

M.L. 2017 Project Abstract

For the Period Ending June 30, 2021

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

PROJECT MANAGER: Edward A. Nater

AFFILIATION: University of Minnesota

MAILING ADDRESS: Department of Soil, Water, and Climate, 439 Borlaug Hall, 1991 Upper Buford Circle

CITY/STATE/ZIP: Saint Paul, MN 55108

PHONE: 612-6384-9779

E-MAIL: nater001@umn.edu

WEBSITE: <http://swac.umn.edu/people/ed-nater>

FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2017, Chp. 96, Sec. 2, Subd. 04i as extended by M.L. 2020, First Special Session, Chp. 4, Sec. 2

APPROPRIATION AMOUNT: \$300,000

AMOUNT SPENT: \$300,000

AMOUNT REMAINING: \$0

Sound bite of Project Outcomes and Results

Objectives were to determine if peatland degradation from increased temperatures will exacerbate mercury and sulfur impairments of surface waters. Results predict slightly decreased export of sulfate and methylmercury, slightly increased export for total mercury, and large increases in mercury volatilization to the atmosphere, with negligible local impact to surface waters.

Overall Project Outcome and Results

Mercury contamination of surface waters constitutes a human and ecological health problem in Minnesota. Peatlands have accrued substantial quantities of mercury and sulfur from atmospheric deposition over thousands of years. Will they become sources of legacy contamination to the environment if peatlands degrade under future, warmer climates, as hypothesized? Increased export of mercury and sulfur to surface waters could further contaminate already impaired surface waters and exacerbate existing human health problems in northern Minnesota. The study was conducted at the [SPRUCE](#) ecosystem warming research site located on a bog north of Grand Rapids, MN. We collected peat outflow waters and peat porewaters from multiple depths in the bog from 2017-2019 and analyzed them for total mercury, methylmercury, and sulfate concentrations. We also measured rates of volatilization of mercury to the atmosphere with passive atmospheric mercury collectors. Regional climate estimates from the [USGS Climate Change Viewer](#) were used to estimate future changes in peatland water export, which is predicted to decrease by about 15% by 2100. Methylmercury and sulfate concentrations were unaffected by temperature, whereas total mercury increased approximately 15% with a 9°F increase. When combined with a small decrease in water export, methylmercury and sulfate exports should remain the same or decrease slightly from current levels. Total mercury exports are expected to remain the same or increase no more than 10-20%. Warmer temperatures caused large increases in mercury volatilization rates to increase to the point where peatlands becoming sources of mercury to the atmosphere. Overall, future environmental and human health impacts from peatlands to surface waters should be relatively similar to current day impacts. Increased mercury release to the atmosphere will have negligible local to regional impacts.

Project Results Use and Dissemination

Numerous oral presentations have been given to citizen groups, high school and college classes, the Minnesota Tribal Environmental Council, TV news and interest programs, and numerous visitors to the SPRUCE project site. Project members have also made presentations at national and international scientific meetings and to the SPRUCE project annual meetings. Three peer-reviewed scientific manuscripts of related work have been published and a fourth is in revision. Future plans are to share our final report to the ad hoc state agency mercury group (MPCA, MDH, MDNR) and the Minnesota Tribal Environmental Council and to meet with them if desired.



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

Date of Submission: September 15, 2021

Final Report

Date of Work Plan Approval: 06/07/2017

Project Completion Date: June 30, 2021

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

Project Manager: Ed Nater

Organization: University of Minnesota

Mailing Address: 439 Borlaug Hall, 1991 Upper Buford Circle

City/State/Zip Code: St Paul, MN 55108

Telephone Number: (612) 384-9779

Email Address: enater@umn.edu

Web Address: <http://www.swac.umn.edu/directory/faculty/ed-nater>

Location: Itasca County, northern Minnesota

Total ENRTF Project Budget:

ENRTF Appropriation: \$300,000

Amount Spent: \$300,000

Balance: \$0

Legal Citation: M.L. 2017, Chp. 96, Sec. 2, Subd. 04i as extended by M.L. 2020, First Special Session, Chp. 4, Sec. 2

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.

M.L. 2020 - Sec. 2. ENVIRONMENT AND NATURAL RESOURCES TRUST FUND; EXTENSIONS. [to June 30, 2021]

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:

As of 1 January, 2018 we have:

- hired one 1.00 FTE technician/lab manager and one 0.80 FTE technician on project funds; and
- recruited one PhD student to work on the project on other funds.

We have:

- conducted our annual peat core sampling and have processed those samples for analysis;
- collected porewater and outflow samples on a biweekly basis; and
- collected surface peat samples at two different dates.

We have analyzed:

- peat core samples collected in 2015 and 2016 for sulfur, carbon, and nitrogen;
- peat porewater and outflow samples for total mercury and methylmercury;
- peat core samples collected in 2017 for total mercury;
- peat core samples collected in 2016 for sulfur speciation analysis (S-XANES) at the Canadian Light Source synchrotron; and
- have begun analyzing peat samples for ¹³C PLFA (microbial lipid analysis).

We have begun statistical analysis of data collected during and prior to the project period, including:

- developed a computer program to batch fit sulfur XANES spectra for SPRUCE project samples to a reference library of organic sulfur species; and
- have two graduate students conducting statistical analyses of chemical data for trend analysis.

Project Status as of July 1, 2018:

Between January 1, 2018 and July 1, 2018 we have:

- collected porewater and outflow samples on a biweekly basis; and
- collected outflow DOC samples on a biweekly basis

We have analyzed

- all peat core samples collected in 2017 for total mercury and methylmercury
- all remaining peat core samples collected in 2016 and a portion of the peat core samples collected in 2017 for sulfur speciation (S-XANES) at the Canadian Light Source synchrotron;
- all peat porewater samples and outflow samples collected so far in 2018 for total and methylmercury;
- all peat samples collected in 2015 and a portion of those collected in 2016 and 2017 for ¹³C PLFA analysis. The 2015 data are being presented in a manuscript in preparation at this time.
- a portion of the outflow samples collected in 2017 and 2018 for sulfur speciation in the dissolved organic carbon.

We are performing statistical analyses of data for:

- predictive relationships between sulfur speciation, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in peat;
- predictive relationships between sulfur concentrations, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in outflow samples; and
- relationships between chemical and environmental variables in peat porewaters.

Project Status as of January 1, 2019:

Between July 1, 2018 and January 1, 2019 we have:

- collected porewater and outflow samples on a biweekly basis; and

- collected outflow DOC samples on a biweekly basis

We have analyzed

- all peat core samples collected in 2018 for total mercury
- all remaining peat core samples collected in 2017 for sulfur speciation (S-XANES) at the Canadian Light Source synchrotron (the instrument has been down for the last 6 months so we have not made any progress on the 2018 samples);
- all peat porewater samples and outflow samples collected in 2018 for total and methylmercury;
- all peat samples collected in 2015 and the majority of those collected in 2016 ¹³C PLFA analysis.
- all outflow samples collected in 2017 and a portion of those collected in 2018 for sulfur speciation in the dissolved organic carbon.

We are performing statistical analyses of data for:

- predictive relationships between sulfur speciation, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in peat; this work was completed for the 2012 - 2016 data and forms the basis of a MS thesis by Anna Lucia Krupp.
- predictive relationships between sulfur concentrations, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in outflow samples; and
- relationships between chemical and environmental variables in peat porewaters.

Project Status as of *July 1, 2019:*

Between January 1, 2019 and July 1, 2019 we have:

- collected porewater and outflow samples on a biweekly basis; and
- collected outflow DOC samples on a biweekly basis

We have analyzed

- all peat samples collected in 2018 for methylmercury,
- all peat porewater samples and outflow samples collected in the latter half of 2018 for total and methylmercury,
- all peat samples collected in 2015 and the majority of those collected in 2016 for ¹³C PLFA (carbon-13 isotope phospholipid fatty acid) analysis,
- all outflow samples collected in 2017 and a portion of those collected in 2018 for sulfur speciation in the dissolved organic carbon, and
- all 2016, 2017, and 2018 peat samples for carbon, nitrogen, and sulfur elemental content and isotope ratios.

We continue to perform statistical analyses of data for:

- predictive relationships between sulfur concentrations, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in outflow samples; and
- relationships between chemical and environmental variables in peat porewaters.

Project Status as of *January 1, 2020:*

Between July 1, 2019 and January 1, 2020 we have:

- collected porewater and outflow samples on a biweekly basis; and
- collected outflow DOC samples and standpipe samples on a biweekly basis

We have analyzed

- a portion of the peat samples collected in 2019 for total mercury and methylmercury,

- all peat porewater and outflow samples for total and methylmercury,
- the first round of passive atmospheric samplers for total mercury,
- peat samples collected from inception through 2017 for sulfur speciation at the Canadian Light Source synchrotron facility,
- all 2019 peat samples for ¹³C PLFA (carbon-13 isotope phospholipid fatty acid) analysis,
- a portion of 2017 peat samples for ¹³C PLFA, and
- all 2016, 2017, and 2018 peat samples for carbon, nitrogen, and sulfur elemental content and isotope ratios.

We continue to perform statistical analyses of data for:

- predictive relationships between sulfur concentrations, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in outflow samples,
- relationships between chemical and environmental variables in peat porewaters,
- passive sampler concentrations and other environmental variables (temperature and enclosure air exchange rates) to determine atmospheric fluxes of mercury, and
- relationships between ¹³C PLFA results and other variables.

Amendment Request as of 28 June, 2020

We request an amendment to move funds between budget categories. The explanation for these moves is provided below.

1. We would like to reduce budget category "Travel expenses in Minnesota" from \$15,492 to \$1,953. We were able to increase efficiency by paying half the salary of an individual working at the Marcell Experimental Forest (our research site) to collect samples and take measurements for us rather than have our personnel travel to the Marcell Experimental Forest on a biweekly basis.
2. We would like to reduce budget category "Other" from \$12,000 to \$6,316. We were unable to travel to the Synchrotron Beamline in Saskatoon, Saskatchewan in Fall 2019 due to a shutdown of the Beamline for repairs and upgrades. Further, we were unable to travel to the Beamline in Spring 2020 due to COVID-19.
3. We would like to reduce budget category "Professional/Technical/Service Contracts" from \$17,000 to \$10,205. Dr. Carl Mitchell, University of Toronto-Scarborough, provided his services as an in-kind contribution (budgeted for \$7,400) which helped reduce our expenses in this category.
4. We would like to reduce budget category "Equipment/Tools/Supplies" from \$34,677 to \$30,984. We were unable to collect samples from our project site during the COVID-19 shutdown and thus spent less than we had anticipated. We have a remaining balance of \$1,722 in that category to be moved into the 2020-2021 budget year to pay for supplies required to complete the passive atmospheric mercury sampling and porewater sample collection this year.
5. We would like to increase budget category "Personnel" from \$220,831 to \$250,542. This increase is needed to pay for sample collection by the individual working at the Marcell Experimental Forest.

Approved June 7, 2020

Project Status as of July 1, 2020:

Project extended to June 30, 2021 by LCCMR 6/18/20 as a result of M.L. 2020, First Special Session, Chp. 4, Sec. 2, legislative extension criteria being met.

Between January 1, 2020 and July 1, 2020 we have:

- collected a portion of the porewater and outflow water samples. Due to COVID-19, we were unable to collect samples until University approval for employee field travel, which occurred on April 9, 2020.
- collected outflow DOC samples and standpipe samples on a biweekly basis

We have analyzed:

- all peat samples collected in 2019 for total mercury and methylmercury,
- all peat porewater and outflow samples collected in 2019 for total and methylmercury,
- all peat samples collected in 2019 for carbon, nitrogen, and sulfur elemental content and isotope ratios.

We continue to perform statistical analyses of data for:

- predictive relationships between sulfur concentrations, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in outflow samples,
- relationships between chemical and environmental variables in peat porewaters,
- passive sampler concentrations and other environmental variables (temperature and enclosure air exchange rates) to determine atmospheric fluxes of mercury, and
- relationships between ¹³C PLFA results and other variables.

