



Environment and Natural Resources Trust Fund (ENRTF) M.L. 2017 LCCMR Work Plan

Date of Submission: January 29, 2017
Date of Next Status Update Report: January 1, 2018
Date of Work Plan Approval: 06/07/2017
Project Completion Date: June 30, 2020
Does this submission include an amendment request? No

PROJECT TITLE: Assessing Release of Mercury and Sulfur on Aquatic Communities

Project Manager: Ed Nater

Organization: University of Minnesota

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Location: Itasca County, northern Minnesota

| | | |
|------------------------------------|-----------------------------|------------------|
| Total ENRTF Project Budget: | ENRTF Appropriation: | \$300,000 |
| | Amount Spent: | \$0 |
| | Balance: | \$300,000 |

Legal Citation: M.L. 2017, Chp. 96, Sec. 2, Subd. 04i

Appropriation Language:

\$300,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota to determine the effects of increased temperatures on the release of mercury and sulfur from Minnesota peatlands to predict impacts on aquatic communities and fish health. This appropriation is available until June 30, 2020, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Assessing Release of Mercury and Sulfur on Aquatic Communities

II. PROJECT STATEMENT: Minnesota has a mercury problem. Eight percent of infants born in the Lake Superior Basin in Minnesota have mercury concentrations in fetal cord blood that exceed human health standards, apparently related to fish consumption by their mothers. In addition, 95% of the stream reaches and lakes assessed for mercury in fish have been listed as impaired, posing a threat to human and environmental health.

This problem may be exacerbated by increased temperatures expected with climate change. Minnesota has more than 6 million acres of peatlands (bogs and fens). Peatlands contain vast stores of mercury and sulfur which have accumulated over several millennia from both natural and anthropogenic sources in atmospheric deposition. Increasing temperatures and longer frost-free seasons will increase the rates of microbial activity in peatlands, which will increase the rate of peat decomposition, thereby releasing mercury and sulfur back into the environment. The potential fate of both mercury and sulfur released from peatlands is unclear, as both mercury and sulfur may be released to surface waters or to the atmosphere.

Release of mercury and sulfur to surface waters would increase existing concentrations in those waters and in fish and other aquatic organisms. In addition, increased aquatic sulfur concentrations may enhance the formation of methylmercury, the most toxic form of mercury in the environment and the form most readily taken up by aquatic organisms. Alternatively, mercury and sulfur could be released to the atmosphere, where they would add to the overall global load but would have relatively negligible local environmental effects. These two pathways have very different outcomes for Minnesota, but currently we do not have enough information to predict which pathways mercury and sulfur will follow.

We have a unique opportunity now to determine how climate change will affect Minnesota peatlands and the mercury and sulfur stored within them: it is called the Spruce and Peatlands Under Climatic and Environmental Change (SPRUCE) project (<http://mnspruce.ornl.gov>), a 10 year, 50 million dollar Department of Energy-funded climate change experiment located on a peat bog at the Marcell Experimental Forest north of Grand Rapids, MN. The SPRUCE infrastructure consists of 10 large (40 ft dia., 30 ft tall) open-topped, controlled-environment enclosures. The atmosphere and soil (peat) in the enclosures will be maintained at 5 different temperatures (no change, +4, +8, +12, and +16° F) relative to temperatures measured outside the enclosures throughout the 10 year period of the experiment.

To answer these questions about the fate of mercury and sulfur, we will measure the effects of increased temperature on the release and fate of mercury and sulfur in the SPRUCE environmental enclosures and use that knowledge to predict their impacts on Minnesota's aquatic ecosystems. Specifically, we will measure the effect of increasing temperatures on the rates of microbial activity and peat decomposition, and the release of mercury and sulfur to surface waters, and the release of mercury to the atmosphere. These data will be used, in combination with other data being collected at the SPRUCE site, to determine the fate of mercury and sulfur in a warming environment and to predict what potential impact that may have on Minnesota's fish, lakes and rivers, and human health.

