Environment and Natural Resources Trust Fund

2023 Request for Proposal

General Information

Proposal ID: 2023-063

Proposal Title: Finding, Capturing, and Destroying PFAS in Minnesota Waters

Project Manager Information

Name: William Arnold

Organization: U of MN - College of Science and Engineering

Office Telephone: (612) 625-8582

Email: arnol032@umn.edu

Project Basic Information

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.

Funds Requested: $500,000

Proposed Project Completion: June 30, 2026

LCCMR Funding Category: Water Resources (B)

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

Narrative

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 under-regulation 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.

Activities and Milestones

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

Activity Budget: $60,000

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	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
ublish methods	December 31, 2024

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

Activity Budget: $200,000

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	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: $120,000

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	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: $120,000

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 feammox 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 feammox and the enhanced sorbents versus when they are in the presence of feammox 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	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	University of Minnesota, Department of Chemistry	Co-investigator. Dr. Hillmyer will lead the development of the sorbent material and the development of the biological carriers for PFAS degradation.	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	Pro-bono consulting on NMR method development and data interpretation.	No

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 Sustainable Pharmaceuticals	M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04b	$415,000

Project Manager and Organization Qualifications

Project Manager Name: William Arnold

Job Title: Professor

Provide description of the project manager's qualifications to manage the proposed project.

Distinguished McKnight University and Joseph T. and Rose S. Ling Professor
Department of Civil, Environmental, and Geo- Engineering, University of Minnesota

B.S., Chemical Engineering, 1994, Massachusetts Institute of Technology, Cambridge, MA.
M.S., Chemical Engineering, 1995, Yale University, New Haven, CT.
Ph.D., Environmental Engineering, 1999, The Johns Hopkins University, Baltimore, MD.

Dr. William Arnold will be responsible for overall project coordination and supervision He has been studying the fate of mircopollutants, including pharmaceuticals, pesticides, and PFAS compounds in aquatic environments for twenty years.

As part of these studies, he has determined the transformation rates and identified reaction products of numerous compounds. He has published over twenty five peer-reviewed papers on emerging contaminant detection, fate, and treatment since 2003, and he is the co-author of a textbook on water chemistry (1st edition 2011, 2nd edition 2022). Past ENTRF funded work has been impactful to Minnesota, particularly work on triclosan and quaternary ammonium compounds. Dr. Arnold is a Fellow of the University of Minnesota Institute on the Environment, an Associate Fellow of the Minnesota Supercomputing Institute, and a member of the graduate faculty in Water Resources Science.

Organization: U of MN - College of Science and Engineering

Organization Description:
The University of Minnesota is one of the largest, most comprehensive, and most prestigious public universities in the United States (http://twin-cities.umn.edu/about-us). The College of Science and Engineering is one of the premier public institutes in the country for graduate and undergraduate education and research. The laboratories and offices of the PI contain the necessary fixed and moveable equipment and facilities needed for the proposed studies.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified 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
Undergraduate 2		assist graduate student 2			0%	0.4		$9,500
							Sub Total	**$407,411**
Contracts and Services								
							Sub Total	**-**
Equipment, Tools, and Supplies								
	Tools and Supplies	Laboratory Supplies	Chemicals, solvents, materials, and labware necessary to perform the experiments					$36,589
	Tools and Supplies	Instrument maintenance	repair and upkeep of laboratory instruments needed for the project					$20,000
	Tools and Supplies	Instrument time	Hourly fees for use of NMR instrumentation					$15,000
							Sub Total	**$71,589**

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					$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					$15,000
							Sub Total	**$15,000**
Other Expenses								
							Sub Total	**-**
							Grand Total	**$500,000**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request

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	$220,000
			Non State Sub Total	**$220,000**
			Funds Total	**$220,000**

Attachments

Required Attachments

Visual Component

File: e4d527b4-6bc.pdf

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 or Other

Title	File
Letter of Commitment UMN	b840b668-56e.doc

Administrative Use

Does your project include restoration or acquisition of land rights?

No

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?

N/A

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?

N/A

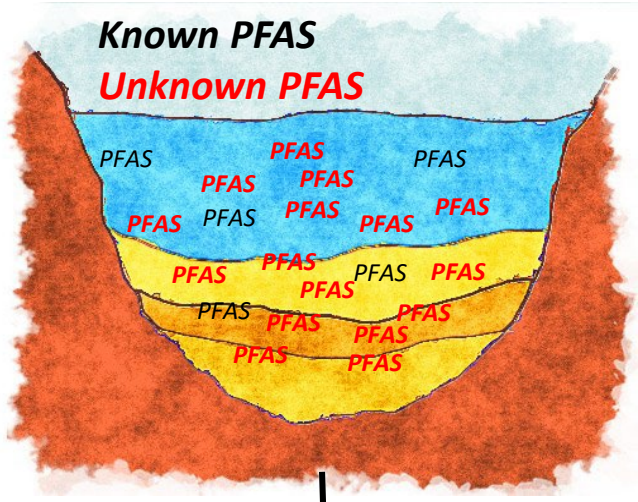
Does your project include original, hypothesis-driven research?

