

Final Abstract

Final Report Approved on October 1, 2026

M.L. 2023 Project Abstract

For the Period Ending June 30, 2026

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

Project Manager: William Arnold

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Funding Source:

Fiscal Year:

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

Appropriation Amount: \$478,000

Amount Spent: \$477,747

Amount Remaining: \$253

Sound bite of Project Outcomes and Results

This project i) developed a robust method for measuring the total amount of fluorinated pollutants present in environmental matrices; ii) developed new sorbents for fluorinated pollutant capture from contaminated water and iii) attempted to stimulate fluorinated pollutant biodegradation by creating a microenvironment for specialized bacteria.

Summary of Project and Outcomes

Poly- and perfluoroalkyl substances (PFAS) represent pressing risks to water quality in Minnesota. This study established a methodology for quantifying the total amount of PFAS or organofluorine present in environmental samples using nuclear magnetic resonance spectroscopy (NMR). The measurement includes traditional short- and long-chain PFAS as well as fluorinated pesticides and pharmaceuticals, and the analysis reveals that NMR detects four to ten times more fluorine in samples than traditional targeted mass spectrometry methods. This indicates that current methods may be underestimating the amount of organofluorine present in the environment. Removal of the wide variety of PFAS present in aquatic systems was investigated using a multipronged approach. NMR experiments with proteins and other model molecules were used to understand how PFAS bind to substrates. PFAS structure was a key variable in binding, with longer chain compounds binding more strongly to protein structures. Additionally, competitive and cooperative binding

of multiple PFAS was observed. This knowledge was used to design two new polymer sorbents for PFAS. One of these resins takes up the more mobile and hard to capture short chain PFAS faster than current commercial resins and has stronger affinity than previously observed. A second material also developed and showed rapid uptake. The materials are tunable in terms of their morphology, which will allow optimization of the rate of PFAS capture. Lastly, an iron-zeolite-polymer composite material was designed to bring together iron and ammonium to stimulate the growth of a PFAS degrading bacteria. While the material did effectively take up ammonium, there was only a slight enhancement of growth of the targeted bacteria, and a PFAS degrading culture could not be established. While only partially successful, this portion of the work did point to areas where improvements can be made in terms of PFAS capture and bacterial growth stimulation.

Project Results Use and Dissemination

Four conference presentations, four peer-reviewed journal articles, an MS Thesis, and Ph.D. dissertation were disseminated and can be shared with the public as a result of this project. Two more journal articles and one more Ph.D. dissertation will also arise from the work.



Environment and Natural Resources Trust Fund

M.L. 2023 Approved Final Report

General Information

Date: October 5, 2026

ID Number: 2023-063

Staff Lead: Lisa Bigaouette

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

Project Budget: \$478,000

Project Manager Information

Name: William Arnold

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Project Reporting

Final Report Approved: October 1, 2026

Reporting Status: Project Completed

Date of Last Action: October 1, 2026

Project Completion: June 30, 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 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 ENTRF-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 “stickiest” 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 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	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	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
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 Sustainable Pharmaceuticals	M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04b	\$415,000

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	\$ Amount	\$ Amount Spent	\$ Amount Remaining
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		\$106,396	-	-
Undergraduate 1		Assist graduate student 1			0%	0.22		\$3,500	-	-
Postdoctoral Researcher		Assist with development of sorptive materials			21%	0.2		\$15,108	-	-
Temporary casual employee		assist graduate student 2			0%	0.14		\$3,000	-	-
							Sub Total	\$372,169	\$372,087	\$82
Contracts and Services										
UMN Core Facilities	Internal services or fees (uncommon)	Provide NMR instrument time for analysis of samples by graduate students.				0		\$40,272	\$40,272	-
							Sub Total	\$40,272	\$40,272	-
Equipment, Tools, and Supplies										
	Tools and Supplies	Laboratory Supplies	Chemicals, solvents, materials, and labware					\$34,205	\$34,205	-

