Environment and Natural Resources Trust Fund (ENRTF) M.L. 2016 Work Plan

Date of Report: May 29, 2016

Date of Next Status Update Report: January 1, 2017

Date of Work Plan Approval: June 7, 2016

Project Completion Date: June 30, 2019

Does this submission include an amendment request? No

PROJECT TITLE: Engineered Biofilter for Sulfate and Metal Removal from Mine Waters

Project Manager: Sebastian Behrens

Organization: University of Minnesota, Department of Civil, Environmental, and Geo-Engineering

Mailing Address: 500 Pillsbury Drive S.E.

City/State/Zip Code: Minneapolis, MN, 55455

Telephone Number: (651) 756-9359

Email Address: sbehrens@umn.edu

Web Address: http://www.cege.umn.edu/directory/faculty-directory/behrens.html

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Location: NE Minnesota, Aitkin, Carlton, Cook, Itasca, Lake, St. Louis

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Total ENRTF Project Budget:	**ENRTF Appropriation:**	**$440,000**
	Amount Spent:	**$0**
	Balance:	**$440,000**

Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 04p

Appropriation Language:
$440,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop an efficient, low-cost, biomass-derived adsorbent material for use in bioactive filters able to remove sulfate and metals from mining-impacted waters. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2019, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Engineered biofilter for sulfate removal from mine waters

II. PROJECT STATEMENT:

Minnesota is currently facing the challenge to balance the economic gain of ongoing and intended mining activities in the Northeast with the potential offset by environmental damage from sulfate and toxic metals in mine discharge waters. Iron mineral mining in the State of Minnesota produces waters with high sulfate concentrations. Currently proposed non-iron, copper-nickel mining activities can even produce waters that contain besides high sulfate concentrations also elevated concentrations of toxic metals. Existing and proposed mining operations in Minnesota are located within the Mississippi River, Lake Superior, and Rainy River watersheds that comprise many pristine wetlands, floodplains, streams and lakes. Elevated heavy metal and sulfide concentrations are toxic to many plants (e.g. wild rice) and animals living in these impacted areas. Biological, passive water filters with an efficient, low-cost, and environmentally-friendly absorbent material (biochar = biomass-derived, carbon-rich solids obtained by heating biomass with little to no oxygen in a process called pyrolysis) are a simple solution to remove sulfate and toxic metals from mining impacted waters.

The purpose of this research is to develop an efficient, bioactive filter to remove sulfate and metals from water. The outcomes of this work will be:

- A mineral-enriched, biomass-derived adsorbent material (composite biochar) optimized to stimulate biological sulfate reduction and adsorption of metal sulfides and heavy metals.
- An effective and low-cost biochar filter to remove sulfate and toxic metals from mine waters.
- Application guidelines for scale-up and field implementation of the new bio-filtration technology.

The treatment of mine waters by passive filtration systems is a low cost, broadly applicable approach for non-point source clean-up of sulfate and heavy metals from water. The availability of effective low cost water treatment methods for sulfate and heavy metal-rich waters will lower the environmental impact of mining in Minnesota. Results from this research will be key for the Minnesota Department of Natural Resources (MNDNR) and the Minnesota Pollution Control Agency (MPCA) to use in support of the decision making process on protecting wild rice from excess sulfate and promote the development of new technologies to remove sulfate and heavy metals from waters impacted by mining operations. Motivation for the project comes from Minnesota’s need for an environmentally-friendly, sustainable water treatment technology that can be applied to lower the environmental impact of mining in order to protect Minnesota’s water resources and pristine aquatic ecosystems.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 1, 2017:

Project Status as of July 1, 2017:

Project Status as of January 1, 2018:

Project Status as of July 1, 2018:

Project Status as of January 1, 2019:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Production of mineral-biochar composite material for heavy metal and metal sulfide sorption.
Description:
The main objective of this activity is the study of engineered biochars (modified with iron sulfate, magnesium chloride, and magnesium hydroxide) as sorption materials for heavy metal and metal sulfide (copper and nickel) removal from solution. We will produce mineral oxide–enriched biochars by blending waste biomass with metals prior to thermochemical decomposition of the organic material at elevated temperatures in the absence of oxygen. Biochars will be produced from woods chips. Prior to pyrolysis the feedstock will be mixed with iron sulfate, magnesium chloride, and magnesium hydroxide. Biochars will be produced at 400°C and 700°C in a PYREG pyrolysis reactor.
The modified sorbents will be rinsed three times in deionized water, dried, and sieved to a homogenous particle size (0.125-0.5 mm). The physico-chemical properties of the prepared biochar-based sorbent materials (pH, EC, metal leaching and mass loss at pH 3, 5, and 6.5) will be characterized. The sorption behaviors of the produced mineral-biochar composite materials will be studied in batch arrangements at different initial concentrations of copper and nickel (1-100 mg L^{-1}). Copper and nickel will be quantified by flame atomic absorption spectroscopy (FAAS) and/or inductively coupled plasma mass spectrometry (ICP-MS). The obtained equilibrium sorption data will be analyzed by mathematical equations of adsorption models. Parameters of adsorption isotherms will be calculated by non-linear regression analysis using the programs MATLAB (MathWorks, Inc. MA, USA) and SigmaPlot (Systat Software, Inc., CA USA).