Project Status as of January 1, 2021:

Between July 1, 2020 and January 1, 2021, we have:

- collected porewater and outflow water samples
- collected outflow DOC samples and standpipe samples on a biweekly basis
- there was no solid peat sampling in 2020 due to Covid-19

We have analyzed:

- a portion of peat porewater and outflow samples collected in 2020 for total and methylmercury,
- 422 samples of peat and freeze-dried outflow waters for sulfur speciation data, and
- a portion of peat samples collected in 2020 for carbon, nitrogen, and sulfur elemental content and isotope ratios.

We continue to perform statistical analyses of data for:

- predictive relationships between sulfur concentrations, soil temperature, elevated CO₂ concentrations, and other environmental variables with total mercury and methyl mercury in outflow samples,
- metagenomic data from Oak Ridge National lab to identify hgcAB and merAB operons responsible for the methylation and demethylation of mercury as a measure of mercury methylation and demethylation activity within peat porewaters,
- relationships between chemical and environmental variables in peat porewaters,
- passive sampler concentrations and other environmental variables (temperature and enclosure air exchange rates) to determine atmospheric fluxes of mercury, and
- relationships between ¹³C PLFA results and other variables.

Amendment Request June 11, 2021

The requested current changes in the personnel category reflect reimbursement of personnel expenses that were erroneously charged to the budget after July 1, 2020. Unfortunately the amount reimbursed was \$4,184 higher than the erroneous expenditures leaving an excess of funds in the personnel expense category. Consequently, we are requesting that this amount be transferred to the Equipment/Tools/Supplies category to allow us to balance the budget.

Budget Explanation: As of July 1, the budget matched that presented in the July 1, 2020 budget update, where \$1,722 remained in supplies. However, accounting continued to pay a postdoc and a technician from this project, even though we asked them to not do so. Consequently this budget was in deficit.

At that point I asked them to remove all salaries and fringe spent after July 1. Unfortunately, they also removed 2 weeks of salary and fringe spent prior to July 1, which then left us with a surplus in the salary and fringe category. At this point they will not correct that mistake.

Therefore I am requesting that the budget be amended to the figures provided, with a total salary of \$246,358 and a total Equipment/Tools/Supplies budget of \$35,168.

My apologies for not catching this sooner, but the University suspended my ability to view my own budgets upon my retirement in January 15, 2021.

Approved June 11, 2021

Project Status as of July 1, 2021:

Overall Project Outcomes and Results:

Mercury contamination of surface waters constitutes a human and ecological health problem in Minnesota. Peatlands have accrued substantial quantities of mercury and sulfur from atmospheric deposition over thousands of years. Will they become sources of legacy contamination to the environment if peatlands degrade under future, warmer climates, as hypothesized? Increased export of mercury and sulfur to surface waters could further contaminate already impaired surface waters and exacerbate existing human health problems in northern Minnesota. The study was conducted at the [SPRUCE](#) ecosystem warming research site located on a bog north of Grand Rapids, MN. We collected peat outflow waters and peat porewaters from multiple depths in the bog from 2017-2019 and analyzed them for total mercury, methylmercury, and sulfate concentrations. We also measured rates of volatilization of mercury to the atmosphere with passive atmospheric mercury collectors. Regional climate estimates from the [USGS Climate Change Viewer](#) were used to estimate future changes in peatland water export, which is predicted to decrease by about 15% by 2100. Methylmercury and sulfate concentrations were unaffected by temperature, whereas total mercury increased approximately 15% with a 9°F increase. When combined with a small decrease in water export, methylmercury and sulfate exports should remain the same or decrease slightly from current levels. Total mercury exports are expected to remain the same or increase no more than 10-20%. Warmer temperatures caused large increases in mercury volatilization rates to increase to the point where peatlands becoming sources of mercury to the atmosphere. Overall, future environmental and human health impacts from peatlands to surface waters should be relatively similar to current day impacts. Increased mercury release to the atmosphere will have negligible local to regional impacts.

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: \$ 298,278
Balance: \$ 1,722

Outcome	Completion Date
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	January 1, 2020

<i>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>	
2. <i>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, 2021
3. <i>Write reports and disseminate information to collaborators and state agencies.</i>	June 30, 2021

Activity 1 Status as of January 1, 2019: See overall for updates

Final Report Summary:

This study was conducted at the US Department of Energy's [SPRUCE](#) ecosystem warming project site located on a bog at the US Forest Service's Marcell Experimental Forest north of Grand Rapids, MN. Porewater samples were collected on a biweekly basis from all ten enclosures and two unenclosed ambient plots at 4 depths during 2017 to 2019. Samples were collected when sufficient water was present during the unfrozen season. Samples were analyzed for total mercury, methylmercury, sulfate, and other chemicals of interest. A network of passive mercury atmospheric samplers was also deployed in the enclosures and others sites. The samplers were analyzed to determine atmospheric mercury concentrations over the period of deployment; these data were then used to determine the rate of mercury volatilization to the atmosphere.

The analytical results were statistically analyzed to determine the effects of a warming climate on the concentrations of total mercury, methylmercury, and sulfate, and on the rate of mercury volatilization. Our results showed no influence of temperature on sulfate and methylmercury concentrations in porewaters or outflow waters. Total mercury concentrations, however, increased with increasing temperatures, approximately 15% with a 5°C increase, close to the temperature increase expected by 2100. The rate of mercury volatilization also increased significantly with increasing temperatures, although the relationship was less clear in the warmer (+6.75 and +9°C) enclosures.

Regional climate projections from the USGS Climate Change Viewer were used to predict future water export from peatlands to surface waters and were combined with concentration data to predict future changes in the export of mercury, methylmercury, and sulfate from peatlands. Future water export from peatlands is predicted to decrease approximately 15% by the year 2100, but confidence in this prediction is lower than for some of the other climate variables because peatland export is dependent on the balance between temperature, evaporative demand, and precipitation, all variables that are expected to increase, making predictions less clear. Snow melt has a disproportionately higher impact on bog outflow than on upland runoff due to lack of infiltration in frozen ground and high volumes resulting from an often rapid rate of snowmelt. Because regional climate predictions show large (50%) reductions in snowfall by 2100, it is likely that water export from peatlands will decrease more than upland runoff, providing more confidence in future predictions for decreased peatland water exports.

When combined with regional predictions of peatland outflow, future exports of sulfate and methylmercury to surface waters are predicted to decrease due to a reduction in peatland outflow. Total mercury exports to surface waters are predicted to remain largely the same due to an increase in total mercury concentrations and a comparable, offsetting decrease in peatland outflow. Because there is some uncertainty around outflow estimates, it is possible that sulfate and methylmercury exports may not change and that total mercury exports may increase somewhat. The rates of mercury volatilization to the atmosphere are expected to increase significantly. A 2.25% increase in average temperature led to more than a doubling of volatilization rates within the enclosures.

Based on this study and on regional climate change modeling, peatland exports of mercury and sulfate are not predicted to cause a significant increase in mercury impairment of surface waters in the future, nor should they exacerbate existing human and ecosystem health impacts.

Increases in mercury volatilization rates will quickly outstrip atmospheric deposition rates in the region and peatlands will become net sources of mercury to the atmosphere. Volatilization losses will be incorporated into the global atmospheric pool and should produce negligible local-to-regional impacts. Legacy mercury will be released to the atmosphere and redistributed as part of the global mercury cycle.

Under these scenarios, the degradation of peatlands predicted to occur with warming temperatures will not cause significant additional impairment of surface waters nor exacerbate existing human and ecosystem health impacts. Future management options for surface waters will be similar to current options.

We originally proposed to use passive samplers to capture hydrogen sulfide (H₂S) gas emitted from the peat. Hydrogen sulfide gas emissions are a potential sulfur loss pathway. We had originally proposed to measure the hydrogen sulfide captured at the Minnesota Science Museum's St. Croix Research Laboratory at Marine on St. Croix as they had the equipment and expertise to do so. However, their labs were shut down for a significant period of time due to Covid-19 and they lost the laboratory personnel who had this expertise.

Matching funds were used to support two postdoctoral fellows, provided full or partial support for five graduate students, and full or partial support for three technicians. They also paid for additional supplies, shipping of samples and supplies, analysis of passive atmospheric mercury samplers, and analysis of porewater and outflow water samples for sulfate. Matching funds will be used to continue this study into the future and we have already collected, but have not fully analyzed, samples from 2020 and 2021. Although not technically matching funds, our free use of the SPRUCE infrastructure and of data collected by the SPRUCE project and some of the other one hundred-plus researchers working at the SPRUCE site constituted a massive leverage of tens of millions of dollars of external funds for our project.

V. DISSEMINATION:

Description:

Status as of January 1, 2018:

no dissemination activities

Status as of July 1, 2018:

The following presentations disseminated preliminary results of this project to academic and other audiences:

- Gutknecht, J., and C.M. Blake. Microbial C use under whole ecosystem warming, as determined with isotopic methods. Contributed Oral Presentation for the annual Ecology Society of America meeting, New Orleans, August 5-10, 2018.
- Gutknecht, J., and C.M. Blake. Microbial C and S use under whole ecosystem warming, as determined with isotopic methods. Poster Presentation for the SPRUCE all-hands meeting, May 2018.
- Toner, B.M. (2018) Effect of climate change on coupled biogeochemistry of sulfur and mercury in organic soils. Soils for a Sustainable Future Workshop. National Synchrotron Light Source II User Meeting, Brookhaven National Laboratory, May 22, 2018 (invited talk).

Status as of January 1, 2019:

The following presentations disseminated preliminary results of this project to academic and other audiences:

- Gutknecht, J., and C.M. Blake. Microbial $\delta^{13}\text{C}$ profiles in peat soils under warming. Oral presentation, Ecological Society of America annual meetings, New Orleans, LA, August 5-10, 2018.

- Druschel, G., Dvorski, S., Kafantaris F.-C., Toner, B., Philippe S.-K. A holistic view of organic sulfurization. Goldschmidt Geochemistry Conference, Boston, MA USA, Aug 12-17, 2018. Oral Presentation.
- Fakhraee, M., Crow, S. A., Toner, B. M., Katsev, S. Low sulfate systems: does organic sulfur affect isotopic fractionations? Goldschmidt Geochemistry Conference, Boston, MA USA, Aug 12-17, 2018. Oral Presentation.

Status as of July 1, 2019:

The following presentations disseminated preliminary results of this project to academic and other audiences:

- Caroline E. Pierce, Sona Psarska, James Brozowski, Stephen D. Sebestyeny, Randall K. Kolka, Natalie Griffiths, Diana Karwin, Edward A. Nater, and Brandy M. Toner (2019). The Effect of Climate Change on Methylmercury in Boreal Peatlands. Abstract accepted for the 14th International Conference on Mercury as a Global Pollutant, Krakow, Poland, Sep 8 –13, 2019

Status as of January 1, 2020:

The following presentations disseminated preliminary results of this project to academic and other audiences:

- Kolka, R.K., and P.J. Hanson. 2019. Changing environments in northern peatlands: The SPRUCE experiment. Congress of the International Union of Forestry Research Organizations. Curitiba, Brazil.
- Pierce, C.E., S. Psarska, J. Brozowski, S.D. Sebestyeny, R.K. Kolka, N. Griffiths, D. Karwan, E.A. Nater, and B.M. Toner (2019). The Effect of Climate Change on Methylmercury in Boreal Peatlands. Abstract to the International Conference on Mercury as a Global Pollutant 2019 Conference Abstract.
- Fissore, C., E.A. Nater, K.J. MacFarlane, and A.S. Klein. 2019. Carbon dynamics over the last 50 years in three boreal peatlands in northern Minnesota, USA. *Biogeochemistry* (145): 1-2, 63-79.