			necessary to perform the experiments							
	Tools and Supplies	Instrument maintenance	repair and upkeep of laboratory instruments needed for the project					\$26,781	\$26,610	\$171
							Sub Total	\$60,986	\$60,815	\$171
Capital Equipment										
							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					-	-	-
	Conference Registration Miles/ Meals/ Lodging	conference attendance by graduate students (2 conferences for each student)	disseminate results	X				\$115	\$115	-
							Sub Total	\$115	\$115	-
Travel Outside Minnesota										
							Sub Total	-	-	-
Printing and Publication										
	Publication	Open access journal fees	maximize dissemination of results of the project					\$4,458	\$4,458	-
							Sub Total	\$4,458	\$4,458	-
Other Expenses										
							Sub Total	-	-	-

							Grand Total	\$478,000	\$477,747	\$253
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Classified Staff or Generally Ineligible Expenses

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

Non ENRTF Funds

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

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....

Supplemental Attachments

Capital Project Questionnaire, Budget Supplements, Support Letter, Photos, Media, Other

Title	File
Letter of Commitment UMN	b840b668-56e.doc
Background check certification form	dc98e430-594.pdf
Closing PFAS analytical gaps: Inter-method evaluation of total organofluorine techniques for AFFF-impacted water	c3fbae6f-a74.pdf
Conference Presentation (AEESP)	da6f5b02-2a9.pptx
Conference Presentation (UCOWR)	cb04076e-f10.pptx
IPRIME poster presentation	3c9ffdb5-817.pdf
Conference Presentation (Amer Chem Soc)	f093ac13-c9b.pptx
Revealing Organofluorine Contamination in Effluents and Surface Waters with Complementary Analytical Approaches: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy (19F-NMR) and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)	90537a41-be4.docx
Anion exchange beads for PFAS capture using a polymerization-induced microphase separation approach	9e2ebda6-324.pdf
Evaluation of porous polyethylene-supported zeolite carriers to support feamnox-based perfluorooctanoic acid biotransformation	483f3cb6-e44.pdf
Enhancing Feamnox-Based Perfluorooctanoic Acid Biotransformation Using Porous Polyethylene-Supported Zeolite Carriers	65cf4fda-069.pdf
Anion Exchange Resins through Polymerization-Induced Microphase Separation for PFAS Capture	269b8b45-7cb.pdf

Media Links

Title	Link
Closing PFAS analytical gaps: Inter-method evaluation of total organofluorine techniques for AFFF-impacted water	https://www.sciencedirect.com/science/article/pii/S2666911024000212?via%3Dihub
Revealing Organofluorine Contamination in Effluents and Surface Waters with Complementary Analytical Approaches: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy (19F-NMR) and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)	https://pubs.acs.org/doi/10.1021/acs.est.5c05079

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 understand that travel expenses are only approved if they 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 understand the UMN Policy on travel applies.

Does your project have potential for royalties, copyrights, patents, sale of products and assets, or revenue generation?

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

Do you understand that a named service contract does not constitute a funder-designated subrecipient or approval of a sole-source contract? In other words, a service contract entity is only approved if it has been selected according to the contracting rules identified in state law and policy for organizations that receive ENRTF funds through direct appropriations, or in the DNR's reimbursement manual for non-state organizations. These rules may include competitive bidding and prevailing wage requirements

