

Environment and Natural Resources Trust Fund

M.L. 2023 Approved Work Plan

General Information

ID Number: 2023-063 Staff Lead: Mike Campana Date this document submitted to LCCMR: May 22, 2023 Project Title: Finding, Capturing, and Destroying PFAS in Minnesota Waters Project Budget: \$478,000

Project Manager Information

Name: William Arnold Organization: U of MN - College of Science and Engineering Office Telephone: (612) 625-8582 Email: arnol032@umn.edu Web Address: https://cse.umn.edu/

Project Reporting

Date Work Plan Approved by LCCMR: June 22, 2023

Reporting Schedule: April 1 / October 1 of each year.

Project Completion: June 30, 2026

Final Report Due Date: August 14, 2026

Legal Information

Legal Citation: M.L. 2023, Chp. 60, Art. 2, Sec. 2, Subd. 04d

Appropriation Language: \$478,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota to develop novel methods for the detection, sequestration, and degradation of poly- and perfluoroalkyl substances (PFAS) in Minnesota's lakes and rivers.

Appropriation End Date: June 30, 2026

Narrative

Project Summary: Novel methods for the detection, sequestration, and degradation of poly- and perfluoroalkyl substances (PFAS) will be developed to address a pressing contamination issue in Minnesota's lakes and rivers.

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

Poly- and perfluoroalkyl substances (PFAS), also called "forever chemicals," are common contaminants present in Minnesota's lakes, rivers, and groundwaters. PFAS are of critical concern because they have known and suspected environmental and human health impacts. Because of their widespread use in consumer and industrial products, such as in pizza boxes, stain-resistant clothing, and firefighting foam, they are also continuously released in wastewater discharges, landfill leachates, and storm water. Unfortunately, we do not yet know the full extent of the PFAS problem. Current estimates indicate there are hundreds to thousands of different PFAS chemicals in the environment, and we do not yet know how to measure the abundance of them all. In addition, current technologies for the capture and destruction of PFAS are expensive or of limited effectiveness. Together, this could lead to under-treatment or underregulation of PFAS, with the resulting exposure of humans and wildlife to PFAS. Methods to detect the full suite of PFAS present, to effectively capture PFAS, and to efficiently degrade PFAS are needed to solve this pervasive issue.

What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

A new, rapid method to determine the total amount of PFAS in water and sediment samples will be developed so that the risks posed to humans or the environment can be evaluated quickly (Activity 1). This method, using nuclear magnetic resonance (NMR) spectroscopy instead of mass spectrometry, is inspired by a previously funded ENTRF project. The advantage of NMR is that it allows quantification of total PFAS, a particular advantage when so many unidentified and unquantifiable PFAS exist. Because many individual PFAS have similar adverse impacts, it is logical to measure and treat them in total. The new method will determine total PFAS concentrations in Minnesota water and sediment samples and quantify the fraction of PFAS being overlooked (Activity 2). The NMR technique also enables the determination of how well PFAS stick to proteins or sorbents. By measuring these interactions, we will identify which chemical structures are "stickiest", which in turn will lead to the development of new sorbents to remove PFAS from water or sediment (Activity 3). By leveraging previous ENRTF-funded research focused on concentrating bacteria on non-hazardous and inert plastic carriers, we will also devise a PFAS treatment material that brings PFAS and PFAS-degrading bacteria together (Activity 4).

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

PFAS represent an urgent and pervasive problem in Minnesota's environment. The presence of PFAS threatens drinking water sources, leads to fish consumption advisories, and impacts human and ecosystem health. Additionally, the presence of PFAS burdens water and wastewater treatment systems, landfills, and other facilities with increased treatment costs. Better understanding the extent of PFAS contamination and combined with the development of ways to remove and degrade PFAS will lead to better protection and enhancement of Minnesota's resources, benefits to human health, and cost effective ways to protect the environment.

Project Location

What is the best scale for describing where your work will take place? Statewide

What is the best scale to describe the area impacted by your work? Statewide

When will the work impact occur?

During the Project and In the Future

Activities and Milestones

Activity 1: Establish the optimal sample processing and analysis protocols for measurement of total PFAS

Activity Budget: \$59,000

Activity Description:

Under a previous ENTRF project, we developed an NMR method to quantify antibiotics and pesticides that contain fluorine in their structure. Here, we will extend the method to be used for PFAS. Because the amounts of PFAS present in water and sediments are small, we will test pre-concentration methods for water and sediments. For water samples, two options are freeze drying and solid-phase extraction techniques. Solid samples will be dried and extracted with solvent. The optimization will also include using agents to reduce the number of NMR measurement cycles needed. The experiments will use laboratory-made clean samples as well as natural waters and sediments spiked with a known amount of PFAS. It is expected that both time and cost will be substantially reduced compared to the current extraction and mass spectrometry methods. The activity is a critical first step that will enable the detection of PFAS in environmental samples and development of methods for PFAS removal/degradation.

