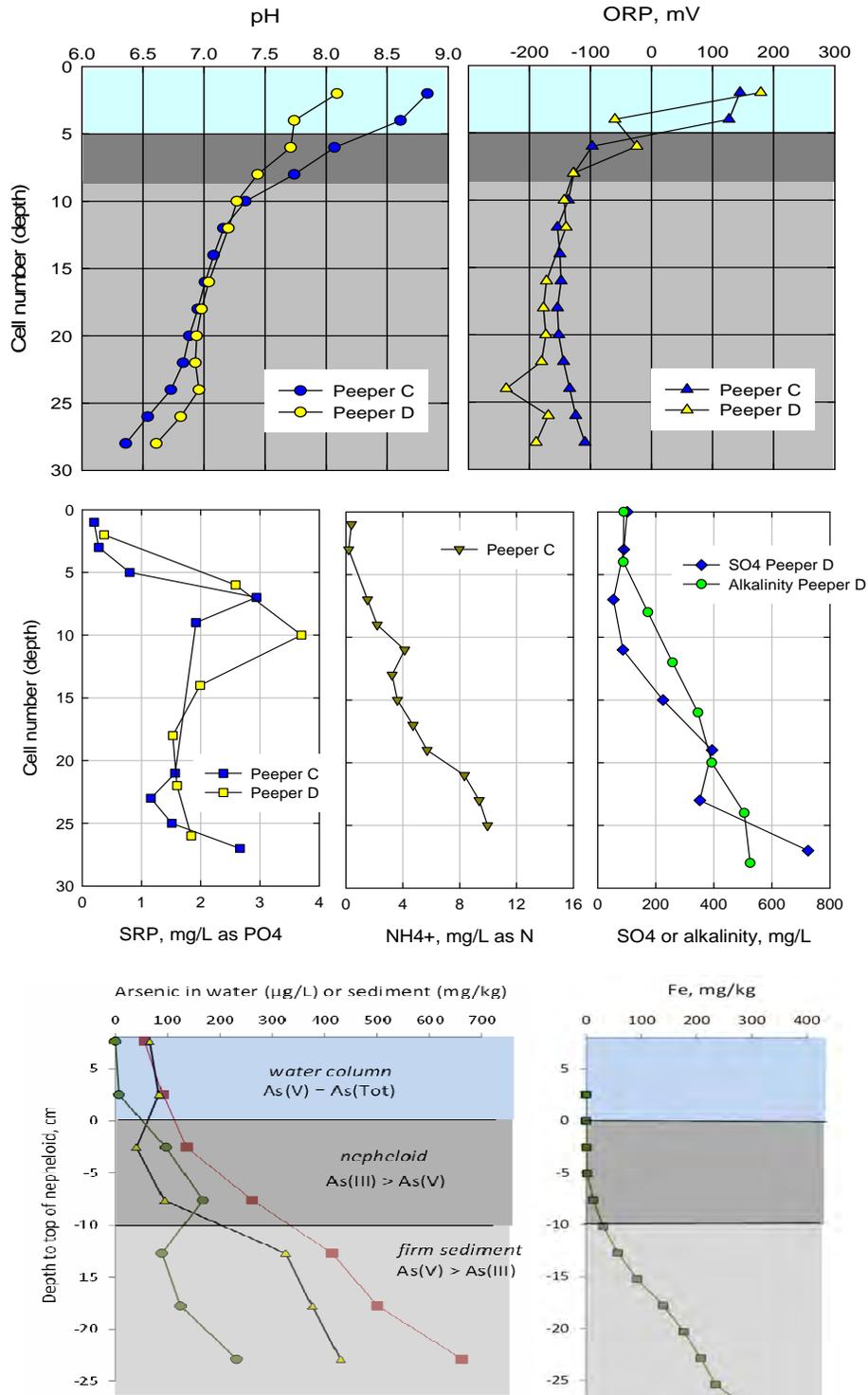
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Figure 3. Examples of peeper data collected in sediment of the Warm Springs Ponds (from Josh Lee's M.S. thesis, 2012). The top two panels show pH and ORP (oxidation-reduction potential) gradients with depth. The middle panels show soluble reactive phosphorus (SRP), ammonium, sulfate, and alkalinity. The bottom panels show arsenic and dissolved iron. Note that we were able to speciate arsenic between the As(V) and As(III) redox states.