N/A

Work Plan Amendments

Amendment ID	Request Type	Changes made on the following pages	Justification For Amendment Request (word limit 75)	Date Submitted	Approved	Date of LCCMR Action
1	Amendment Request	• Other • Budget - Personnel	We are requesting to move \$15,108 in the personnel category from the graduate student line (\$12,108) and undergraduate student line (\$3000) to partially support a postdoctoral researcher to help with the materials synthesis portion of the project. Having the additional, more established person will help us more rapidly make materials that we can test in the biological PFAS degradation experiments.	August 16, 2024	Yes	August 28, 2024
2	Amendment Request	• Budget - Personnel	We request to move \$3000 from the undergraduate student line to the category "temporary casual employee". The hourly rate and responsibilities will be the same. The new budget line is necessary to allow hiring of a post-secondary enrollment option student. The student is on the UMN campus daily but is not categorized as an undergraduate.	February 5, 2025	Yes	February 7, 2025
3	Amendment Request	• Budget - Personnel • Budget - Professional / Technical Contracts • Budget - Capital, Equipment, Tools, and Supplies • Budget - Travel and Conferences • Budget - Printing and Publication • Budget - Non-ENRTF Funds Contributed	To align with expenditures as the project finalizes analyses, the budget of Graduate Student 2 was reduced by \$19,911. We request these funds be moved to the service category (\$35,000), as additional NMR analyses were needed. Other changes are an increase in maintenance (\$26,781, instrument repair of mass spectrometer needed for PFOA analyses for sorption/degradation experiments), supplies (\$32,000). Funds for publication and travel were reduced (\$5,519 and \$700)	May 11, 2026	Yes	May 12, 2026
4	Amendment Request	• Other • Budget - Personnel • Budget - Professional / Technical	To finalize the work, additional funds were used for supplies and analyses. Necessary funds were moved from the graduate	September 22, 2026	Yes	September 22, 2026

		Contracts • Budget - Capital, Equipment, Tools, and Supplies • Budget - Travel and Conferences • Budget - Printing and Publication • Budget - Non-ENRTF Funds Contributed • Attachments	student 2 salary and unspent travel and publication funds to cover the necessary expenditures. The increased funds for consumable supplies and analyses were spent during the final reporting period of the project			
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Status Update Reporting

Final Status Update August 14, 2026

Date Submitted: September 9, 2026

Date Approved: September 22, 2026

Overall Update

Analyses of water and solid samples for PFAS with our fluorine NMR method were completed. The NMR method measures total organic fluorine. In some scenarios (e.g., wastewater) traditional PFAS only make up a fraction of the total fluorine present. Assessment of binding of PFAS by proteins is also complete. A key finding is that for one protein, PFAS compete for binding sites, while with another, they synergistically bind. This has both sorbent design and toxicological implications. The development and characterization of a sorbent for short chain PFAS was completed. This material has tunable morphology which allows for potential optimization of PFAS uptake rate.

Activity 1

We have optimized our procedure for analysis of water samples and extracts from solid materials (completion of Milestones 1-3), and two publications document the method (Milestone 4; Closing PFAS analytical gaps: Inter-method evaluation of total organofluorine techniques for AFFF-impacted water and Revealing Organofluorine Contamination in Effluents and Surface Waters with Complementary Analytical Approaches: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy (19F-NMR) and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)). The methods have been documented and uploaded to the "Supplemental Attachments" section of the Attachments page (Tab 7). There has been substantial interest from researchers and practitioners regarding the method. Thus, we will continue to further optimize the method and expand the capabilities moving forward (using other, non-ENRTF funds).

(This activity marked as complete as of this status update)

Activity 2

We have analyzed numerous water samples to quantify the total amount of fluorinated compounds in samples. We have worked with our Minnesota partners to collect surface water and solid samples from around the state, including paired samples from passive samplers, biosolids, and landfill leachates. The fraction of total PFAS missed by mass spectrometry has been complete (Milestone 3) and the published paper (Revealing Organofluorine Contamination in Effluents and Surface Waters with Complementary Analytical Approaches: Fluorine-19 Nuclear Magnetic Resonance Spectroscopy (19F-NMR) and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)) has been uploaded to the "Supplemental Attachments" section of the Attachments page (Tab 7). Analysis of all samples relevant to the projects using the optimized, published NMR method is complete, and we are combining this data with samples from non-ENRTF funded work into a future publication (Milestone 4).

(This activity marked as complete as of this status update)

Activity 3

The competition experiments for PFAS binding to proteins were completed (Milestone 1). Interestingly, for one protein, the PFAS molecules compete with each other for binding sites and for the other protein, PFAS synergistically bind. These findings have implications both for design of bio-inspired sorbents as well as toxicology of PFAS molecules. Using targeted competitors, we were able to identify specific binding sites on a human protein.