Oral presentations in the field were given to the following local groups in 2019:

- Greenway High School Science Class
- Landscape Ecology, Bemidji State University
- Forest Ecology, Itasca Community College
- Trek North High School Science Class from Bemidji for Science Day
- Wilderness Inquiry Youth Group
- Field Study of Soils, University of Minnesota
- Michigan Tech Society of Wetlands Science Student Chapter
- Natural Resources, Leech Lake Tribal College

Status as of July 1, 2020:

The following presentations disseminated preliminary results of this project to academic and other audiences:

- Pierce C., Kolka R., Sebestyeny S., Griffiths N., Nater E. & Toner B. (2020) Warming causes increased total mercury and decreased methylmercury in porewaters. *2020 SPRUCE all-hands annual meeting*. May 12-13, 2020.
- Pierce, C., Sebestyeny, S., Kolka, R., Griffiths, N., Nater, E., Toner, B. (2020) The effect of climate change on methylmercury in boreal peatlands. *Goldschmidt International Geochemistry Conference*. June 21-26, 2020.
- Gutknecht J., Felice M., Pierce C., Nater E., Kolka R. & Sebestyeny S. (2020) Determining Future Potential Release of Mercury and Sulfur from Peatlands to the Lake Superior Basin. *2020 SPRUCE all-hands annual meeting*. May 12-13, 2020.

- Kolka, R. 2020. The Spruce and Peatland Responses Under Changing Environments (SPRUCE) Experiment on the Marcell Experimental Forest: Cutting edge peatland climate change research. Webinar. *The Nature Conservancy Regional Brown Bag Lunch Meeting*. May 28, 2020.
- Kolka, R. 2020. The Spruce and Peatland Responses Under Changing Environments (SPRUCE) Experiment on the Marcell Experimental Forest: Cutting Edge Peatland Climate Change Research. *Michigan Technological University College of Forest Resources and Environmental Science Seminar Series*. Houghton, MI. February 13, 2020.

Oral presentations in the field were given to the following local groups in 2020:

- Ely, MN Climate Change Discussion Group, Ely, MN

We also disseminated preliminary results of this project to Duluth area and Twin Cities area TV programs:

- Kolka, R. 2019. Special Report: Rising Concerns. Television Interview. WDIO 13 News, Duluth, MN, aired 11/13/2019 and 11/14/2019. <https://www.wdio.com/news/rising-concerns-temperatures-global-warming-climate-change-northland/5549961/>
- Kolka, R. 2019. Tucked away in a northern Minnesota forest, researchers work on first-of-its-kind climate change experiment. Television Interview. KARE 11 News, Minneapolis, aired 10/24/2019 and 10/25/2019. <https://www.kare11.com/article/news/local/northern-mn-climate-change-experiment-has-global-implications/89-90b32992-3b4a-4033-bc72-0df3686d641f>

Status as of January 1, 2021:

The following are presentations at professional meetings or conferences:

- Gutknecht J., Felice M., Pierce C., Nater E., Kolka R. and Sebestyen S. Determining Future Potential Release of Mercury and Sulfur from Peatlands to the Lake Superior Basin. Volunteered presentation to the 2020 SPRUCE all-hands virtual annual meeting. May 12-13, 2020.
- Pierce, C.E., Sebestyen, S.D., Kolka, R.K., Griffiths, N., Nater, E.A., Toner, B.M. Mercury and Sulfur Characterization of Peat in the SPRUCE Project at Marcell Experimental Forest. 2020 Canadian Light Source User's Meeting, virtual, October 2020. (poster)
- Pierce, C.E., Sebestyen, S.D., Kolka, R.K., Griffiths, N., Nater, E.A., Toner, B.M. Warming Causes Increased Total Mercury and Decreased Methylmercury in Boreal Peatland Porewaters. 2020 Goldschmidt Geochemical Society Conference, virtual, June, 2020. (presentation)
- Pierce, C.E., Sebestyen, S.D., Kolka, R.K., Griffiths, N., Nater, E.A., Toner, B.M. Warming Causes Increased Total Mercury and Decreased Methylmercury in Porewaters. Spruce and Peatland Responses Under Changing Environments (SPRUCE) Annual All-Hands Meeting, Minneapolis, MN, May, 2020. (presentation)

The following presentations were provided to interested groups in Minnesota:

- Invited presentation, Minnetonka High School Vantage Program, "Marcell Experimental Forest and the Spruce and Peatland Responses Under Changing Environments (SPRUCE) Experiment (Peatlands & Mercury)", February 25, 2020
- Invited presentation, Macalester College Ecosystem Ecology class, "Peering into a warmer world: Effects of experimental warming on Peatlands", April 17, 2020
- Invited Presentation, Minnesota Tribal Environmental Council quarterly meeting "Future Release of Mercury and Sulfur from Peatlands" July 29, 2020.

Status as of July 1, 2021:

The following are presentations at professional meetings or conferences:

- Pierce, C.E., Furman, O.S., Nicholas, S.L., Coleman Wasik, J., Sebestylen, S.D., Kolka, R.K., Mitchell, C.P.J., Griffiths, N., Nater, E.A., Toner, B.M. The Role of Ester Sulfate and Organic Disulfide in Mercury Methylation in Peat Soils. 2021 Spruce and Peatland Responses Under Changing Environments (SPRUCE) Annual All-Hands Meeting, virtual, May 12, 2021 (presentation)
- Felice, M., and J. Gutknecht. Measuring sulfur-cycling processes in peatlands. 2021 Spruce and Peatland Responses Under Changing Environments (SPRUCE) Annual All-Hands Meeting, virtual, May 12, 2021 (presentation)
- Pierce, C.E., Furman, O.S., Nicholas, S.L., Coleman Wasik, J., Sebestylen, S.D., Kolka, R.K., Mitchell, C.P.J., Griffiths, N., Nater, E.A., Toner, B.M. The Role of Ester Sulfate and Organic Disulfide in Mercury Methylation in Peat Soils. 2021 International Peatland Conference, virtual, May 5, 2021 (presentation)
- Kolka, R. 2021. Simulating climate change in a northern peatland: Early results of the SPRUCE experiment. Virtual Presentation, International Peat Congress.
- Pierce, C.E., Furman, O.S., Nicholas, S.L., Coleman Wasik, J., Sebestylen, S.D., Kolka, R.K., Mitchell, C.P.J., Griffiths, N., Nater, E.A., Toner, B.M. The Role of Ester Sulfate and Organic Disulfide in Mercury Methylation in Peat Soils. 2021 UMN Earth Student Research Symposium, virtual, April 1, 2021 (presentation)
- Kolka, R. 2021. The Marcell Experimental Forest, peatlands and the Spruce and Peatlands Response to Changing Environments (SPRUCE) experiment. Virtual Graduate Student Seminar, Department of Soil Science. University of Wisconsin. Madison, WI.

The following presentations were provided to interested groups in Minnesota:

- Kolka, R. 2021. The Marcell Experimental Forest, peatlands and the Spruce and Peatlands Response to Changing Environments (SPRUCE) experiment. Virtual Seminar, The Nature Conservancy of Minnesota, North Dakota, and South Dakota.
- Kolka, R. 2021. The Marcell Experimental Forest, peatlands and the Spruce and Peatlands Response to Changing Environments (SPRUCE) experiment. Virtual Seminar, Detroit Lakes, MN Festival of Birds.

The following scientific publications were published:

- Woerndle, G.E., M. T-K. Tsui, S.D. Sebestylen, J.D. Blum, X. Nie, and R.K. Kolka. 2018. New insights on ecosystem mercury cycling revealed by stable isotopes of mercury in water flowing from a headwater peatland catchment. *Environmental Science and Technology*. 52: 1854-1861.
- Haynes, K.M., E. Kane, L. Potvin, E. Lilleskov, R.K. Kolka, and C.P.J. Mitchell. 2017. Gaseous mercury fluxes in peatlands and the potential influence of climate change. *Atmospheric Environment*, 154: 247-259.

The following scientific manuscript has been submitted and is in revision:

- Pierce, C.P., O.S. Furman, S.L. Nicholas†, J. Coleman Wasik, C.M. Gionfriddo, A.M. Wymore, S.D. Sebestylen, R.K. Kolka, C.P.J. Mitchell, N. Griffiths, D.A. Elias, E.A. Nater, and B.M. Toner. 2021. The Role of Ester Sulfate and Organic Disulfide in Mercury Methylation in Peat Soils. Submitted to *Environmental Science & Technology*. In Revision.

Final Report Summary:

Project members have presented various aspects of this work to professional colleagues at national meetings and at the SPRUCE project annual meetings.

Project members have given numerous oral presentations to interested parties in the region, including students in several high school and college courses, the Leech Lake Tribal College, wilderness advocacy groups, the Ely, MN Climate Change Discussion Group, local television news programs, the Minnesota Tribal Environmental Council, The Nature Conservancy of MN, ND, and SD, and numerous presentations to individuals and groups visiting the SPRUCE research site at the Marcell Experimental Forest north of Grand Rapids, MN.

We have also published 3 peer-reviewed scientific manuscripts of related work conducted on site and have a fourth manuscript in revision at this time.

Future plans for dissemination include share our report to the ad hoc environmental mercury group from the Pollution Control Agency, Department of Health, and Department of Natural Resources and meeting with them to discuss its implications for Minnesota surface waters and fisheries in the future. Likewise, we will share our report with the Minnesota Tribal Environmental Council and will meet with them if they desire to do so.

We also plan to publish the results of this study in one or more peer-reviewed scientific manuscripts.

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	Amended \$ Amount	Overview Explanation
Personnel:	\$220,831	<u>\$246,358</u>	Postdoctoral Fellow \$55,080 (81.7% salary, 18.3% fringe), 100% FTE for 2 years total (estimated \$111,812). Scientific Technician \$40,768 (78.5% salary, 21.5% fringe), 100% for 2 years total (estimated \$82,759). Undergraduate Researchers \$11.00 per hour (100% salary), 600 hrs over 2 years (estimated \$13,200). Dr. Brandy Toner \$125,456 (74.8% salary, 25.2% fringe), 0.05 FTE for 0.5 years (estimated \$4,000).
Professional/Technical/Service Contracts:	\$7,400	<u>\$0</u>	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) Dr. Carl Mitchell, University of Toronto-Scarborough, has provided his services as an in-kind contribution to this project.

Professional/Technical/Service Contracts:	\$9,600	\$10,205	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)
Equipment/Tools/Supplies:	\$34,677	\$35,168	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, 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	\$1,953	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	\$6,316	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	\$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 Equivalent (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	\$329,896	Develop methods and collect background data. Collect water and peat samples, analyze water samples for carbon, nitrogen, and sulfur. Support personnel
National Science Foundation	\$102,000	\$102,000	Graduate Fellowship. Supports one PhD student.
USDA Forest Service	\$47,030	\$47,030	General supplies and personnel support for sampling and analyses
US Department of Energy through USDA Forest Service	\$120,000	\$120,000	General support for personnel and supplies
USDA Forest Service	\$160,000	\$160,000	Post doc support and limited support for supplies and other salaries.