We will have completed three years of method development and baseline measurements at the SPRUCE site prior to the project start date. The project will leverage these preliminary results as well as the SPRUCE infrastructure and data collected by SPRUCE partners (currently more than 100 scientists). SPRUCE is the largest environmental warming project in existence and is extensively instrumented to collect a wide array of data. Protocols for data sharing and data archival have been established and implemented. As project partners, we will have access to those data to provide contextual background for interpretation of our own results.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of *January 1, 2018:*

Project Status as of *July 1, 2018:*

Project Status as of *January 1, 2019:*

Project Status as of *July 1, 2019:*

Project Status as of *January 1, 2020:*

Project Status as of *July 1, 2020:*

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Determine the effects of increased temperatures on the fate of mercury and sulfur released from peatlands to aquatic ecosystems.

Description:

We will make measurements across the temperature gradient in the SPRUCE environmental chambers over two frost free seasons. Samples of peat and peat surface and pore waters will be collected beginning at the start of the frost free period in 2017 to the end of the frost free season in fall 2017. Samples prior to the project start date (prior to 30 June, 2017) will be collected and analyzed using existing (non LCCMR) funds or will be stored and analyzed after the project start date.

Measurements across the temperature gradient include:

- concentrations and speciation of mercury (ionic mercury or methylmercury) and sulfur (sulfate, sulfide, or organic species) in peat soil at multiple depths;
- concentrations and speciation of mercury (ionic mercury or methylmercury) and sulfur (sulfate, sulfide, or organic species) in surface water and peat porewaters at multiple depths;
- concentrations of mercury vapor in the atmosphere within the chambers;
- the rates of microbial activity and the determination of peat decomposition rates at multiple depths in the peat; and
- concentrations of dissolved organic carbon and suspended particulate organic carbon in surface waters and peat porewaters at multiple depths.

Peat soil will be sampled once per year as it will undergo the least amount of change over the period of the project. Surface water and peat porewater samples will be collected on a monthly basis during the frost free period (which will vary in different enclosures due to different temperature treatments). Almost all of the processes we are concerned about are microbially driven. Because the availability of oxygen decreases with depth in peat, the microbial community also changes with depth. Consequently, most measurements will be taken at multiple depths in the peat to determine how these microbially-driven processes are affected by warming. Atmospheric mercury concentrations will be measured on a monthly basis using passive atmospheric mercury samplers. All measurements will be coordinated with other SPRUCE scientists to leverage results across studies.

The resulting data will be statistically analyzed to determine significant relationships with warming. The microbial measurements and dissolved organic carbon measurements will be used in conjunction with carbon

dioxide release measurements obtained by SPRUCE scientists to determine peat decomposition rates. The mercury and sulfur analyses will be used to determine their environmental fate and potential warming effects on their rate of release, as well as the potential for enhanced mercury methylation in surface waters. All results will be analyzed for trends in their response to increased temperatures. Measurements collected by other SPRUCE scientists will allow us to develop a comprehensive understanding of how these processes are affected by temperature and how they may respond to climatic drivers. All results will form the basis for determinations of how future temperature increases will influence the amount of mercury and sulfate released to MN surface waters or volatilized to the atmosphere

Summary Budget Information for Activity 1:

ENRTF Budget: \$ 300,000
Amount Spent: \$ 0
Balance: \$ 300,000

| Outcome | Completion Date |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| <i>1. Collect samples of peat (two sets of 330 samples) and water (two sets of 1200 samples) across the full range of warming treatments; measure the concentrations of mercury, methylmercury, carbon, nitrogen, and sulfur in peat and water; measure microbial activity and peat decomposition rates over the full range of warming treatments; deploy a network of passive samplers to determine atmospheric mercury and hydrogen sulfide concentrations (~ 700 analyses total) in the environmental enclosures.</i> | January 1, 2019 |
| <i>2. Datasets compiled and statistically analyzed; interpretation of data to determine fate of mercury and sulfur and potential impacts to Minnesota's lakes, rivers, and fish.</i> | June 30, 2019 |
| <i>3. Write reports and disseminate information to collaborators and state agencies.</i> | June 30, 2019 |

Activity 1 Status as of January 1, 2019:

Final Report Summary:

V. DISSEMINATION:

Description:

Status as of January 1, 2018:

Status as of July 1, 2018:

Status as of January 1, 2019:

Status as of July 1, 2019:

Status as of January 1, 2020:

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:

A. Preliminary ENRTF Budget Overview:

***This section represents an overview of the preliminary budget at the start of the project. It will be reconciled with actual expenditures at the time of the final report.**

| Budget Category | \$ Amount | Overview Explanation |
|------------------------|------------------|-----------------------------|
|------------------------|------------------|-----------------------------|

| | | |
|-------------------------------------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Personnel: | \$220,831 | <p>Postdoctoral Fellow \$55,080 (81.7% salary, 18.3% fringe), 100% FTE for 2 years total (estimated \$111,812).</p> <p>Scientific Technician \$40,768 (78.5% salary, 21.5% fringe), 100% for 2 years total (estimated \$82,759).</p> <p>Undergraduate Researchers \$11.00 per hour (100% salary), 600 hrs over 2 years (estimated \$13,200).</p> <p>Dr. Brandy Toner \$125,456 (74.8% salary, 25.2% fringe), 0.05 FTE for 2 years (estimated \$13,060).</p> |
| Professional/Technical/Service Contracts: | \$7,400 | <p>Contract for supply and analysis of passive mercury monitors. Dr. Carl Mitchell, University of Toronto - Scarborough, is the inventor and sole source supplier of the most accurate passive mercury monitors currently in existence. Purchase and analysis of 190 passive samplers for atmospheric mercury @\$39 = \$7,400. (see note 1 that follows)</p> |
| Professional/Technical/Service Contracts: | \$9,600 | <p>Contract for analysis of 1200 samples of peat and water for sulfur-34 isotopic analyses. Dr. Jessica Gutknecht, project partner, performs these analyses in her laboratory and has developed an Internal Sales agreement with the University that allows her to charge other researchers for these services. Because she has an Internal Sales agreement, the University also wants her to charge herself for analyses for her own projects. Consequently, we transferred funds from the supplies category of the 2016 budget to the contracts category of this, the 2017 budget. (See note 2 that follows)</p> |
| Equipment/Tools/Supplies: | \$34,677 | <p>Collect 330 samples of peat and 1,200 samples of water across the full range of warming treatments for multiple analyses. Construct 175 passive samplers for hydrogen sulfide monitoring and made 175 analyses of air for hydrogen sulfide (@ \$20 = \$3,500). Materials and supplies for mercury and methylmercury analyses of peat and water include ultraclean sample bottles (1200), analytical standards, analytical reagent gases (argon and nitrogen), reagent chemicals, filters, cleanroom gloves and wipes, and miscellaneous (1,530 samples @ \$10 = \$15,300). Materials and supplies for carbon-13 PLFA microbial analyses (800 samples @ \$10 = \$8,000), Materials and supplies for analysis of water samples for sulfide ion (1,200 samples @ \$5 = \$6,000) include teflon vials, caps, and tubing, chemical reagents, sample containers,</p> |

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|--------------------------------------|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| | | and reagent gases. Miscellaneous expenses include dry ice for sample preservation, protective gloves, labcoats, eyewear, containers for archiving samples, pipettors and pipette tips, and other expenses (\$1,877). |
| Travel Expenses in MN: | \$15,492 | 30 sampling trips (15 per year) to research site north of Grand Rapids, MN. Includes mileage reimbursement (\$240 per trip), lodging (\$83 per night for 2 individuals each trip), and meals (\$46 per person per day, 18 days per year). All expenses will follow University of Minnesota travel guidelines. |
| Other: | \$12,000 | Travel to Synchrotron Beamline in Saskatoon, Saskatchewan to analyze solid samples to determine sulfur speciation. Four trips total, including airfare, lodging, meals, estimated from experience at \$3,000 per trip. There are no synchrotron facilities in Minnesota. All expenses will follow University of Minnesota travel guidelines. |
| TOTAL ENRTF BUDGET: \$300,000 | | |

Note 1: This note describes changes to the budget from the original 2016 Work Plan. We moved \$7,400 from the Equipment/Tools/Supplies category to the Professional/Technical/Service Contracts category to accommodate changes in how we will fund the passive atmospheric mercury monitors needed for this project. We initially planned to develop (\$3,900) and analyze (\$3,500) our own passive atmospheric monitors as existing ones did not meet our needs. During that time, however, a colleague of ours (Dr. Carl Mitchell, University of Toronto - Scarborough) has developed and tested passive atmospheric mercury monitors that completely fulfill our needs. He is the sole source supplier for these monitors. We will contract with him to supply and analyze the passive mercury monitors for this project. Contract for supply and analysis of 190 passive samplers for atmospheric mercury @\$39 = \$7,400.