Activity Milestones:

Description	Approximate Completion Date
Optimize NMR spectroscopy measurement parameters	December 31, 2023
Optimize water sample pre-concentration method	May 31, 2024
Develop sediment extraction method	August 31, 2024
Publish methods	December 31, 2024

Activity 2: Measure total PFAS concentrations in a variety of water and sediment samples.

Activity Budget: \$186,000

Activity Description:

Because there are known to be thousands of PFAS chemicals, mass spectrometric analysis of PFAS, which focuses on a subset of PFAS, misses a potentially substantial portion of the PFAS mass present in environmental samples. Because recent work suggests PFAS could be regulated as a class instead of as individual compounds, a method to measure total PFAS concentration is urgently needed. By comparing NMR and mass spectrometry data, it will be possible to assess the fraction of PFAS that are missed and obtain a more accurate assessment of total PFAS concentrations from the NMR analyses. We will collect approximately 100 samples from lakes, rivers, groundwater, wastewater treatment plants, and landfill or compost leachates in which to measure total PFAS. These samples will be geographically dispersed in the state to capture various degrees of impact but will be focused on sites where PFAS contamination is suspected or known. We will coordinate sampling with other academic researchers and state agencies using mass spectrometry to leverage costs and allow direct comparison of the two PFAS measurement methods. When this is not possible, we will conduct the mass spectrometry measurements. The results will provide new insight into the extent of PFAS contamination in Minnesota.

Activity Milestones:

Description	Approximate Completion Date
Collect water and sediment samples	October 31, 2024
Quantify total PFAS in water and sediment samples	June 30, 2025
Assess fraction of total PFAS missed by mass spectrometry	October 31, 2025
Publication/dissemination of results	January 31, 2026

Activity 3: Quantify binding of PFAS to biomolecules and develop sorbent materials

Activity Budget: \$116,000

Activity Description:

Binding of PFAS to biological materials and surfaces is important for PFAS transport in the environment and their uptake/toxicity to biota. A deeper mechanistic understanding of these interactions will aid understanding how PFAS move in the environment and affect biota, and will lead to effective ways to remove PFAS by mimicking these interactions in a controlled way on an engineered surface. These engineered surfaces, also called sorbents, will have use for treating water or for concentrating PFAS to facilitate their biodegradation (Activity 4). By monitoring changes in the NMR spectra in the presence of sorbent molecules, we will quantify the interaction strength of PFAS with model proteins and engineered surfaces that are known or suspected to bind PFAS. By finding the "stickest" materials, we can develop optimal sorbents. PFAS chain length will be a key variable, and NMR spectroscopy will also be used to assess the portion of the PFAS molecules that interact with various materials that can then be grafted onto a non-hazardous plastic or clay base to develop sorbents for treatment of PFAS contaminated water or sediment.

Activity Milestones:

Description	Approximate Completion Date
Assess binding on model proteins	August 31, 2024
Assess binding on polymer materials	March 31, 2025
Prepare and test optimized sorbent	September 30, 2025
Publication/dissemination of results	December 31, 2025

Activity 4: Evaluate a bioactive sorbent for the capture and degradation of PFAS

Activity Budget: \$117,000

Activity Description:

A recently discovered bacterium, known as feammox, is able to degrade PFAS. This bacteria requires specialized conditions, specifically the presence of both iron and ammonium, to grow. We will leverage our collaborative relationship with the researcher who discovered PFAS-degrading feammox and previous ENTRF-inspired research that developed materials coated in zeolite particles, that concentrate ammonium on their surface to provide an ideal environment for ammonium-utilizing bacteria. The sorption of PFAS on these materials will be enhanced by the research in Activity 3, incorporating other materials that increase PFAS concentration on the surfaces, along with ammonium. These enhanced sorbents, able to locally increase both ammonium and PFAS concentration, will be tested to determine the extent to which they sorb PFAS, ammonium, and iron. These materials will then be tested to see how well they enrich PFAS-degrading fearmox bacteria. Finally, the degradation of individual and mixtures of PFAS compounds will be tested to determine if they are degraded more effectively in the presence of fearmox and the enhanced sorbents versus when they are in the presence of fearmox bacteria alone. The NMR method will allow us to determine whether the degradation leads to fluoride, which is desirable, or other, smaller PFAS.

Activity Milestones:

Description	Approximate Completion Date
Grow microorganisms; test their enrichment on the materials	September 30, 2025
Test extent of PFAS degradation enhancement in the presence of the materials	March 31, 2026
Publication/dissemination of results	June 30, 2026

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Marc Hillmyer	arc Hillmyer University of Co-investigator. Dr. Hillmyer will lead the development of the sorbent material and the development of the biological carriers for PFAS degradation. Department of Chemistry		Yes
Paige Novak	University of Minnesota, Department of Civil, Environmental, and Geo- Engineering	Co-investigator. Dr. Novak will work on the testing of the biological carriers for PFAS degradation.	Yes
William Pomerantz	University of Minnesota, Department of Chemistry	Minnesota, Department of	
Peter Jaffe	Princeton University	Advisor on Feammox	No

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines. For each of the four activities, results will be disseminated by open access peer reviewed publications in archival journals. Making the products open access will ensure maximum accessibility for stakeholders and decision makers. Data regarding measurements of PFAS concentrations in environmental samples will also be archived in the open access data repository for the University of Minnesota. In both cases, this will make information from the project widely accessible to Minnesotans and other interested parties that are working on PFAS. Results from the project will also be presented at local/regional conferences. We will also communicate key findings to scientists in the Minnesota Pollution Control Agency directly. The Environment and Natural Resources Trust Fund will be acknowledged through use of the trust fund logo or attribution language on project print and electronic media, publications, signage, presentations.