C. Project Benefits

There are a number of benefits, both short-term and longer-term, that will stem from this project. These include:

- We will collect new scientific data that will help us to better understand *where* and *how* the streams that pass through Butte Area One become contaminated with COCs, including trace metals and nutrients.
- We will collect new data on a reach of the stream where there is an ongoing debate as to whether the existing groundwater collection system is 100% effective.   New data on this stream reach may inform future management and reclamation decisions about Butte Area One.
- Funding from this project will be used to support a graduate student research project at Montana Tech.
- We will coordinate our field activities with a parallel study of microbial abundance and speciation in Blacktail and Silver Bow Creeks that is being undertaken by Dr. Alysia Cox and her group of students at Montana Tech. The data we collect on sediment pore-water geochemistry will help inform her genomic work, and likewise the data that Dr. Cox collects on the types of microbes present in the sediment of the stream will help us interpret the chemical gradients that are obtained from the peepers.
- There is a high probability that the results of this study will result in a paper in a scientific journal. This will cast a wider net in terms of dissemination of the results, and will also add recognition to the caliber of research being performed at Montana Tech.

D. Project Implementation

D.1. Peeper deployment and sampling

The PI has extensive experience with peepers, having deployed more than two dozen peepers into various types of sediment in wetlands, shallow lakes, and slow-moving streams.   Some of our peeper data were recently published in two papers dealing with sediment-water interaction in Georgetown Lake, Montana (Shaw et al., 2013; Parker et al., 2016). Before a peeper can be deployed, it must be assembled with deionized water that is de-oxygenated. This is accomplished by bubbling an inert gas, such as N_2 or Ar, through a cooler containing the lab water for 12 hours (overnight). A portable argon tank connected to a simple glovebag can insure that no oxygen enters the peeper during transport to the field. Once the desired location is reached, the peeper is inserted vertically into the sediment, leaving 2 or 3 rows of sample cells above the sediment-water interface. In summer, the peeper is left in place for at least 2 weeks to allow equilibration. In cold weather, this time is increased to 3 weeks. When it is time to sample a peeper, one simply pulls it out of the sediment, gently wipes off most of the muck in the stream, and then inserts the peeper horizontally into a glovebag with a continuous flow of Ar gas. The peeper cells are sampled by inserting a syringe needle through the glovebag and membrane into the sample cell. Water in the cell is extracted into the syringe, and then pushed through a disposable filter into a pre-massed plastic bottle. Any necessary dilutions and

additions of preserving reagents are typically done in the field, and all sample masses are recorded with a portable balance to accurately determine dilution factors.

Figure 3 shows an example sampling plan for a peeper. The sequence in which the peeper is sampled is shown by the column headings 1 to 8 across the top row from left to right. Thus, the first thing we would do is extract all of the even-numbered sample cells for measurement of pH and ORP (using microelectrodes) and collection of filtered samples for ICP-MS analysis. The next task would be to collect samples for H_2S analysis, then soluble reactive phosphorus (SRP), ammonium ion, and so on. In the end, 42 discrete samples are collected from a single peeper.

ORDER	1	2	3	4	5	6	7	8
Cell	pH/ORP	ICP-MS	H2S	SRP	NH4	IC-anions	ICP-AES	alkalinity
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 3. Example sampling plan for a peeper. The image at left shows the layout of a peeper. The even-rowed cells are 12 mL volume, whereas odd rows have a left and right cell, each 5 mL volume.   The image at right shows which cells are used to sample for which parameters, and also shows the order in which each group of cells is sampled (e.g., pH/Eh and ICP-MS first, alkalinity last).

Depending on the start date of the project, we anticipate installing roughly 10 peepers in the first field season. After scrutinizing the results, we will resample some locations the following field season, or move to new locations. The budget allows for a full set of sampling and analysis of 20 peepers. However, it is possible to stretch the funds to do more deployments but analyze each peeper for fewer parameters, or with less close vertical spacing. In this way, it should be possible to place peepers in additional locations of interest, such as the wetlands that fringe Blacktail Creek to the north and south.

D.2. Solids Characterization

Representative samples of stream and wetland sediment at each peeper location will be collected for laboratory characterization. The samples will be dry-sieved to determine the grain size distribution. The fine fraction, where most of the mass of metal is expected to reside, will be analyzed for metal content by sequential extraction. The purpose of the sequential extraction method (as opposed to a single-step, total digestion) is to quantify the relative amount of each element of interest that is present in different mineralogical forms. Amacher (1998) developed a leaching sequence that can be used to speciate a given metal between six different mineral forms: 1) exchangeable (weakly bound) metal; 2) carbonate minerals; 3) manganese oxides; 4) amorphous Fe-oxides; 5) crystalline Fe-oxides; and 6) organic matter, sulfides and other residual phases. Other methods of sediment characterization could include scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy, as well as traditional reflected and transmitted light microscopy.

D.3. Analytical Methods

Most of the analytical work in this project will be done at the Montana Bureau of Mines and Geology. This lab follows standard EPA procedures for quantification of anions by ion chromatography (IC), major solutes by inductively-coupled plasma atomic emission spectrometry (ICP-AES) and trace elements by inductively-coupled plasma mass spectrometry (ICP-AES). We will use colorimetric methods and our own portable spectrophotometer for quantification of dissolved phosphate, ammonium, and H_2S (dissolved sulfide). We will also perform our own alkalinity titrations on diluted peeper samples. Semiquantitative analyses of the metal content of sediments will be performed using a portable X-ray fluorescence (pXRF) meter. The pXRF will be a handy tool to locate "hot spots" of high metal concentration along the streambed.