Yes

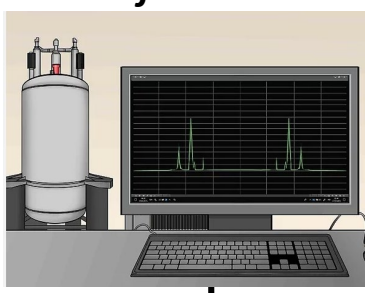
Does the organization have a fiscal agent for this project?

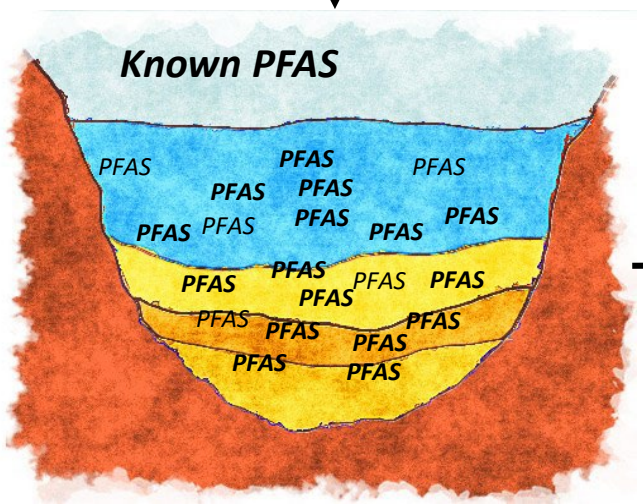
Yes, Sponsored Projects Administration

Tools are needed to measure, capture, and destroy PFAS



Develop new NMR method for total PFAS

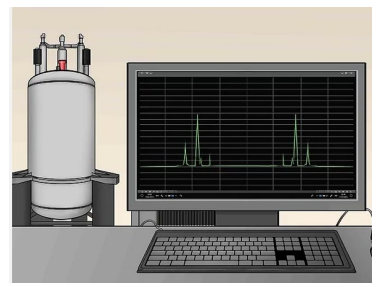


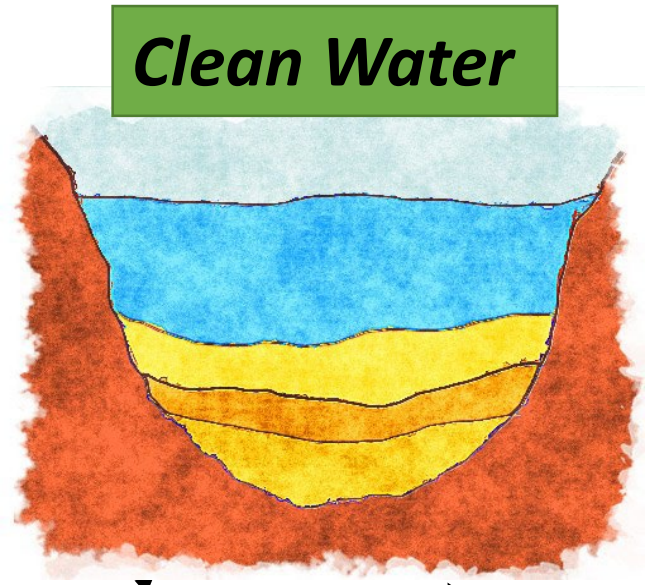


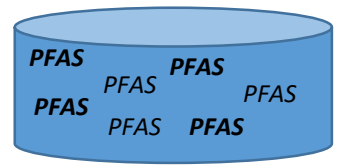
Outcomes:

A. Develop and verify NMR PFAS method.
B. Measurement of *<u>total PFAS</u>* in Minnesota's water and sediment.
C. Optimize sorbents for PFAS capture to clean water.
D. Develop a bioactive sorbent for PFAS destruction to clean water.

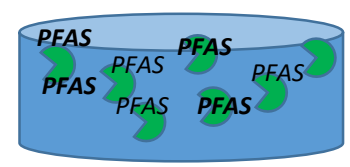
NMR quantifies PFAS binding





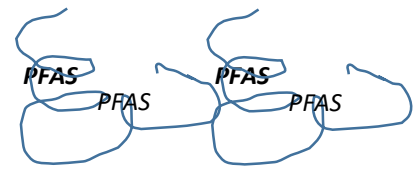


PFAS Sorbent



Bioactive PFAS Sorbent

Prepare sorbents



Design molecules to capture PFAS