Work was completed on two new polymer sorbents for PFAS (Milestones 2 and 3). The styrene based resin was developed that takes up short chain PFAS faster than current commercial resins. Additionally, the material has stronger affinity for PFAS than the standard commercial material. This combination is particularly valuable for uptake of PFAS at the typical low concentration present in the environment or water treatment systems. A second acrylic-based anion exchange resin was also developed with rapid uptake and high capacity for short chain PFAS. A key advantage of this

material is tunable morphology, which can be optimized to tailor the rate of update. These studies provide design guidelines for optimized materials. One manuscript has been published, one submitted, and one is in draft form (Milestone 4; see Attachments page (Tab 7)).

(This activity marked as complete as of this status update)

Activity 4

Our experiments with materials that contain both iron and ammonium sorbents to feed the feammox bacteria are complete (Milestone 1 and 3). While only partially successful, this work did point to areas where improvements can be made in terms of PFAS capture and bacterial growth stimulation. A manuscript on the work (Evaluation of porous polyethylene-supported zeolite carriers to support feammox-based perfluorooctanoic acid biotransformation) has been published and has been uploaded to the “Supplemental Attachments” section of the Attachments page (Tab 7).

(This activity marked as complete as of this status update)

Dissemination

Two additional open access manuscripts have been published.

Arshad, A., Back, J., Faber, K.A., Arnold, W.A., Buhlmann, P., Hillmyer, M.A. 2026. Anion Exchange Beads For PFAS Capture Using a Polymerization-Induced Microphase Separation Approach. RSC Applied Polymers, accepted.
<https://doi.org/10.1039/d6lp00075d>

Pearson, M.C., Novak, P.J., Huang, S., Jaffe, P.R., Hillmyer, M.A., Arnold, W.A. 2026. Evaluation of porous polyethylene-supported zeolite carriers to support feammox-based perfluorooctanoic acid biotransformation. Front. Environ. Eng. 5: 1878655:<https://doi.org/10.3389/fenv.2026.1878655>

McKenzie Pearson completed her M.S. degree and her thesis is available in the University of Minnesota Digital Conservancy (<https://hdl.handle.net/11299/277323>). Dr. Ali Arshad's Ph.D. thesis will be available in the Conservancy soon. They have also been uploaded to the “Supplemental Attachments” section of the Attachments page (Tab 7).

One manuscript has been submitted (protein binding of PFAS) and another in draft form on the acrylic exchange resins. We will also have an additional paper on environmental detections once those data are combined with non-ENTRF funded work.

Status Update Reporting

Status Update April 1, 2026

Date Submitted: May 11, 2026

Date Approved: May 12, 2026

Overall Update

We are finalizing our analyses of water and solid samples for PFAS with our NMR method. We have all the samples we plan to analyze collected and will complete them before the end of the project. For the binding studies, we are also on track to complete our evaluation of proteins as models for sorbents, and we are continuing to optimize the production of materials that bind PFAS quickly with high capacity. Our biodegradation experiments are complete, and while not fully successful, have provided key information for the development of the sorbent materials and future directions for facilitating biodegradation.

Activity 1

We are continuing to optimize the solids extraction process and to pursue opportunities to improve the throughput and detection limit of the NMR method. Analysis of solids samples is ongoing. We are also exploring expanding the NMR method to include trifluoroacetic acid (TFA), an ultrashort-chain PFAS of emerging concern.

Activity 2

We have analyzed numerous water samples to quantify the total amount of fluorinated compounds in samples. We are continuing to work with our Minnesota partners to collect surface water and solid samples from around the state, including paired samples from passive samplers, biosolids, and landfill leachates. Analysis of these samples using the optimized, published NMR method is ongoing.

Activity 3

The experiments exploring PFAS binding with human serum albumin protein and proteins in cow's milk and human breast milk are expected to soon. The remaining planned experiments will explore competition between different PFAS and between other protein ligands to understand how the presence of other molecules influences PFAS binding. Our results continue to show that PFAS structure is an essential factor influencing binding strength. We are developing insight into the different binding sites on these proteins that PFAS may bind to, which will guide continuing sorbent development.