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?

The results will be disseminated to PFAS testing laboratories, agencies, stakeholders and practitioners through open access publications, direct meetings, and conference presentations. We will seek partners to produce the materials to sorb and degrade PFAS. If additional work is needed, funding from federal sources will be sought.

Other ENRTF Appropriations Awarded in the Last Six Years

Name	Appropriation	Amount Awarded
Wastewater Nitrogen Removal Technology to Protect Water Quality	M.L. 2017, Chp. 96, Sec. 2, Subd. 04b	\$450,000
Benign Design: Environmental Studies Leading to	M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2,	\$415,000
Sustainable Pharmaceuticals	Subd. 04b	

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineli gible	% Bene fits	# FTE	Class ified Staff?	\$ Amount
Personnel								
Principal Investigator - William Arnold		Project coordination			25%	0.18		\$52,865
co-Principal Investigator - Marc Hillmyer		Lead sorbent development			25%	0.06		\$28,254
co-Principal Investigator - Paige Novak		Coordinate PFAS biodegradation experiments			25%	0.06		\$18,800
Graduate Student 1		Perform NMR method development and PFAS quantification studies			47%	1.5		\$144,246
Graduate Student 2		Perform sorption and biodegradation experiments			47%	1.5		\$144,246
Undergraduate 1		Assist graduate student 1			0%	0.4		\$9,500
							Sub Total	\$397,911
Contracts and Services								
UMN Core Facilities	Internal services or fees (uncommon)	Provide NMR instrument time for analysis of samples by graduate students.				-		\$15,000
							Sub Total	\$15,000
Equipment, Tools, and Supplies								
	Tools and Supplies	Laboratory Supplies	Chemicals, solvents, materials, and labware necessary to perform the experiments					\$34,089
	Tools and Supplies	Instrument maintenance	repair and upkeep of laboratory instruments needed for the project					\$15,000
							Sub Total	\$49,089

Capital Expenditures						
					Sub Total	-
Acquisitions and Stewardship						
					Sub Total	-
Travel In Minnesota						
	Miles/ Meals/ Lodging	collection of water and sediment samples	Collect samples for use in Activity 2			\$4,500
	Conference Registration Miles/ Meals/ Lodging	conference attendance by graduate students (2 conferences for each student)	disseminate results	X		\$1,500
					Sub Total	\$6,000
Travel Outside Minnesota						
					Sub Total	-
Printing and Publication						
	Publication	Open access journal fees	maximize dissemination of results of the project			\$10,000
					Sub Total	\$10,000
Other Expenses						
					Sub Total	-
					Grand Total	\$478,000

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
Travel In	Conference	conference attendance by graduate	presenting at conferences is an important educational experience and critical to
Minnesota	Registration	students (2 conferences for each	dissemination of the results to stakeholders in the PFAS area
	Miles/Meals/Lodging	student)	

Non ENRTF Funds

Category	Specific Source	Use	Status	\$ Amount
State				
			State Sub	-
			Total	
Non-State				
In-Kind	U of MN indirect costs	U of MN facilities and administrative support	Secured	\$208,000
			Non State	\$208,000
			Sub Total	
			Funds	\$208,000
			Total	

Attachments

Required Attachments

Visual Component File: <u>e4d527b4-6bc.pdf</u>

Alternate Text for Visual Component

A lake contains known and unknown PFAS. A method is developed to measure both types of PFAS in Minnesota's water and sediment. The same tool is used to find molecules that bind PFAS. With this information, sorbents to capture and/or destroy PFAS are developed, leading to clean water....

Optional Attachments

Support Letter, Photos, Media, Other

Title	File
Letter of Commitment UMN	<u>b840b668-56e.doc</u>
Background check certification form	<u>dc98e430-594.pdf</u>

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

Peter Jaffe (Princeton University) was added as a project partner (non-funded)

The budget for the individual activities and the overall project was adjusted to match the amount recommended. One of the undergraduate students was eliminated and the supply, maintenance, and publication budgets were reduced. The in-kind contribution was adjusted accordingly.

The dissemination plan was added.

The background check certification form was uploaded.

Made indicated changes to budget and dissemination sections.

Fiscal agent name and contact updated

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes? N/A

Do you agree travel expenses must follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan? Yes, I agree to the UMN Policy.

- Does your project have potential for royalties, copyrights, patents, or sale of products and assets? No
- Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10? $$\rm N/A$$
- Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF? N/A
- Does your project include original, hypothesis-driven research? Yes
- Does the organization have a fiscal agent for this project?

Yes, Sponsored Projects Administration