USDA Forest Service	\$142,243	\$142,243	Support for post doc, personnel and supplies
USDA Forest Service	\$128,502	\$128,502	Support for personnel and supplies
Dr. Carl Mitchell, University of Toronto - Scarborough	\$7,400	\$0	In-kind contribution. Dr. Mitchell has agreed to analyze the passive atmospheric mercury samplers for free.
Minnesota Sea Grant	\$146,709	\$106,709	Graduate student, supplies, analyses
State			
University of Minnesota	\$40,380	\$40,380	Graduate Student Assistantship, develop microbial methods and collect background data
University of Minnesota	\$40,380	\$40,380	Graduate Student Fellowship, analyzing samples for mercury and sulfur
University of Minnesota, indirect cost recovery waiver	\$156,000	\$0	Matching funds
TOTAL OTHER FUNDS:	\$1,420,540	\$1,267,221	\$1,217,140

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.	September 1, 2016 - August 31, 2018	\$80,760
USDA Forest Service, supplies and personnel support for sampling and analyses	December 22, 2017 - July 24, 2020	\$47,030
US Department of Energy through USDA Forest Service, general support for this project	July 12, 2017 - August 25, 2019	\$60,000
NSF Graduate Research Fellowship - supports one graduate student for 3 years	September 1, 2019 to August 31, 2022	\$102,000
USDA Forest Service, support for a postdoctoral researcher and limited support for supplies and other salaries	October 1, 2017 to September 30, 2022	\$160,000
USDA Forest Service, general support for personnel and supplies	June 27, 2018 - June 1, 2023	\$142,243
USDA Forest Service, general support for personnel and supplies	September 30, 2019 = September 29, 2020	\$128,502
Minnesota Sea Grant, partial support for 2 more years of this study, including graduate student salaries, analyses, and supplies	July 1, 2020 to June 30, 2022	\$146,709
Dr. Carl Mitchell, University of Toronto-Scarborough, in-kind contribution of services for analysis of passive atmospheric mercury samplers	July 1, 2018 - June 30, 2021	\$7,400
		\$1,264,540

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. 04i as extended by M.L. 2020, First Special Session, Chp. 4, Sec. 2*

Project Manager: *Ed Nater*

Organization: *University of Minnesota*

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

Project Length and Completion Date: 4 years, June 30, 2021

Date of Report: *September 15, 2021*

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Revised Budget (6/11/2021)	Amount Spent	Activity 1 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM					
Personnel (Wages and Benefits)	\$246,358	\$246,358	\$0	\$246,358	\$0
<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	\$10,205	\$10,205	\$0	\$10,205	\$0
<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. 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	\$35,168	\$35,168	\$0	\$35,168	\$0
<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	\$1,953	\$1,953	\$0	\$1,953	\$0
<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	\$6,316	\$6,316	\$0	\$6,316	\$0
<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	\$0	\$300,000	\$0

**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. 04i as extended by M.L. 2020, First Special Session, Chp. 4, Sec. 2*

Project Manager: *Ed Nater*

Organization: *University of Minnesota*

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

Project Length and Completion Date: 4 years, June 30, 2021

Date of Report: June 11, 2021

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Revised Budget (06/30/2020)	Activity 1 Revised Budget (6/11/2021)	Amount Spent	Activity 1 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM						
Personnel (Wages and Benefits)	\$250,542	\$246,358	\$246,358	\$0	\$246,358	\$0
<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	\$10,205	\$10,205	\$10,205	\$0	\$10,205	\$0
<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. 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	\$30,984	\$35,168	\$29,857	\$5,311	\$35,168	\$5,311
<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	\$1,953	\$1,953	\$1,953	\$0	\$1,953	\$0
<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	\$6,316	\$6,316	\$6,316	\$0	\$6,316	\$0
<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	\$294,688	\$5,311	\$300,000	\$5,311

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



Project Title: *Assessing Release of Mercury and Sulfur on Aquatic Communities*
Legal Citation: *\$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.*

Project Manager: *Ed Nater*

Organization: *University of Minnesota*

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

Project Length and Completion Date: *4 years, June 30, 2021*

Date of Report: *January 8, 2021*

	Activity 1 Revised Budget (06/30/2020)	Activity 1 Revised Budget (01/01/2021)	Amount Spent	Activity 1 Balance	TOTAL BUDGET	TOTAL BALANCE
ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET						
BUDGET ITEM						
Personnel (Wages and Benefits)	\$250,542	\$246,358	\$246,358	\$0	\$246,358	\$0
<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	\$10,205	\$10,205	\$10,205	\$0	\$10,205	\$0
<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>						

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

Equipment/Tools/Supplies	\$30,984	\$35,168	\$29,857	\$5,311	\$35,168	\$5,311
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.						
Travel expenses in Minnesota	\$1,953	\$1,953	\$1,953	\$0	\$1,953	\$0
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	\$6,316	\$6,316	\$6,316	\$0	\$6,316	\$0
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.						
COLUMN TOTAL	\$300,000	\$300,000	\$294,688	\$5,311	\$300,000	\$5,311

Graphics

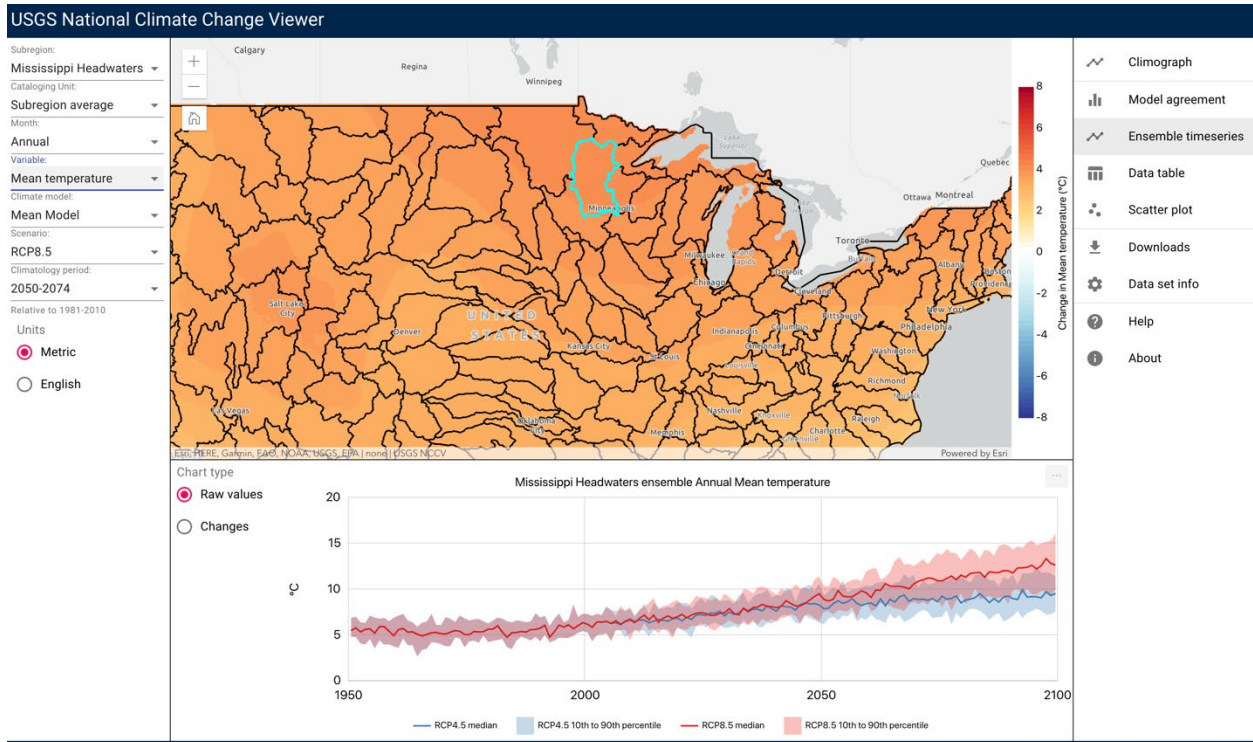


Figure 1. The USGS National Climate Change Viewer showing the Mississippi Headwaters Watershed and the climate model predictions for average annual maximum temperature from 1950 to 2100. Predictions are based on ensemble calculations from 20 different climate models, each using two different (RCP4.5 and RCP8.5) scenarios.

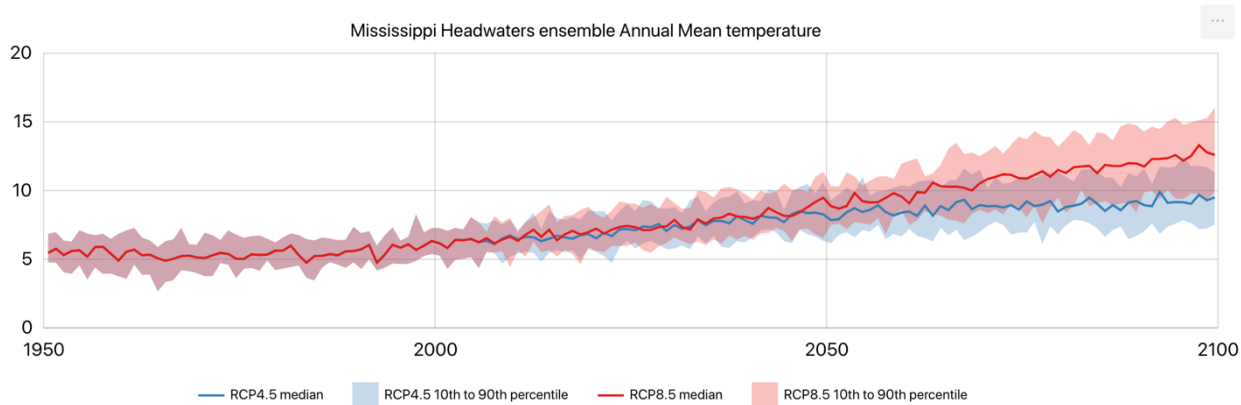


Figure 2. Annual average temperatures (degrees C) in the Upper Mississippi River watershed predicted by USGS Climate Change Viewer for the years 1950 to 2100 based on ensemble climate modeling. All models predicted a statistically significant increase in temperature over this period.

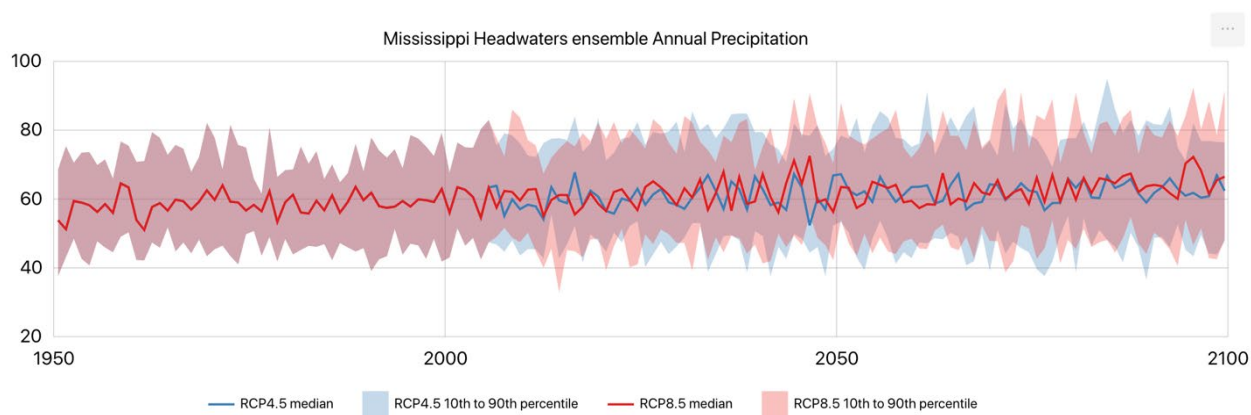


Figure 3. Annual precipitation (mm per month) in the Upper Mississippi River watershed predicted by USGS Climate Change Viewer for the years 1950 to 2100 based on ensemble climate modeling. 65% of the models predicted an increase in precipitation, with 15% of those predicting a statistically significant increase.

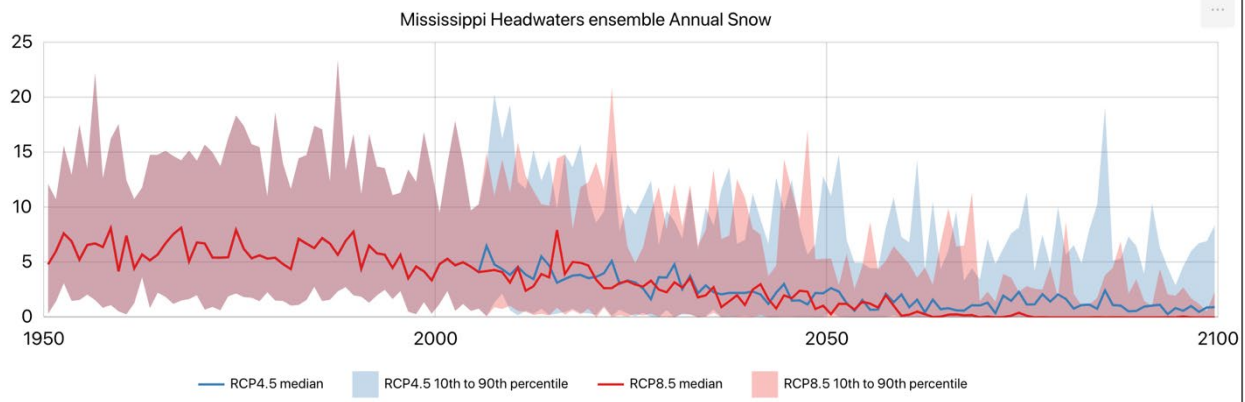


Figure 4. Annual snowfall (water content, in units of mm per month) in the Upper Mississippi River watershed predicted by USGS Climate Change Viewer for the years 1950 to 2100 based on ensemble climate modeling. All models predicted a decrease in snowfall, with 95% of those predicting that it would be statistically significant.