Activity 4

Our experiments with materials that contain both iron and ammonium sorbents to feed the Feamox bacteria are complete. While only partially successful, this work did point to areas where improvements can be made in terms of PFAS capture and bacterial growth stimulation. A manuscript on the work is under review. We are continuing our work on PFAS sorbents, optimizing the synthetic routes for two distinct PFAS sorbents: styrene-based and acrylate-based anion exchange resins. The styrenic anion exchange resin is synthesized via thermal polymerization using 4-vinylpyridine, whereas the acrylic resin is prepared through photopolymerization. Notably, the acrylic anion exchange resin exhibits significantly faster PFAS sorption kinetics compared to commercially available sorbents. However, further investigation is required for the acrylic system to ensure the stability of the structure. For kinetic and isotherm studies, we are also optimizing the mass spectrometry conditions to enable PFAS analysis at ppb-level concentrations, which are closer to environmentally relevant conditions than those used in our previous tests.

Dissemination

We have published a paper comparing NMR and mass spectrometry analysis. Presentations have been given at five different forums directly related to the work. Presentations have been uploaded as attachments and a link to the journal paper provide.

Status Update Reporting

Status Update October 1, 2025

Date Submitted: September 22, 2025

Date Approved: December 8, 2025

Overall Update

We have established the utility of the NMR method for the quantification of total organofluorine in water samples and published an article comparing traditional mass spectrometry with this new method. The NMR method detects more organofluorine than targeted mass spectrometry in most samples. We are continuing to optimize the methods and collecting samples from additional matrices to compare different quantification techniques. We are also pursuing two strategies for PFAS sorbents because we have found that one material is better for capture of carboxylates and the other sulfonated. The materials developed to date have superior kinetics to commercial ion exchange resins, and we are working to improve the capacity. Experiments with polymer "pucks" that contain iron oxide and sorb ammonium were used to try to sustain the growth of feammox bacteria that are able to degrade PFAS. While the feammox appeared to slightly stimulated by the pucks, we were unable to sustain growth or facilitate degradation of perfluorooctanoic acid (PFOA). These experiments will be continued at the point at which we have PFAS sorbents that can be included in the experimental matrix.

Activity 1

The paper comparing mass spectrometry and NMR quantification of PFAS in water samples has been published. We are continuing to optimize the solids extraction process and to pursue opportunities to improve the throughput and detection limit of the NMR method.

Activity 2

We are continuing to work with our Minnesota partners to collect surface water and solid samples from around the state, including paired samples from passive samplers, biosolids, and landfill leachates. Analysis of these samples using the optimized, published NMR method is ongoing.

Activity 3

Experiments investigating the interactions of PFAS with biomolecules and polymers are ongoing. Follow-up experiments investigating interactions with the human serum albumin protein showed that different PFAS molecules may bind at different sites on the protein surface. Understanding why PFAS bind to some sites and not others can help guide ongoing sorbent design. Additionally, a new set of experiments is underway exploring PFAS interactions with proteins present in human breast milk and cow's milk. We expect that comparing interactions between these milk proteins and human serum albumin will further illuminate why PFAS stick to some proteins more strongly than others.

For the capture of PFAS, we are developing two distinct polymer-based sorbents: styrene-based and acrylate-based resins. For the styrenic anion exchange resin, we are seeking to synthesize mesoporous materials through a sustainable route. For the acrylate resin, we are implementing a novel nitrogen-mediated photopolymerization strategy. Further optimization is required to fine-tune the resin composition, ensuring stable mesoporous sorbents. The styrenic anion exchange resin demonstrates strong affinity for capturing carboxylic acid-based PFAS, while the acrylate resin shows higher efficiency toward sulfonic acid-based PFAS. Ongoing and future work will focus on enhancing both sorption kinetics and overall PFAS adsorption capacity.

Activity 4

Experiments conducted with iron-containing, ammonium sorbing materials in the presence of feammox bacteria were completed. The iron-containing materials showed greater sorption of ammonium than those with only zeolite sorbent,

and the ammonium was able to be released, indicating these materials are places where the feammox bacteria could obtain necessary nutrients. While the feammox showed initial increases after inoculation, growth could not be sustained and no perfluorooctanoic acid was degraded. Extraction of the materials, however, did show a greater abundance of feammox on the iron/ammonium loaded materials versus controls. We suspect the lack of success was due to initial cultures containing insufficient feammox. We plan to return to these experiments if materials that sorb PFAS and ammonium are able to be produced.