Note 2: We have moved an additional \$9,600 from the Equipment/Tools/Supplies category to the Professional/Technical/Service Contracts category for the analysis of samples for sulfur-34 isotopic measurements. Because other researchers within the University want to have these analyses, Dr. Gutknecht has established an internal sales organization (ISO), a University financial entity that allows her to charge other researchers within the University for these analyses. Now that she has established an ISO, the University prefers that she charge for all sulfur-34 isotopic analyses, including her own, through it rather than through materials and supplies or other budget categories. Consequently, we moved \$9,600 from Supplies to Service Contracts to accommodate that change. The numbers of analyses and their cost remain unchanged.

Explanation of Use of Classified Staff: n/a

Explanation of Capital Expenditures Greater Than \$5,000: n/a

Total Number of Full-time Equivalent (FTE) Directly Funded with this ENRTF Appropriation: 4.1 FTE

**Total Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF
Appropriation: 0**

B. Other Funds:

| Source of Funds | \$ Amount Proposed | \$ Amount Spent | Use of Other Funds |
|--------------------------------------------------------|--------------------|------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| Non-state | | | |
| USDA Forest Service | \$329,896 | \$250,024 | Develop methods and collect background data. Collect water and peat samples, analyze water samples for carbon, nitrogen, and sulfur. |
| State | | | |
| University of Minnesota | \$40,380 | \$40,380 | Graduate Student Assistantship, develop microbial methods and collect background data |
| University of Minnesota | \$40,380 | \$16,000 | Graduate Student Fellowship, analyzing samples for mercury and sulfur |
| University of Minnesota, indirect cost recovery waiver | \$156,000 | \$0 | Matching funds |
| TOTAL OTHER FUNDS: | \$566,656 | \$306,404 | |

VII. PROJECT STRATEGY:

A. Project Partners:

Partners receiving ENRTF funding

- Dr. Brandy Toner, University of Minnesota: \$13,060 to analyze samples at the synchrotron beamline.

Partners NOT receiving ENRTF funding

- Drs. Ed Nater and Jessica Gutknecht, Department of Soil, Water and Climate, University of Minnesota
- Drs. Randy Kolka and Stephen Sebestyen, USDA Forest Service Northern Forest Research Station.

The Project Partners will conduct the project and oversee the postdoctoral fellow, technicians, undergraduate students, and other personnel working on the project. Ed Nater will be the project director and will coordinate partner efforts and oversee the mercury and methylmercury analyses. Brandy Toner will oversee the sulfur measurements and will conduct analyses of samples at the synchrotron beamline. Jessica Gutknecht will oversee the microbial analyses. Randy Kolka and Stephen Sebestyen will oversee sample collection, coordination of our efforts with the SPRUCE project, and other aspects of the project. All partners will be involved in final analyses of data and interpretation of results. Our colleagues in the Department of Health, Pollution Control Agency, and Department of Natural Resources have expressed interest in the results of this project and will serve as ad hoc advisors for this project.

B. Project Impact and Long-term Strategy: This project will determine the environmental fate of mercury and sulfur released from peatlands by a warming environment. We will use these data to determine their impacts on Minnesota's lakes and rivers, with particular emphasis on fish mercury concentrations and implications for human health. This information will be disseminated to state agencies managing fisheries, surface water quality, and human health and will provide them with an awareness of predicted trends and potential impacts of a warming environment. These results can be used to inform planning processes regarding enhanced monitoring of fish mercury levels in the northern part of Minnesota, where lake and river watersheds often contain large areas of peatlands, and potential changes to fish consumption advisories in those areas.

C. Funding History:

| Funding Source and Use of Funds | Funding Timeframe | \$ Amount |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|-----------|
| USDA Forest Service, method development and collection and analysis of samples to determine background conditions prior to the start of the warming experiment at SPRUCE | July 1, 2012 to June 30, 2017 | \$329,896 |
| University of Minnesota, support of 2 graduate students for development of microbial methods to be used in this project and determination of background mercury and sulfur status prior to warming. | | \$80,760 |
| | | \$410,656 |

VIII. REPORTING REQUIREMENTS:

- The project is for 3 years, will begin on 07/01/2017, and end on 06/30/2020.
- Periodic project status update reports will be submitted 01/01 and 07/01 of each year.
- A final report and associated products will be submitted between June 30 and August 15, 2020.