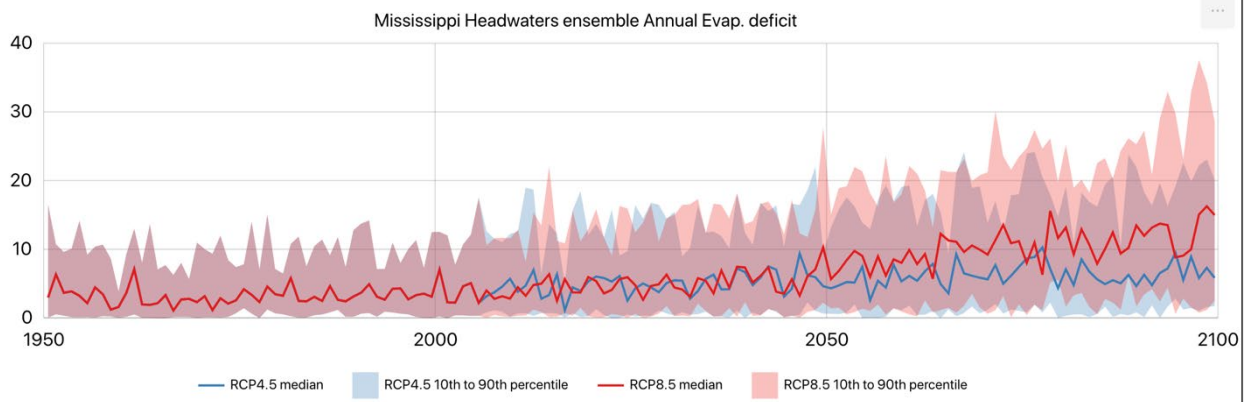


Figure 5. Annual evaporative demand (mm per month) in the Upper Mississippi River watershed predicted by USGS Climate Change Viewer for the years 1950 to 2100 based on ensemble climate modeling. 95% of models predicted an increase in evaporative demand, with 75% of those predicting a statistically significant change.

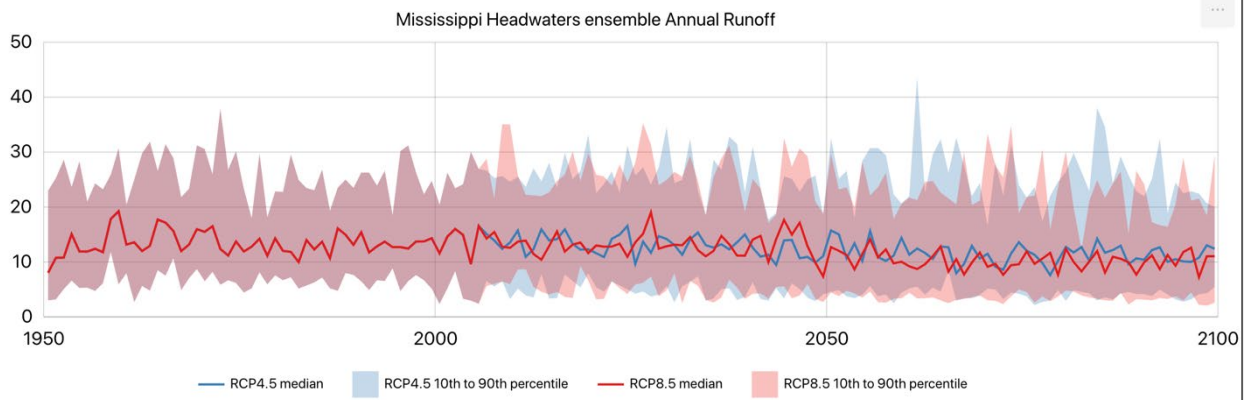


Figure 6. Annual runoff (mm per month) in the Upper Mississippi River watershed predicted by USGS Climate Change Viewer for the years 1950 to 2100 based on ensemble climate modeling. 80% of the models predicted a decrease in runoff, with 45% of those predicting that it would be statistically significant.

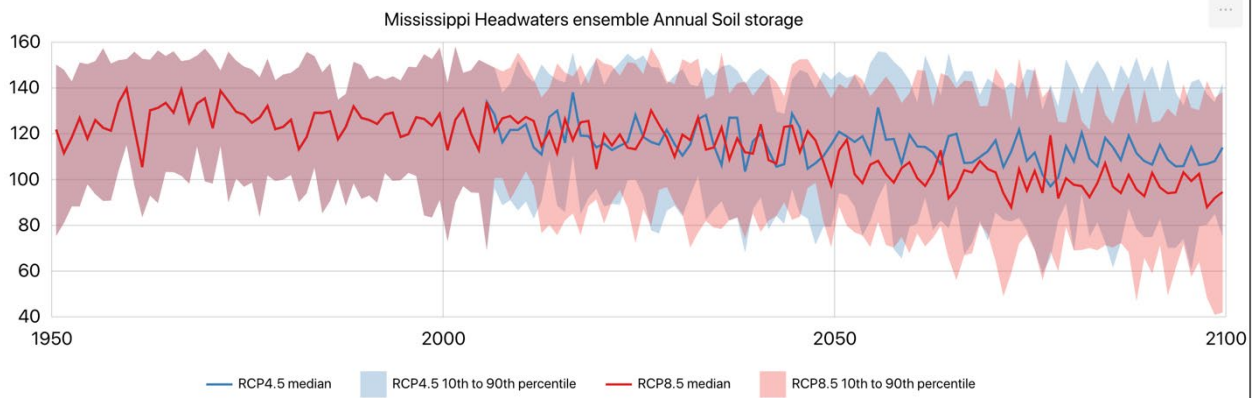


Figure 7. Annual soil water storage (mm) in the Upper Mississippi River watershed predicted by USGS Climate Change Viewer for the years 1950 to 2100 based on ensemble climate modeling. 90% of all models predicted that soil storage would decrease with 75% of those predicting that it would be statistically significant.

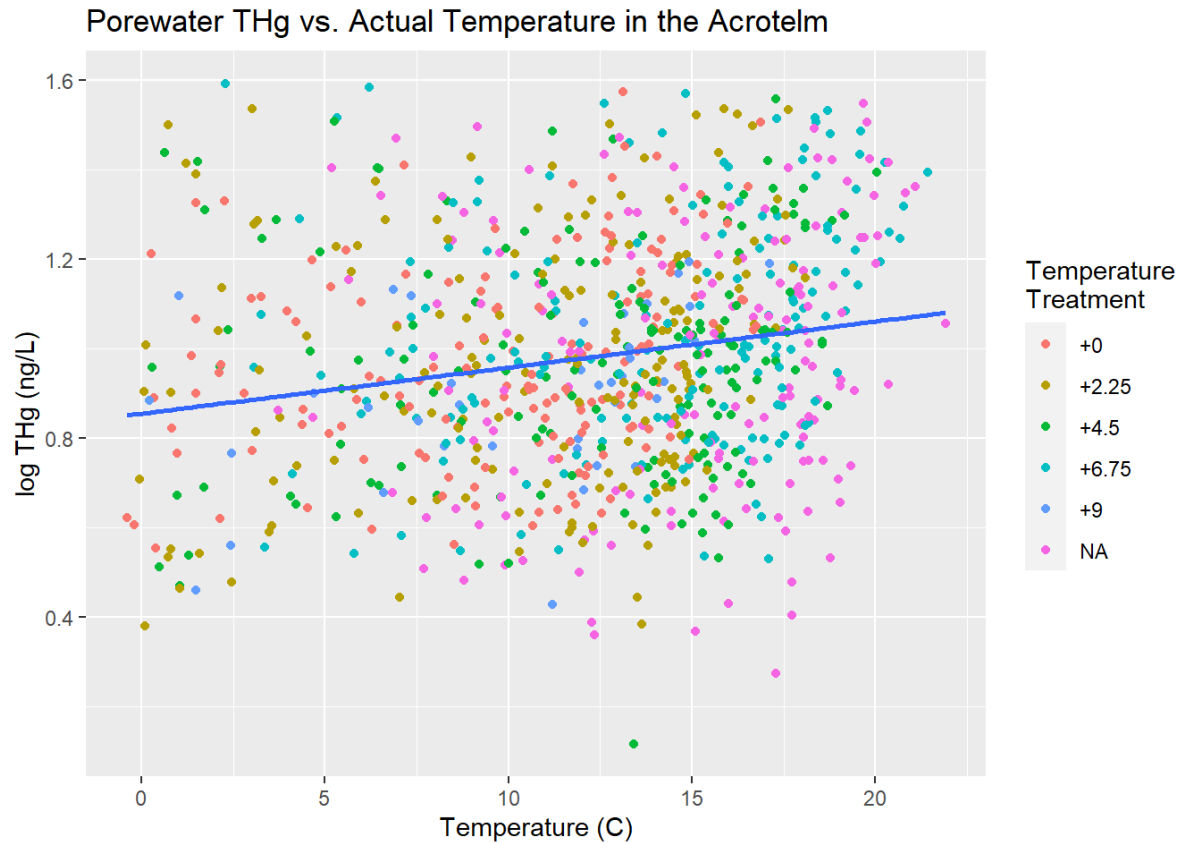


Figure 8. Linear regression of the log of total mercury in porewater vs soil temperature in the acrotelm (porewater samples within 40 cm depths of the surface). The relationship was not significant ($\alpha < 0.5$) in either the ambient CO₂ plots or the elevated CO₂ plots. Statistical parameters for the regression line are: $n = 848$, $R^2 = 0.0356$, $F = 32.26$, $p = 1.856e-08$. The regression equation is: $\log \text{THg} = 0.855665 + 0.010301 * \text{Temp}$.

Porewater THg vs. Actual Temperature in the Catotelm

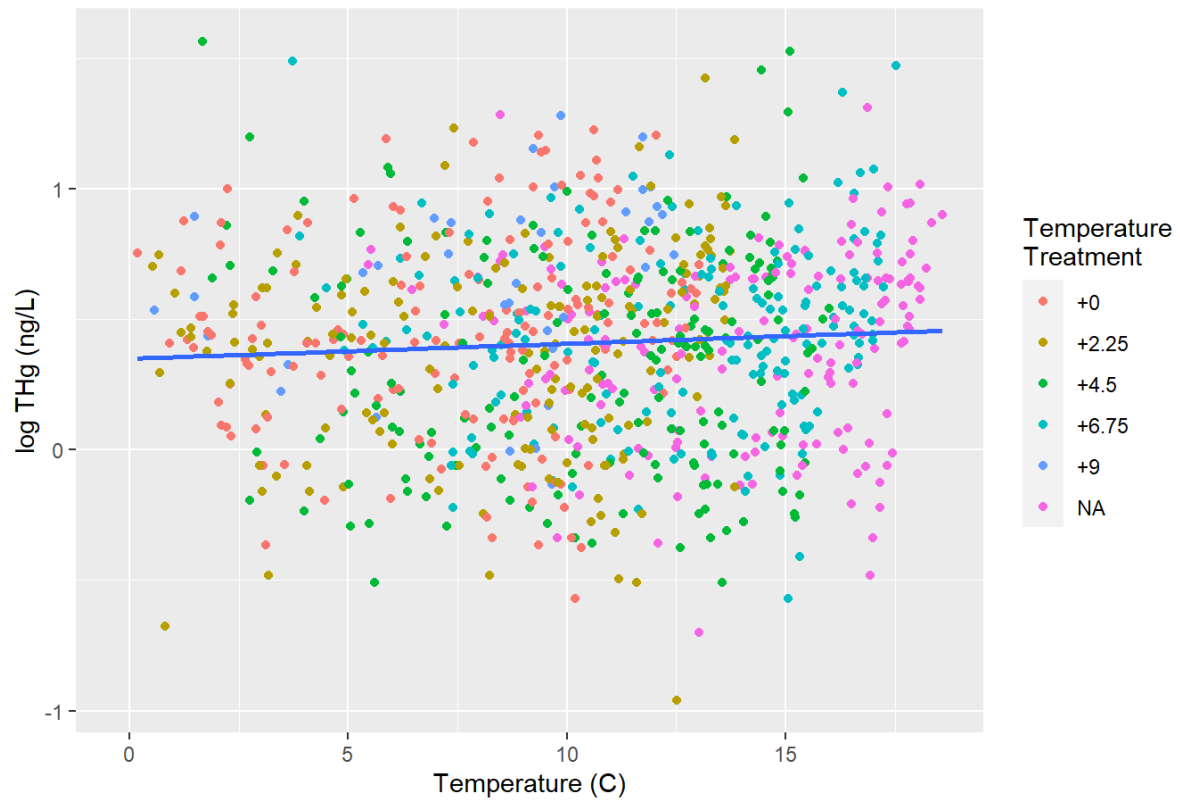


Figure 9. Linear regression of the log of total mercury in porewater vs soil temperature in the catotelm (samples from 50 - 200 cm depths). The relationship was not statistically significant ($p = 0.0607$).