Dissemination

Faber, K.A.; Pomerantz, W.C.K.; Gray, J.L.; Hubbard, L.E.; Kolpin, D.W.; Arnold, W.A. Revealing organofluorine contamination in effluents and surface waters with complementary analytical approaches: fluorine-19 nuclear magnetic resonance spectroscopy (19F-NMR) and liquid chromatography-tandem mass spectrometry (LC-MS/MS). *Environ. Sci. Technol.* 2025, 59 (28), 14695-14706. <https://doi.org/10.1021/acs.est.5c05079>

Presentations:

1. “Exploring the organofluorine gap: 19F-NMR and LC-MS/MS as complementary analytical approaches for PFAS.” K.A. Faber, W.C.K. Pomerantz, J.L. Gray, L.E. Hubbard, D.W. Kolpin, W.A. Arnold. ACS Fall 2025, Washington, DC. August 19, 2025.
2. “Exploring the organofluorine gap: 19F-NMR and LC-MS/MS as complementary analytical approaches for PFAS.” K.A. Faber, W.C.K. Pomerantz, J.L. Gray, L.E. Hubbard, D.W. Kolpin, W.A. Arnold. UCOWR/NIWR Water Resources Conference, Minneapolis, MN. June 4, 2025.
3. “Characterizing protein interactions of PFAS mixtures using fluorine nuclear magnetic resonance spectroscopy.” K.A. Faber, W.C.K. Pomerantz, W.A. Arnold. AEESP Research and Education Conference, Durham, NC. May 22, 2025.

Posters:

1. “Establishing Binding Strength of PFAS to Human Serum Albumin Using 19F-NMR.” M. Hanson, K.A. Faber, W.A. Arnold.

Status Update Reporting

Status Update April 1, 2025

Date Submitted: May 25, 2025

Date Approved: May 30, 2025

Overall Update

Work continues on all aspects of the project. During the reporting period, we have developed a robust and reproducible method to quantify the total PFAS present in a water sample using fluorine NMR. This has been tested on numerous environmental water samples. We are beginning investigations of other matrices and samples, and we will be able to compare our results to those from partners using mass spectrometry and total fluorine methods. Sorbents for ammonia that also contain iron oxide have been developed and characterized. These will provide essential nutrients for PFAS-degrading bacteria. Additionally, a sorbent for PFAS, that takes up PFAS more rapidly than commercial materials, has been synthesized. Binding studies indicate that short chain and long chain PFAS interact with potential sorbents differently, and this information will be used to continue to optimize sorbent design. Biodegradation experiments using the ammonia sorbents are ongoing. Keeping the bacteria alive has proved challenging, and experimental conditions are being adjusted.

Activity 1

We have continued to refine the data processing steps for our optimized NMR method, leading to additional improvements in signal-to-noise ratio beyond our previous report. The refinements enable us to detect PFAS at even lower levels. We are continuing to pursue opportunities to improve the throughput and detection limit of the NMR method.

A paper on the comparison of mass spectrometry and NMR quantification of PFAS in water samples has been submitted, reviewed, and is in revision.

We have obtained samples of solids and are beginning the optimization of this extraction process to assess the conditions needed for NMR analyses.

Activity 2

We have received samples obtained at part of another ENTRF project evaluating passive samplers for PFAS quantification. We will continue to work with this team to collect paired samples this summer. A consulting firm provided samples of biosolids and activated carbon, and these are part of the ongoing solids extraction optimization for Activity 1. We have commitments from two partners to obtain landfill leachates. We are continuing to work with partners to collect Minnesota water and sediment samples.