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

**Environment and Natural Resources Trust Fund
M.L. 2017 Project Budget**



Project Title: Assessing Release of Mercury and Sulfur on Aquatic Communities

Legal Citation: M.L. 2017, Chp. 96, Sec. 2, Subd.

Project Manager: Ed Nater

Organization: University of Minnesota

M.L. 2017 ENRTF Appropriation: \$ 300,000

Project Length and Completion Date: 3 years, June 30, 2020

Date of Report: 10/27/2016

| ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET | Activity 1 Budget | Amount Spent | Activity 1 Balance | TOTAL BUDGET | TOTAL BALANCE |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|--------------|-----------------------|-----------------|------------------|
| BUDGET ITEM | <i>Fill in your activity title here.</i> | | | | |
| Personnel (Wages and Benefits) | \$220,831 | | | \$220,831 | \$220,831 |
| <i>Dr. Brandy Toner \$125,456 (74.8% salary, 25.2% fringe), 0.05 FTE for 2 years (estimated \$13,060)</i> | | | | | |
| <i>Postdoctoral Fellow \$55,080 (81.7% salary, 18.3% fringe), 100% FTE for 2 years total (estimated \$111,812)</i> | | | | | |
| <i>Scientific Technician \$40,768 (78.5% salary, 21.5% fringe), 100% for 2 years total (estimated \$82,759)</i> | | | | | |
| <i>Undergraduate Researchers \$11.00 per hour (100% salary), 600 hrs over 2 years (estimated \$13,200)</i> | | | | | |
| Professional/Technical/Service Contracts | \$17,000 | | | \$17,000 | \$17,000 |
| <i>Contract for supply and analysis of passive mercury monitors. Dr. Carl Mitchell, University of Toronto - Scarborough, is the inventor and sole source supplier of the most accurate passive mercury monitors currently in existence. Purchase and analysis of 190 passive samplers for atmospheric mercury @\$39 = \$7,400.</i> | | | | | |

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| <i>Contract for analysis of 1200 samples of peat and water for sulfur-34 isotopic signatures. Dr. Jessica Gutknecht, project partner, performs these analyses in her laboratory and has developed an Internal Sales organization (ISO) with the University that allows her to charge other researchers for these services. Because she has an ISO, the University wants her to charge herself for analyses for her own projects. Consequently, we transferred funds from the supplies category of the 2016 budget to the contracts category of this, the 2017 budget. 1200 analyses @ \$8 per sample = \$9,600</i> | | | | |
| Equipment/Tools/Supplies | \$34,677 | | \$34,677 | \$34,677 |
| <i>Collect 330 samples of peat and 1200 samples of water for total and methyl mercury @ \$10 = \$15,300. Construct 175 passive samplers for hydrogen sulfide monitoring and make 175 additional analyses of air for hydrogen sulfide (@ \$20 = \$3,500). Materials and supplies for analysis of 800 peat and water samples for carbon-13 PLFA microbial analyses @ \$10= \$8,000 Materials and supplies for analysis of 1200 water samples for sulfide ion @ \$5 = \$6,000. Miscellaneous expenses = \$1,867.</i> | | | | |
| Travel expenses in Minnesota | \$15,492 | | \$15,492 | \$15,492 |
| <i>30 sampling trips (15 per year) to research site north of Grand Rapids, MN. Includes mileage reimbursement (\$240 per trip), lodging (\$83 per night for 2 individuals each trip), and meals (\$46 per person per day, 18 days per year). All expenses will follow University of Minnesota travel guidelines.</i> | | | | |
| Other | \$12,000 | | \$12,000 | \$12,000 |
| <i>Travel to Synchrotron Beamline in Saskatoon, Saskatchewan (there are no synchrotrons in Minnesota) to analyze solid samples for chemical speciation. Two trips per year each year for 2 years, includes airfare, lodging, meals, estimated from experience at \$3,000 per trip. All expenses will follow University of Minnesota travel guidelines.</i> | | | | |
| COLUMN TOTAL | \$300,000 | | \$300,000 | \$300,000 |