Summary Budget Information for Activity 1: **ENRTF Budget: $ 143,110**
Amount Spent: $ 0
Balance: $ 143,110

Outcome	**Completion Date**
1. Production of mineral biochar composites	June 30, 2017
2. Optimal production parameters for most efficient contaminant sorption properties	June 30, 2017
3. Sorption properties of engineered biochars at various heavy metal concentrations	June 30, 2017

Activity Status as of January 1, 2017:

Activity Status as of July 1, 2017:

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

ACTIVITY 2: Determine performance of microbial sulfate reduction in the presence of engineered biochar composites.
Description:
A pure culture of a sulfate-reducing model organism (*Desulfovibrio vulgaris*) and anoxic lake sediments from NE Minnesota containing natural sulfate-reducing microbial communities will be exposed to the engineered biochar composites (produced in *Activity 1*) in the presence of different organic carbon substrates (lactate, ethanol, molasses, organic solids such as hay, sugar beet waste, sawdust, compost) and heavy metal concentrations (iron, copper, nickel) in sulfate containing freshwater medium. Growth and activity of the batch cultures will be monitored. Batch experiments will be performed on triplicates. Sterile setups with the engineered biochars, peat, and microporous, aluminosilicate will serve as negative controls. Sulfate reduction rates will be determined by quantifying sulfate concentrations by ion chromatography (IC) and dissolved as well as

precipitated sulfides using a spectrophotometric assay. Metal concentrations in solution will be quantified by flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma mass spectrometry (ICP-MS). The objectives are to study the effect of the engineered biochars on microbial sulfate reduction and to identify the best practice to mix in biodegradable organic materials as food for the bacteria for efficient and prolonged microbial sulfate reduction performance. The most active sulfate reducing microbial populations will be identified by sequencing 16S rRNA gene amplicons and gene fragments of the dissimilatory sulfite reductase (the *dsrA* gene is a process-specific functional marker gene for microbial sulfate reduction). Quantitative PCR and sequencing of the *dsrA* gene fragments and mRNA transcripts will identify which sulfate reducing microbial populations are most active under the experimental conditions. Knowing which sulfate-reducing microbes perform best in the presence of the engineered biochar materials and elevated metal concentrations will be an important prerequisite to build and operate lab-scale bioactive filter for effective sulfate, heavy metal, and metal sulfide removal from mine waters (*Activity 3*).

Summary Budget Information for Activity 2:	**ENRTF Budget:**	**$ 156,438**
	Amount Spent:	**$ 0**
	Balance:	**$ 156,438**

Outcome	**Completion Date**
1. Determine efficiency of microbial sulfate reduction in the presence of mineral-biochar composites	June 30, 2018
2. Best practice to mix organic substrates (food for the bacteria) with the biochar adsorbent material to optimize bioactivity	June 30, 2018
3. Identification and quantification of most efficient sulfate reducing microbial populations	June 30, 2018

Activity Status as of January 1, 2017:

Activity Status as of July 1, 2017:

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

ACTIVITY 3: Construction of lab-scale bioactive filters for mine water remediation.
Description:
We will construct bench-scale upflow anaerobic packed bed reactors containing organic carbon substrates and the engineered biochars produced in *Activity 1* to study the removal of sulfate and heavy metals from mine waters under continuous flow conditions. Bioreactor will be constructed from columns (diameter 90 mm, height 400 mm, net empty working volume 2.54 L) and equipped with four sampling ports for liquid and solid material. The reactors will be packed with layers of acid washed silica and the reactive adsorbent mixture (engineered biochar + organic substrates + microbial enrichment cultures). The biochar composites will be compared to peat-based sorption materials and microporous, aluminosilicate minerals. Artificial sulfate-rich lake and mine water (based on the composition of leachate from sulfide-bearing rock formations from the Duluth Complex in NE Minnesota) will be pumped from a reservoir tank into the bottom inlet of each reactor. Duplicate column experiments for each column-bed-reactive-mixture type will be conducted in a non-parallel manner. Control experiments containing no sulfate-reducing microbial communities will be performed under the same conditions as the inoculated bioreactor tests. Sulfide concentrations, the amount of sulfate removed, and the