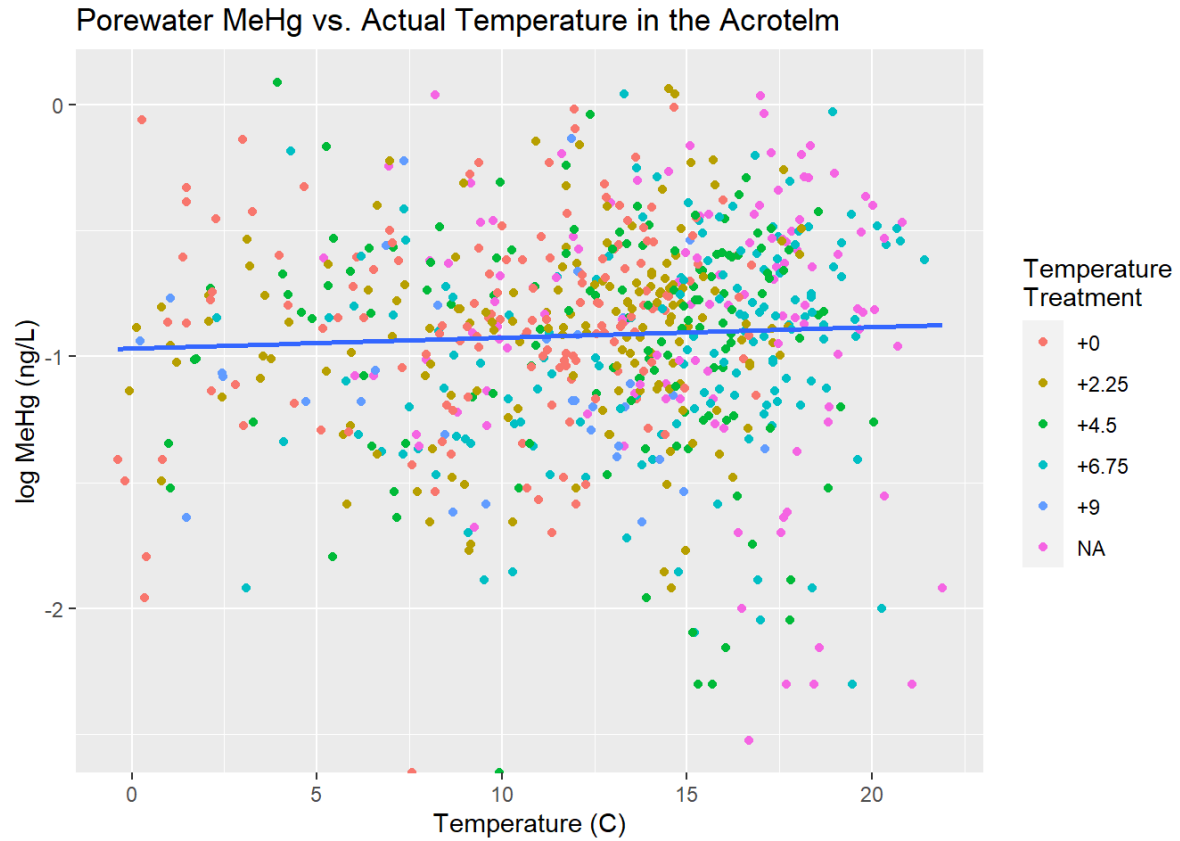


Figure 10. Linear regression of the log of methylmercury in porewater vs soil temperature in the acrotelm (porewater samples within 40 cm depths of the surface). The relationship was not statistically significant ($p = 0.4444$).

Porewater MeHg vs. Actual Temperature in the Catotelm

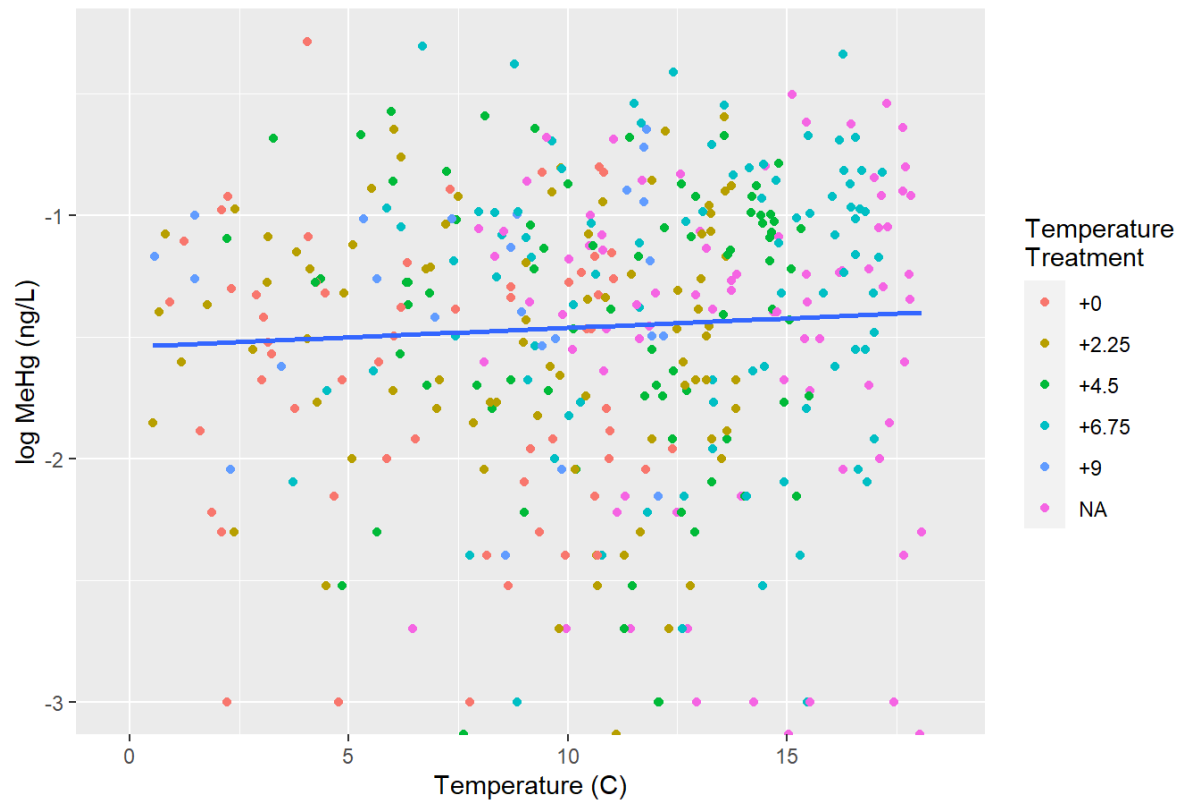


Figure 11. Linear regression of the log of total mercury in outflow vs soil temperature measured at a 20 cm depth. The relationship was not statistically significant ($p = 0.4063$).

Porewater Sulfate vs. Actual Temperature in the Acrotelm

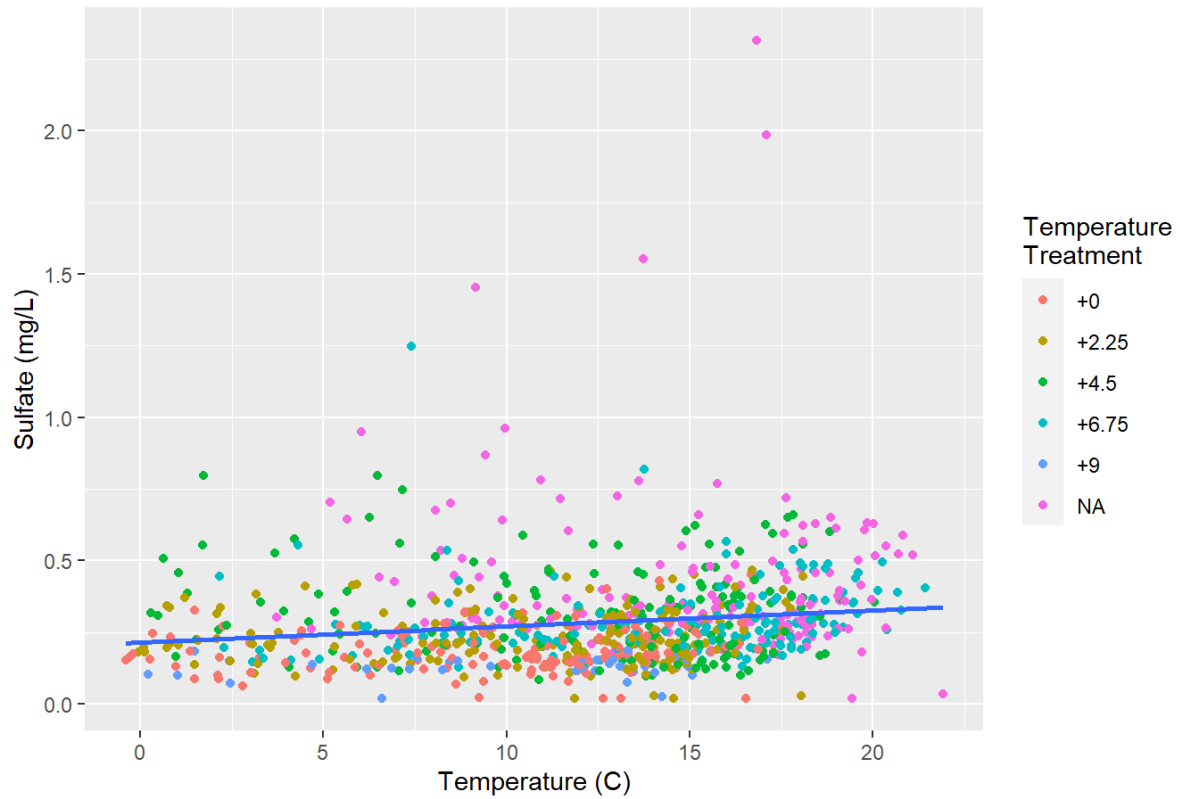


Figure 12. Linear regression of sulfate in porewater vs soil temperature in the acrotelm (porewater samples within 40 cm depths of the surface). Statistical parameters for the regression equation are: $n = 854$, $R^2 = 0.0215$, $f = 19.77$, $p = 9.907e-06$. The regression equation is: $\text{Sulfate} = 0.214543 + 0.005603 * \text{Temp}$.