Activity 3

Experiments using NMR to investigate the interactions of PFAS with various biomolecules and polymers are underway. Results show that PFOA and PFOS associate relatively strongly with human serum albumin protein, while PFBA and PFBS associate less strongly. Interestingly, our results suggest that there are differences among these PFAS in how rapidly the PFAS molecules exchange on and off the surface of the protein. There also seem to be differences in the orientation of the PFAS molecules relative to the protein. Further experiments are planned to explore these effects to understand how they may affect sorbent design. We are also continuing to analyze the binding interactions of more different PFAS, biomolecules, and polymers.

The synthesis of a sorbent material has been successful. The current sorbent material has shown better sorption kinetics for short-chain PFAS and slightly slower sorption kinetics for long-chain PFAS when compared to a commercially

available ion exchange resin. There are still some properties that can be optimized to get faster kinetics and high sorption capacity. Currently, optimization experiments are underway to achieve better results and to test how the fluorinated chain length affects the uptake. Further work will investigate combining the PFAS and ammonia sorbents.

Activity 4

After confirming sufficient ammonium sorption on the zeolite-coated polyethylene sorbent material, a variant was synthesized with an iron oxide (goethite) included in the material. By including goethite, this material provided a centralized location for both iron and ammonium, the nutrients that the Feammox bacteria require. The goethite modified material sorbs ammonium to the same extent as the zeolite sorbent alone.

Batch experiments are currently in progress that include the Feammox bacteria, PFOA, and the zeolite-coated polyethylene sorbent materials (iron and regular). These experiments compare typical growth media with iron and ammonium included to media that uses the sorbent material as the sole iron and ammonium source. After 60 days, the growth of the bacteria and PFOA levels will be compared across experimental setups to determine if the sorbent materials improve activity and biodegradation.

Dissemination

Dixit, F. Antell, E.H., Faber, K.A., Zhang, C., Pannu, M.W., Plumlee, M.H., Van Buren, J., Doroshov, A., Pomerantz, W.C.K., Arnold, W.A., Higgins, C.P., Peaslee, G.F., Alvarez-Cohen, L., Sedlak, D.L., Atiea, M. 2024. Closing PFAS Analytical Gaps: Inter-Method Evaluation of Total Organofluorine Techniques for AFFF-Impacted Water, J. Haz. Mat. Lett. vol 5 Nov 2024, 100122.

<https://doi.org/10.1016/j.hazl.2024.100122>

Presentations:

Arshad, A.; Hillmyer, M. A.; Bühlmann, P. "Ion Exchange Materials Through Polymerization Induced Microphase Separation (PIMS) for PFAS Sorption" Poster Presentation, IPRIME, Minneapolis, MN 2024

K.A. Faber, W.C.K. Pomerantz, J.L. Gray, L.E. Hubbard, D.W. Kolpin, W.A. Arnold. Insight of total PFAS in effluents and surface waters using fluorine nuclear magnetic resonance spectroscopy. American Chemical Society, Fall 2024, Denver, CO. August 21, 2024.

Poster:

K.A. Faber, J.L. Gray, L.E. Hubbard, D.W. Kolpin, W.C.K. Pomerantz, W.A. Arnold. Fluorine Nuclear Magnetic Resonance (^{19}F NMR) for the Quantification of Total PFAS. IPRIME Annual Meeting, Workshop: Challenges, Opportunities, and Perspectives on Replacements for Fluorinated Organic Materials, Minneapolis, MN. May 28, 2024.

Status Update Reporting

Status Update October 1, 2024

Date Submitted: September 18, 2024

Date Approved: September 19, 2024

Overall Update

This status update is waived per guidance from LCCMR staff provided on August 13, 2024.

Activity 1

This status update is waived per guidance from LCCMR staff provided on August 13, 2024.

Activity 2

This status update is waived per guidance from LCCMR staff provided on August 13, 2024.

Activity 3

This status update is waived per guidance from LCCMR staff provided on August 13, 2024.

Activity 4

This status update is waived per guidance from LCCMR staff provided on August 13, 2024.

Dissemination

New journal article: Closing PFAS analytical gaps: Inter-method evaluation of total organofluorine techniques for AFFF-impacted water, Journal of Hazardous Materials Letters, vol 5, Nov 2024, 100122.