concentrations of the dissolved metals will be quantified using the analytical methods described above (*Activity 2*). Liquid and solid samples from each biofilter will also be taken for analyses of the microbial community composition using the molecular methods described in *Activity 2*. The objective of this activity is to optimize filter performance by quantifying filter efficiency at various flow rates, pH values, sulfate, and metal concentrations in order to derive critical parameters for biofilter scale-up and field implementation of the developed technology, e.g. as bioactive barriers. Results will be summarized in a user handbook for guidance on how to use the engineered biochars for the treatment of mine waters.

Summary Budget Information for Activity 3: **ENRTF Budget: $ 140,452**
Amount Spent: $ 0
Balance: $ 140,452

Outcome	**Completion Date**
1. Installation of bench-scale upflow sulfate-reducing packed bed biofilters	June 30, 2019
2. Quantification of filter efficiency at various flow rates, pH values, sulfate, and metal concentrations	June 30, 2019
3. Sorption data for effective use of engineered biochar in field scale bioactive barriers	June 30, 2019
4. Field application handbook on engineered biochars for water treatment	June 30, 2019

Activity Status as of January 1, 2017:

Activity Status as of July 1, 2017:

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

V. DISSEMINATION:
Description: The target audience for results from this research will be professionals in the area of mine water treatment. Specific targets will be environmental engineers and scientists in academia, industry, state agencies such as the DNR and MPCA, and environmental consultants. Results will be disseminated through scholarly publications in peer-reviewed scientific journals and via a publically available final report. Results from the research project will also be presented at local/regional conferences.

Status as of January 1, 2017:

Status as of July 1, 2017:

Status as of January 1, 2018:

Status as of July 1, 2018:

Status as of January 1, 2019:

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
Personnel:	$ 360,772	1 project manager at 15% FTE for each of the 3 years (6 weeks summer salary each year) ($68,518); 1 postdoctoral researcher at 100% FTE for each of the 3 years ($171,938); 1 graduate student at 50% FTE for each of the 3 years ($120,316)
Professional/Technical/Service Contracts:	$ 46,000	University of Minnesota Genomics Center (UMGC) - DNA sequencing, quantitative PCR ($12,000); Research Analytical Laboratory at the University of Minnesota - Inorganic chemical analyses for water, biochar composites, and filter material ($34,000)
Equipment/Tools/Supplies:	$ 30,000	Materials and costs to produce biochars ($10,000); Materials to construct lab-scale biofilters including pumps, tubing, fittings, valves and machining ($15,000); Chemicals, gases, glass ware for anaerobic cultivation and filter operation ($5,000)
Travel Expenses in MN:	$ 3,228	Travel to collect water and sediment samples from aquatic ecosystems in NE Minnesota impacted by high sulfate and heavy metal concentrations
TOTAL ENRTF BUDGET:	**$ 440,000**	

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than $5,000: N/A

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 4.95 FTEs

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0.1 FTEs

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
State			
In-kind: The University of Minnesota does not charge the State of Minnesota its typical overhead rate of 52% of the total modified direct costs (graduate tuition and academic fringe are excluded).	$ 201,020	$ 0	General office and laboratory support during the project period
University of Minnesota - MnDrive Start-Up funds to Sebastian Behrens	$ 80,210	$ 0	Graduate student salary at 50% FTE for 2 years
TOTAL OTHER FUNDS:	**$ 281,230**	**$ 0**	

VII. PROJECT STRATEGY:
A. Project Partners:

The project team consists of the project manager Dr. Sebastian Behrens (Dept. of CEGE, University of Minnesota) and project partner Dr. Kurt Spokas (USDA-ARS; St. Paul, MN). Behrens is an expert on the microbiology of mineral-metal-biochar interactions and Spokas is an expert on the physical sorption/desorption characteristics of engineered biochars. Since Spokas is a federal employee, his participation comes at no cost to the project. The proposed research will be conducted in collaboration with Michael Berndt and Zach Wenz who are geochemists at the Minnesota Department of Natural Resources (MNDNR). The MNDNR will support the proposed project by helping with the selection and facilitating the access to sampling sites at no direct cost to the study.