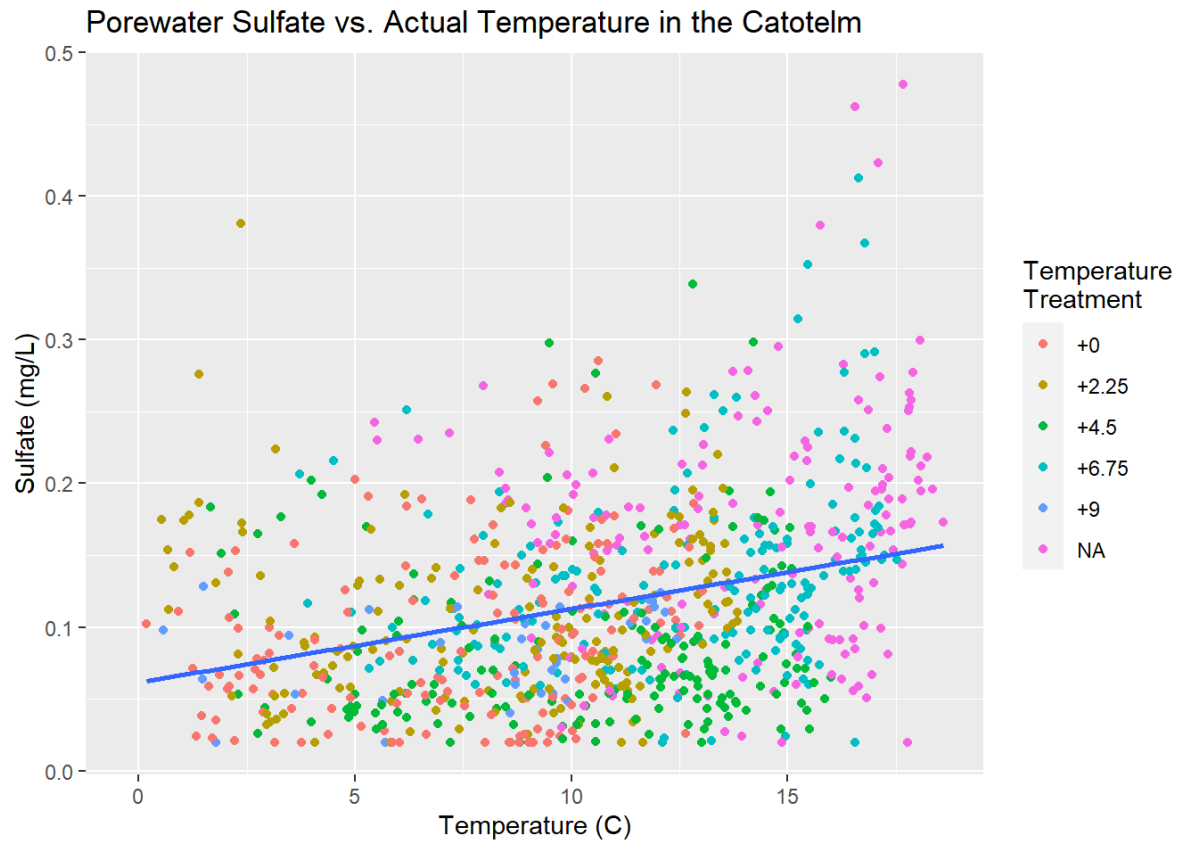


Figure 13. Linear regression of sulfate in porewater vs soil temperature in the catotelm (porewater samples within 40 cm depths of the surface). Statistical parameters for the regression equation are: $n = 869$, $R^2 = 0.09789$, $f = 95.3$, $p < 2.2e-16$. The regression equation is: $\text{Sulfate} = 0.061567 + 0.0051203 * \text{Temp}$.

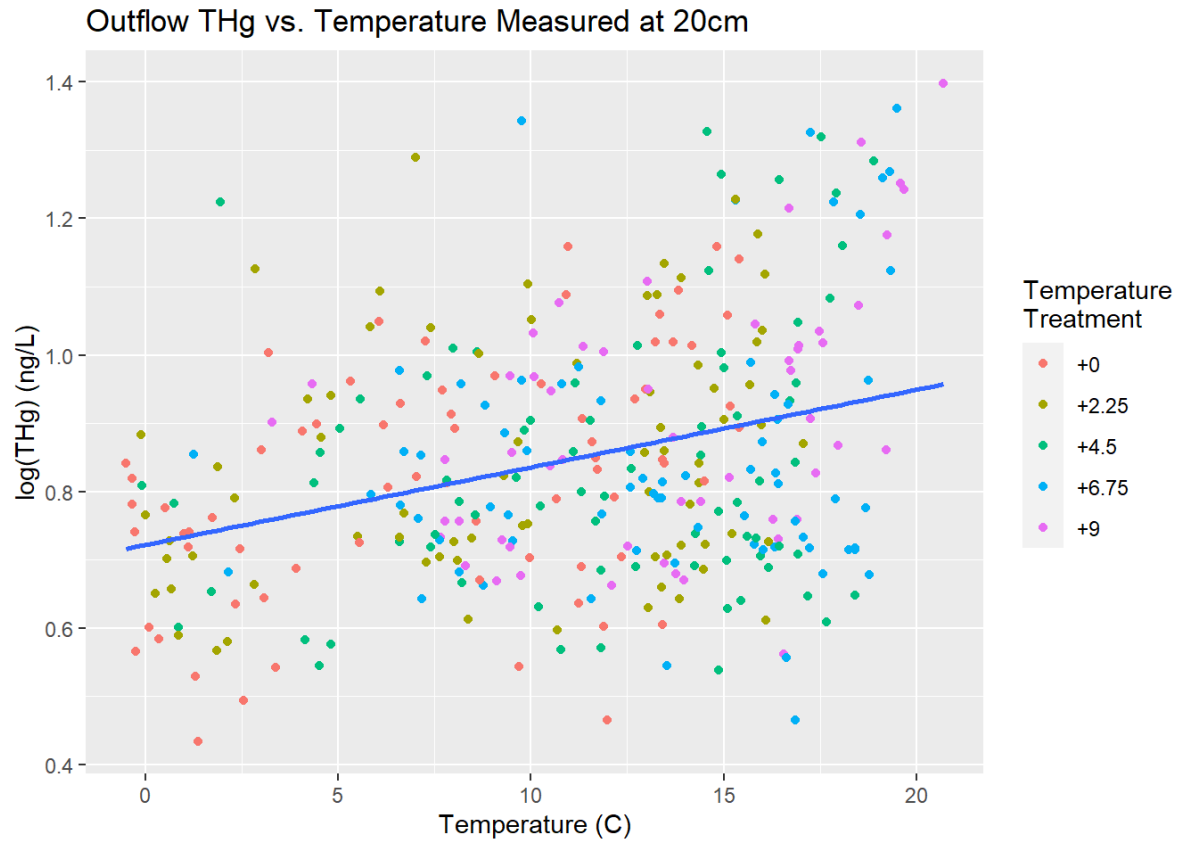


Figure 14. Linear regression of the log of total mercury in outflow vs soil temperature in the enclosure measured at a 20 cm depth. Statistical parameters for regression are: $n = 3430$, $R^2 = 0.1015$, $f = 39.74$, $p = 8.931e-10$. The regression equation is: $\text{THg} = 0.72197 + 0.011373 * \text{Temp}$.

Outflow MeHg vs. Temperature Measured at 20cm

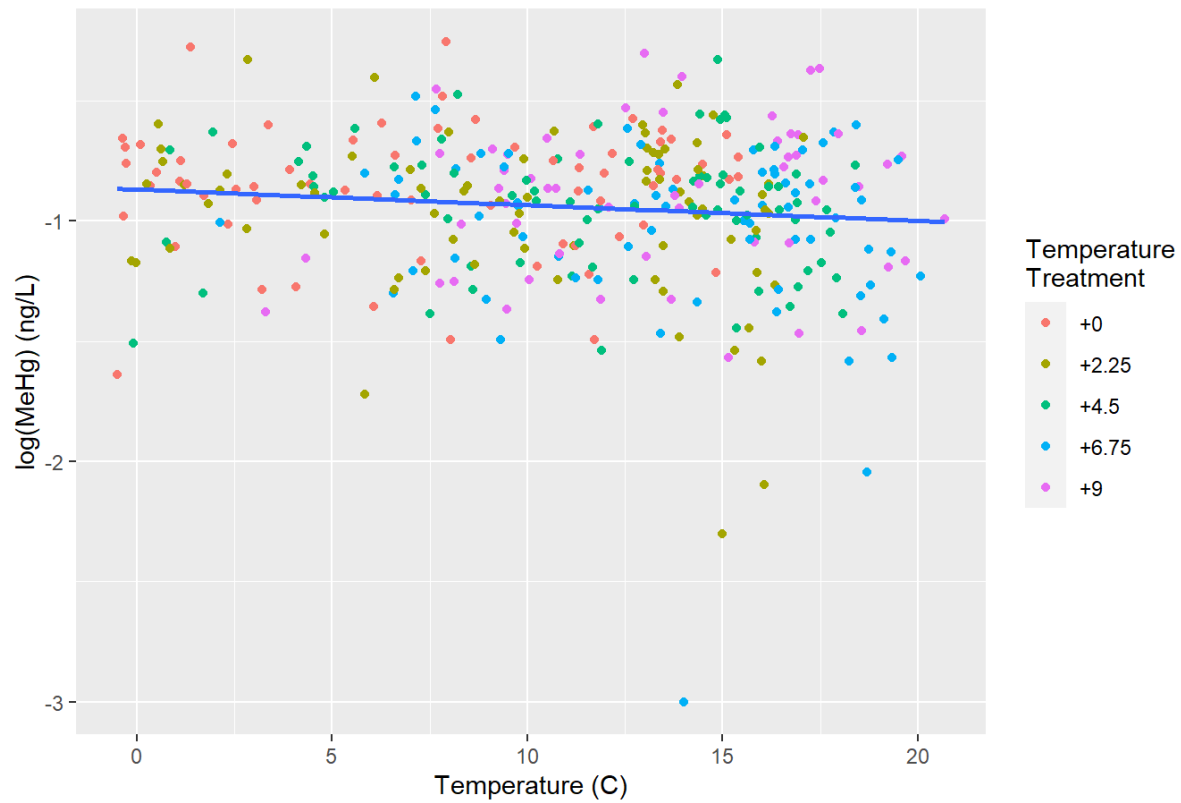


Figure 15. Linear regression of the log of methylmercury concentrations in outflow vs soil temperature measured in the enclosure at a 20 cm depth. The relationship was not statistically significant ($p = 0.4311$).

Outflow Sulfate vs. Temperature Measured at 20cm

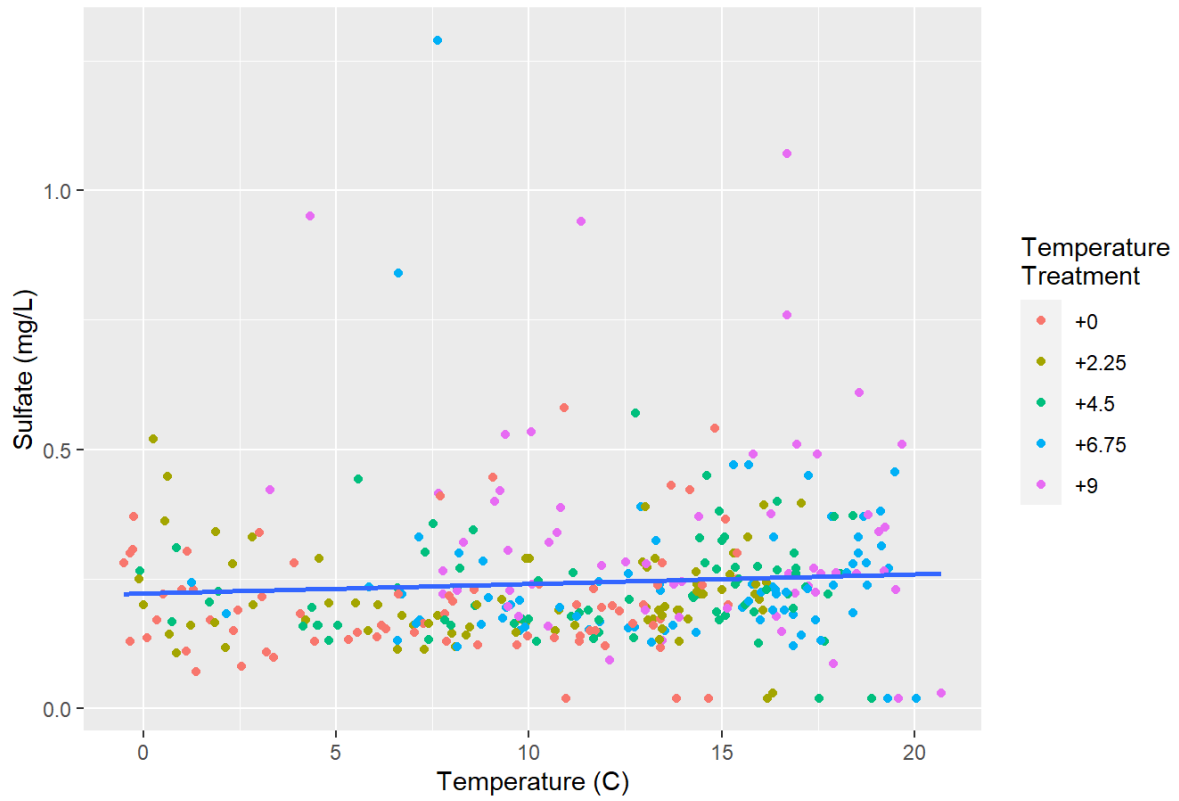


Figure 16. Linear regression of sulfate concentrations in outflow vs soil temperature measured in the enclosure at a 20 cm depth. The relationship was not statistically significant ($p = 0.1944$).