<https://doi.org/10.1016/j.hazl.2024.100122>

Status Update Reporting

Status Update April 1, 2024

Date Submitted: March 20, 2024

Date Approved: May 20, 2024

Overall Update

An nuclear magnetic resonance spectroscopy method was modified to quantify PFAS and other fluorinated compounds using a total fluorine metric. An extraction method for water samples was also optimized. The methodology was tested on water samples, and successfully quantified PFAS on a sample set. We are now working with partners to obtain relevant samples of water and sediment from Minnesota sites. Materials development has proceeded on two fronts. One is focused on producing sorbents for PFAS and a second on testing a previously developed sorbent for ammonium and its affinity for iron. Results to date show the materials can absorb PFAS and ammonium, respectively, but the iron results thus far are inconclusive. Next steps are to evaluate whether using one multifunctional material or a mixture of materials that can sorb the PFAS, ammonium, and iron is the best option to provide a suitable environment for the PFAS degrading bacteria.

Activity 1

Our previously reported NMR method for measuring fluorinated pharmaceuticals and pesticides was successfully adapted for total PFAS analysis. For water sample preparation, we used mixed bed solid phase extraction cartridges to concentrate samples; the mixed bed cartridges improved PFAS retention compared to widely used anion exchange cartridges. For NMR analysis, we used an iron-based relaxation agent to speed up NMR instrument run times. NMR instrumental parameters (e.g. acquisition time, delay time) were re-optimized for the new method. The optimized method incorporating the relaxation agent improved the signal-to-noise ratio about 2.5x compared to our original NMR method, meaning that the new method can more confidently and accurately detect low levels of PFAS. Continuing efforts in Activity 1 are focused on improving our NMR data processing methods to further reduce noise and enable detection of even lower levels of PFAS.

Activity 2

We have tested the optimized NMR method on surface water and industrial effluent samples for a separate project. The method succeeded at detecting both PFAS and non-PFAS fluorinated molecules in the water samples. We are currently working with Minnesota-based partners to collect Minnesota samples for analysis.

Activity 3

Polymeric ion exchange beads were synthesized using polymerization-induced microphase separation (PIMS). A diblock copolymer composed of poly(ϵ -caprolactone)(PCL) and poly(4-vinylbenzyl chloride)(PVBC) was chain extended with styrene and divinylbenzene using suspension polymerization to make microphase-separated beads with an average diameter of 68 μm . PCL domains were chemically etched using basic media to make porous beads and then PVBC domains were treated with trimethylamine (TMA) to introduce positive charges on the pore walls. The ion exchange beads maintained their spherical shape after all the post-polymerization steps.

Separately, we have used NMR to test the binding of PFOA to biomolecules and other large polymers. Initial results indicate that PFOA associates relatively strongly with human serum albumin protein and weakly (if at all) with lysozyme protein. PFOA also associates relatively strongly with polyDADMAC, a cationic polymer used in water treatment, suggesting that similar polymers may be useful for developing effective PFAS sorbents. Upcoming studies will use a similar approach to characterize binding for a larger variety of PFAS and biomolecules.

Activity 4

Perfluorooctanoic acid (PFOA) sorption testing was performed using the polymeric ion exchange beads. When the porous ion exchange beads were soaked in an aqueous solution of PFOA, they showed promising results for PFOA sorption applications. After two hours of soaking the beads in PFOA solution, the beads adsorbed approximately two PFOA molecules per positive charge. In the initial adsorption kinetics experiment with charged porous beads, the data followed the pseudo-second-order kinetics as reported in the previously published literature. Conversely, non-porous neutral beads and porous neutral beads, which were used as controls in the sorption experiments, did not show much sorption behavior for the PFOA.

Isotherms for ammonia sorption on the zeolite-coated polyethylene material were developed through sorption experiments, and the results have shown promising results for A6 growth application. Iron (III) experiments with the same material showed less consistent sorption isotherms, likely due to the insoluble characteristics of iron (III), however more experiments need to be conducted.

Dissemination

Preliminary data on PFAS quantification was presented at the Minnesota Water Resources Conference in October 2023.