B. Project Impact and Long-term Strategy:

Results from this research will be key for the MNDNR and the Minnesota Pollution Control Agency (MPCA) to use in support of the decision making process on protecting wild rice from excess sulfate and promote the development of new technologies to remove sulfate and heavy metals from waters impacted by mining operations. The long-term strategy of the project is to lower the environmental impact of mining in Minnesota and to protect Minnesota's water resources and pristine aquatic ecosystems.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount
German Science Foundation "Iron cycling in freshwater sediments under oxic and anoxic conditions"	2012-2015	$ 185,000
German Science Foundation "Microbial processes and iron-mineral formation in household sand filters used to remove arsenic from drinking water in Vietnam"	2011-2014	$ 307,859
German Science Foundation "Abundance, activity, and interrelation of phototrophic and chemotrophic microbial iron oxidation in freshwater sediments "	2012-2015	$ 300,775
LGFG Fellowship, State of Baden-Württemberg Germany "Biochar effects on microbial nitrous oxide formation in soils - composition and activity of the nitrous oxide-forming microbial community"	2013-2014	$ 113,620
German Science Foundation Research Unit: "Natural halogenation processes in the environment - Direct and indirect formation of organohalogens by microorganisms"	2011-2014	$ 380,644

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:

A. Parcel List: N/A

B. Acquisition/Restoration Information: N/A

IX. VISUAL COMPONENT or MAP(S): "See attached figure"

X. RESEARCH ADDENDUM: "See attached Research Addendum"

XI. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted no later than January 1, 2017; July 1, 2017; January 1, 2018; July 1, 2018, and January 1, 2019. A final report and associated products will be submitted between June 30 and August 15, 2019.

Environment and Natural Resources Trust Fund
M.L. 2016 Project Budget

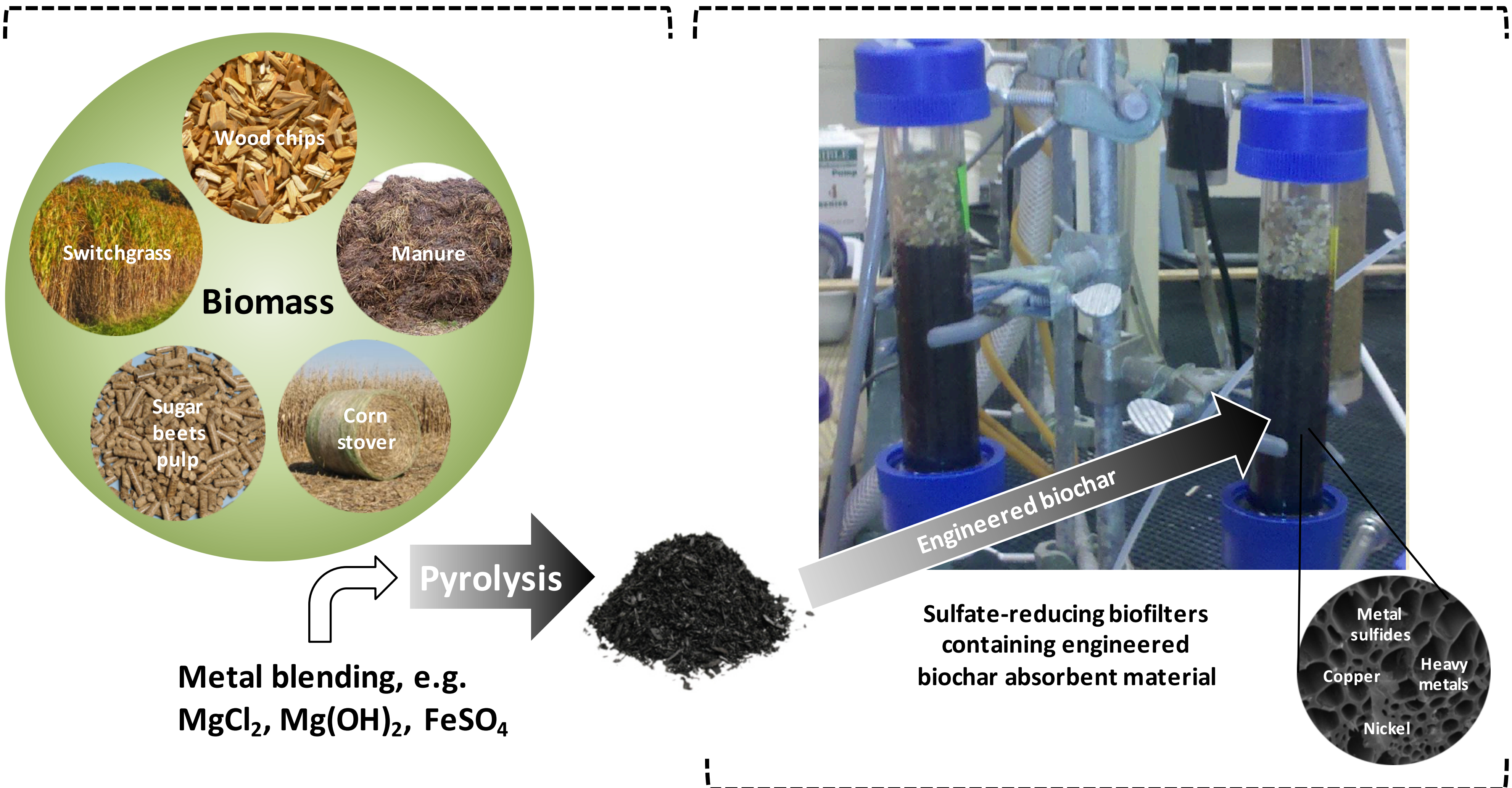
Project Title: Engineered Biofilter for Sulfate and Metal Removal from Mine Waters
Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 04p
Project Manager: Sebastian Behrens
Organization: University of Minnesota - Department of Civil Environmental, and Geo-Engineering
M.L. 2016 ENRTF Appropriation: $440,000
Project Length and Completion Date: 3 Years, June 30, 2019
Date of Report: May 29, 2016