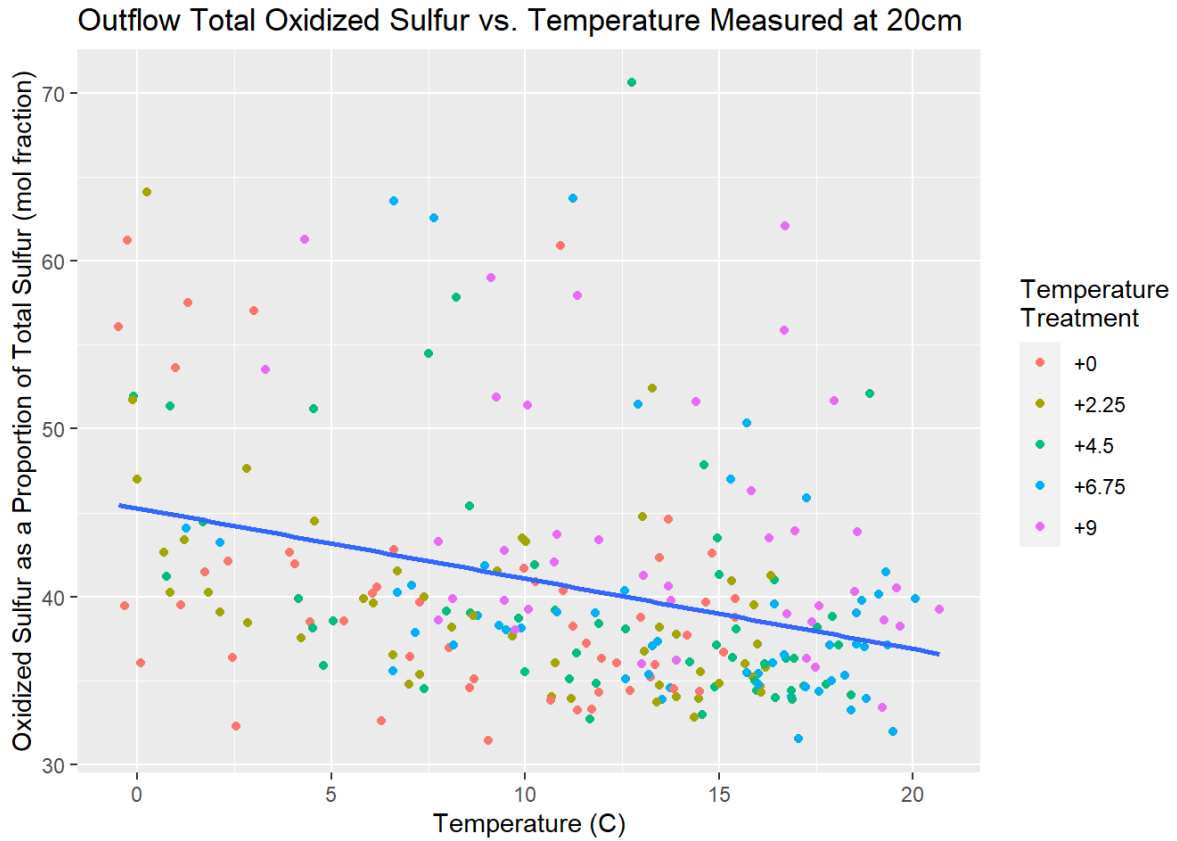


Figure 17. Linear regression of the mole percent of oxidized sulfur species on dissolved organic matter in outflow vs soil temperature measured at a 20 cm depth. Statistical parameters for the regression are: $n = 243$, $R^2 = 0.09791$, $f = 27.37$, $p = 3.632e-07$. The regression equation is: Sulfate = $45.2668 - 0.4185 * \text{Temp}$.

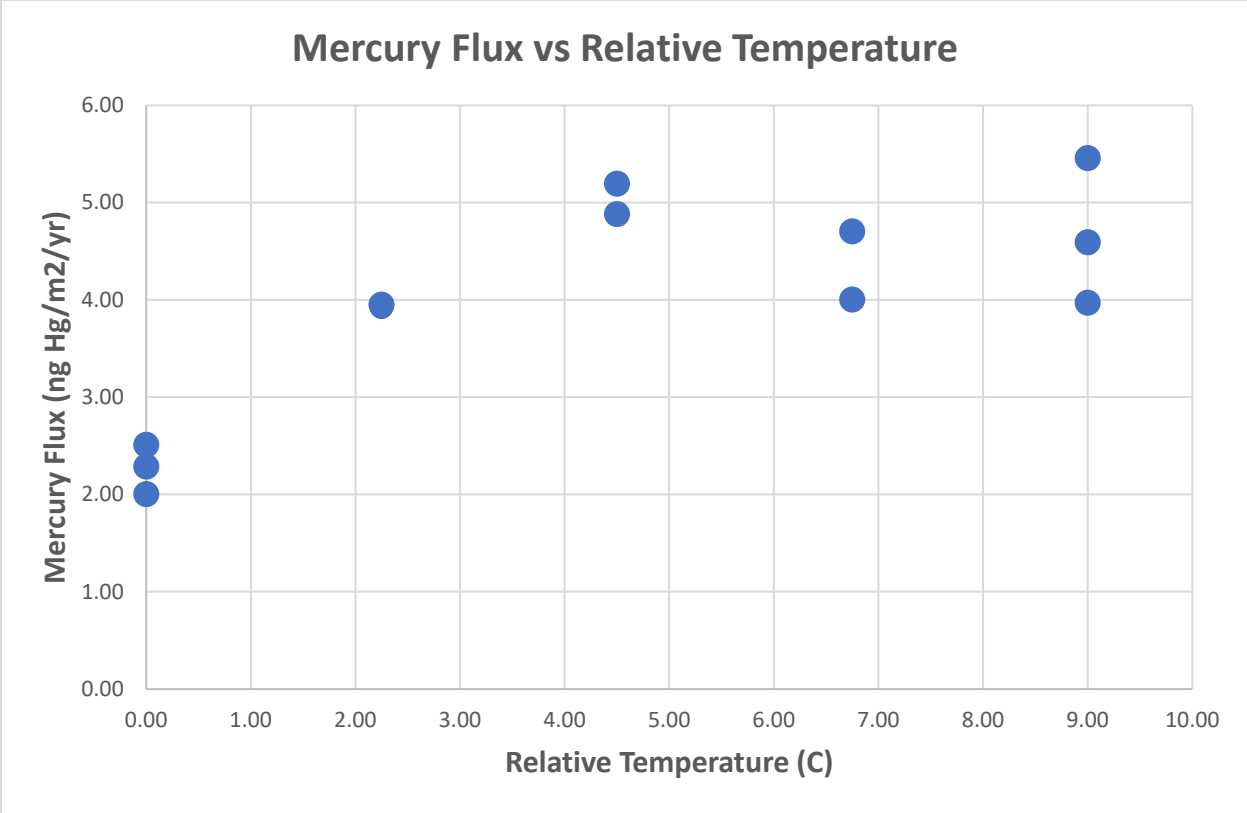


Figure 18. Mercury fluxes (ng of mercury released to the atmosphere per hour from each square meter of peat) in the SPRUCE enclosures. Positive flux values indicate release of mercury from the peat to the atmosphere. These data were measured for the period 9/26/2019 to 7/23/2020. During this period the average ambient air temperature was 2.7° C (36.9° F).

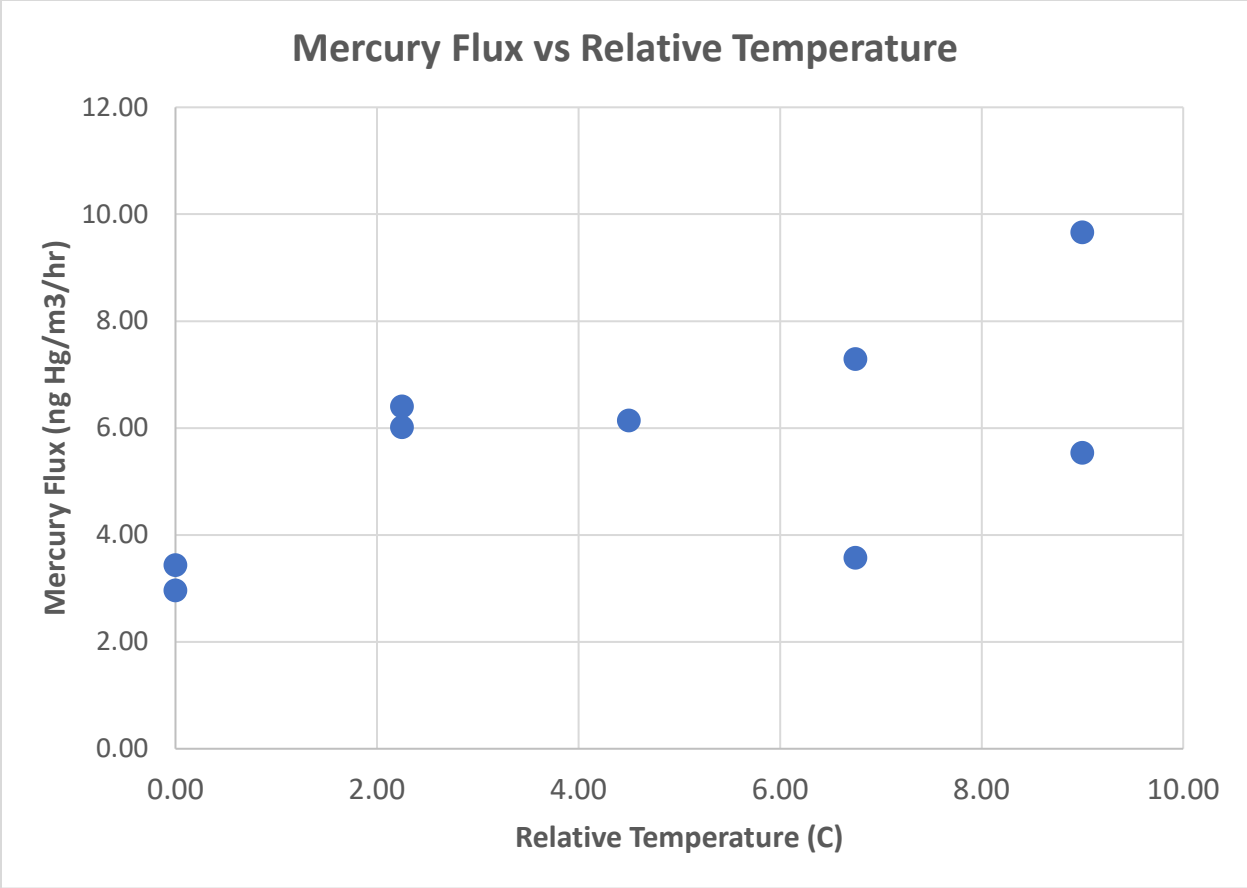


Figure 19. Mercury fluxes (ng of mercury released to the atmosphere per hour per square meter of peat) in the SPRUCE enclosures. Positive flux values indicate release of mercury from the peat to the atmosphere. These data were measured for the period 7/23/2020 to 12/4/2020. During this period the average ambient air temperature was 8.6° C (47.4° F).