D.4. Dissemination of Results

All mineralogy and geochemistry data, along with an interpretation of the results, will be submitted to the NRDP in the form of a technical report, written by the graduate student and/or myself. It is likely that this report will take the form of a Montana Tech thesis. The thesis/report will include all raw laboratory data as appendices. In addition, the PI hopes that the results will lead to publication of a paper in a technical journal, such as Applied Geochemistry, Environmental Science and Technology, or Journal of Contaminant Transport.

E. Project Schedule

Because this project requires a lot of field sampling and laboratory work, and then a fair amount of data interpretation, two years are needed. Ideally, most of the peeper sampling for the proposed project will take place in the summer of 2017. However, if there is a delay in setting up the funding, then some sampling will be done in late summer or fall of 2017, and the rest during the summer of 2018. Most of the sequential extractions and mineralogical

characterization of the sediments will take place during the period October-2017 to April-2018 and September to December-2018.   All data related to the project should be in hand by the end of 2018. The final deliverable will be a graduate student thesis, most likely defended in April of 2019 with the final, edited copy available in June of 2019.

F. Monitoring Activities

There will be no monitoring activities associated with this project.

G. Budget

	NRDP	Match	Total Project
1. Salary			
PI Gammons	0	7,008	7,008
Grad student	12,500	0	12,500
2. Benefits			
PI Gammons	0	1,752	1,752
Grad student	1,250	0	1,250
3. Supplies	10,425	0	10,425
4. Analytical	13,250	13,250	26,500
5. Travel	0	0	0
6. Total	37,425	22,009	59,434

1. Five months of salary at $2500/mo are requested for a Montana Tech graduate student who will perform much of the work described in this proposal. During the summer, it is expected that a student will work full-time on the project. During the semester, this reduces to half-time. The relative proportion of summer and semester work will depend on the project start date.   Gammons will donate 2 weeks of his 9-month academic salary as a match, which represents $7,008, spread over 2 years.

2. Benefits are 10% of salary for students and 25% for Montana Tech faculty.

3. Supplies are budgeted as follows:

	Cost	qty	Total
Peepers	$390	5	$1950
Peeper membranes	$48.75	20	$975
pH microelectrode	$750	2	$1500
Eh microelectrode	$500	2	$1000
Sample bottles and filters			$2500
Chemical reagents			$2500

The PI already has several Hesslein peepers that can be reused in this project, but funds are included for 5 new peepers. Each peeper installation requires a new membrane. A new set of pH and Eh microelectrodes will be needed. These are expensive, but are necessary to be able to measure pH and Eh in the small volumes of water samples in the peeper cells. Also, in our experience, the microelectrodes are only good for about one month of heavy use before they foul or break. For this reason, we have budgeted for a replacement set of electrodes. Although sample bottles are relatively inexpensive, the 0.2 μm PES filters that we use have gone up in price, and are now roughly $2 each. We need to use a different filter for each peeper cell for critical data, such as ICP-MS and ICP-AES samples. Money is needed for reagents related to analysis of hydrogen sulfide, nutrients (ammonia, phosphate) and alkalinity using HACH test kits, for reagents used in sequential leach analyses of the sediments, and for gas cylinders (N_2 gas for the lab, and portable argon tanks used during peeper deployment and sampling).

4. Analytical costs are summarized in the following table:

Analytical	unit price	# samples	total
IC anions	$25	70	$1,750
ICP-AES	$25	250	$6,250
ICP-MS	$37.5	140	$5,250

The reason that we will run so many ICP-AES (major and minor solutes) samples is that this method will likely be used for the sequential leach samples (sediment characterization).

5. No money for travel is requested for this project.

Explanation of the Match

The MBMG analytical lab bills services for Montana Tech student-led research projects at roughly ½ the normal cost. Thus, the $13,250 total for analytical expenses represents a match (cost savings) of $13,250 to the NRDP. In addition, Gammons will donate 2 weeks of his time to the project as a match, which comes to $8,760 of salary + benefits.

References cited

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Timmer, Jackie

BNRC projects for Gammons and Cox

To   Cassidy, Carleen

Cc   Gammons, Chris; Cox, Alysia

Carleen,

The Montana Bureau of Mines and Geology Analytical Lab will provide analysis for Chris Gammons and Alycia Cox BNRC projects, if funded. The analytical lab will provide a 50% discounted rate of which, can be used as cost share in each Dr. Gammons and Dr. Cox's BNRC small project proposals.

Please let me know if you need anything further.

Thanks

JACKIE TIMMER
Chief Chemist

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