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Activity 3 Budget	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	**Production of mineral-biochar composite material for heavy metal and metal sulfide sorption.**			**Determine performance of microbial sulfate reduction in the presence of engineered biochar composites.**			**Construction of lab-scale bioactive filters for mine water remediation.**				
Personnel (Wages and Benefits)	$115,010	$0	$115,010	$119,610	$0	$119,610	$126,152	$0	$126,152	$360,772	$360,772
Sebastian Behrens, Assoc. Professor, 9 month appointment, Dept. CEGE, Project manager, 6 weeks summer salary for each of the 3 years (15%), fringe rate at 33.7% (total $68,518)											
Postdoctoral researcher, full time (100%) for each of the 3 years, fringe rate 22.4% (total $171,938)											
Graduate student, 50% position, full time (100%) for each of the 3 years, fringe rate at 92.89% (includes tuition) (total $120,316)											
Professional/Technical/Service Contracts											
University of Minnesota Genomics Center (UMGC) - DNA sequencing, quantitative PCR -> identification and enumeration of sulfate reducing bacteria; 1680 samples; 210 samples per run = 8 runs x $1500 per run	$3,000	$0	$3,000	$9,000	$0	$9,000				$12,000	$12,000
Research Analytical Laboratory at the University of Minnesota - Inorganic chemical analyses for water, biochar composites, filter material - Ion Chromatography and Flow Injection Analysis: ammonia, nitrate, nitrite, phosphorus, sulfate and chloride; Total C/Total N Analysis: TOC, TIC, TN, ICP-OES: metals; average $ 16 per sample per analysis; 425 samples x 5 = 2125 x $ 16	$13,600	$0	$13,600	$13,600	$0	$13,600	$6,800	$0	$6,800	$34,000	$34,000
Equipment/Tools/Supplies (total costs $30,000)	$10,000	$0	$10,000	$12,500	$0	$12,500	$7,500	$0	$7,500	$30,000	$30,000
Materials and costs to produce biochars (total $10,000)											
Materials to construct lab-scale biofilters including pumps, tubing, fittings, valves and machining (total $15,000)											
Chemicals, gases, glass ware for anaerobic cultivation and filter operation (total $5,000)											
Travel expenses in Minnesota											
Travel to collect water and sediment samples from aquatic ecosystems in NE Minnesota impacted by high sulfate and heavy metal concentrations	$1,500	$0	$1,500	$1,728	$0	$1,728				$3,228	$3,228
COLUMN TOTAL	**$143,110**	**$0**	**$143,110**	**$156,438**	**$0**	**$156,438**	**$140,452**	**$0**	**$140,452**	**$440,000**	**$440,000**

Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2016 Visual Component
Project 054-B: Engineered biofilter for sulfate removal from mine waters

- Metal recovery from biochar
- Recycling of adsorbent

- Feedstocks for biochar production



- Sulfate conversion to sulfide
- Biochar use as adsorbent
- Sulfate and heavy metal removal