



# Environment and Natural Resources Trust Fund

## 2024 Request for Proposal

### General Information

**Proposal ID:** 2024-086

**Proposal Title:** Fluorine Beyond PFAS: Pesticide and Pharmaceutical Degradation

### Project Manager Information

**Name:** William Arnold

**Organization:** U of MN - College of Science and Engineering

**Office Telephone:** (612) 625-8582

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### Project Basic Information

**Project Summary:** The project will assess the fluorinated breakdown products produced from pesticides and pharmaceuticals to identify potentially persistent or toxic byproducts and allow development of sustainable chemistries.

**Funds Requested:** \$560,000

**Proposed Project Completion:** June 30, 2027

**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.**

Rachel Carson brought to light the dangers of persistent chlorinated chemicals in 1962, and we have spent decades dealing with these pollutants. Recently, persistent fluorochemicals, such as perfluorooctane sulfonate (PFOS), rose to prominence, and the poly- and perfluorinated chemicals (PFAS) class is under intense scrutiny by regulators and the public. Fluorine incorporation into organic chemicals is, however, much more ubiquitous than is generally known by the public. There are an increasing number of mass-produced chemicals containing one or more fluorine atoms, including pharmaceuticals, pesticides, and medical contrast agents. Yet, we understand little about the identity and fate of fluorinated byproducts produced in aquatic systems upon degradation of fluorinated pesticides and pharmaceuticals and their degradation products are mostly unknown. It is critically important to understand how the incorporation of fluorine into organic chemicals affects the full suite of potential degradation pathways in natural and engineered aquatic environments and what persistent fluorinated products (i.e., PFAS) form from both chemically and biologically driven natural and treatment processes. This information, in turn, will guide the development of molecules that require fluorine incorporation to obtain a desired effect, yet are able to break down into innocuous products.

### **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.**

There is a need to understand which fluorinated groups in chemicals lead to undesirable byproducts. The proposed work will use a screening assay to measure how much fluoride, which is added to toothpaste and is a benign degradation product, is produced from a suite of fluorinated chemicals via chemical and biological reactions that occur in the environment or during water and wastewater treatment. If all the fluorine initially in the chemical does not get converted to fluoride, that indicates unknown PFAS are forming. The next step will be to isolate and identify the fluorinated products that form. This will also include identifying the specific processes leading to formation of potentially problematic byproducts and assessing how bacteria degrade the fluorinated pesticides and pharmaceuticals. This information will provide the information to assess which compounds and processes are most likely to form persistent fluorinated byproducts, leading to recommendations regarding compound use and water treatment/remediation options to limit these issues. The planned work will also lead to a “benign by design” strategy for the development of compounds that have the desired function yet are not harmful to the environment.

### **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?**

We know that fluorinated pesticides and pharmaceuticals are entering Minnesota's waters. While some of these compounds are degraded into non-toxic byproducts either naturally or during drinking water and wastewater treatment, there is the potential for a myriad of persistent, fluorinated, PFAS-like chemicals to form. By understanding which chemicals lead to problematic byproducts, recommendations about chemical use, water and wastewater treatment, and better chemical design will be made. This will lead to protection and enhancement of Minnesota's water resources.

## Activities and Milestones

### Activity 1: Identify fluorinated groups resistant to abiotic and biological reactions in the environment or water treatment systems.

**Activity Budget:** \$168,000

#### Activity Description:

Because the inclusion of fluorine in pesticides and pharmaceuticals gives rise to favorable properties with minimal changes in molecular shape and potentially more potent activity, a wide variety of fluorinated groups have been and will continue to be incorporated in the synthetic organic compounds. Once present in the environment due to direct (pesticides) or indirect (pharmaceuticals) release, a range of chemical and biological transformations may (or may not) occur giving rise to new fluorinated (PFAS) transformation products. A rapid screening test would allow assessment of the extent of fluoride formation and compound stability. Fluoride (which is added to drinking water and toothpaste) is a desirable reaction product, and if all the fluorine in the molecules is not converted to fluoride, that would indicate other fluorinated organic molecules are forming. We will assess the extent of fluoride release from a suite of model fluorinated molecules and selected pesticides and pharmaceuticals under a variety of chemical and biological conditions to assess which molecules lead to formation of PFAS-like chemicals. We anticipate at least two publications/dissemination events prior to March 31, 2026.

#### Activity Milestones:

Description	Approximate Completion Date
Develop fluoride assay	December 31, 2024
Hydrolysis and nucleophile reactions	June 30, 2025
Photolysis studies	August 31, 2025
Enzymatic and microbial fluoride release	March 31, 2026
Publication/dissemination	March 31, 2026

### Activity 2: Assess the (bio)chemical reactivity of fluorinated pesticides and pharmaceuticals and identify persistent fluorinated byproducts

**Activity Budget:** \$224,000

#### Activity Description:

The experiments in this aim will focus on the molecules that show fluoride yields < 100% in any specific chemical or biological assay, indicating the presence of fluorinated byproducts. The matrix of chemicals studied will be expanded to include as many pesticides and pharmaceuticals as possible that contain fluorinated groups that show persistence. Detailed analysis of reaction kinetics and product formation are required, with isolation of persistent products and synthesis of authentic standards when necessary. Samples will be analyzed by quantitative fluorine nuclear magnetic resonance spectroscopy (NMR) to allocate fluorine between fluoride and organic products. Initial assessment of the fluorine moiety will be made based on chemical shifts compared to the parent compounds, and further characterization will be performed by mass spectrometry. Our previous ENTRF funded work has already identified several pesticides and pharmaceuticals that produce persistent products, but we have not yet isolated and identified them. We will also use a three-pronged approach of literature search, our experimental measurements, and computational chemistry calculation to compile NMR data to allow other researchers to identify fluorinated byproduct produced from pharmaceutical and pesticide degradation.

#### Activity Milestones:

Description	Approximate Completion Date
Reaction kinetics (nucleophiles and photolysis)	August 31, 2025
Database of reaction products and NMR information	June 30, 2026
Reaction kinetics (microbiological and enzymes)	October 31, 2026
Product isolation	December 31, 2026
Publicaiton/dissemination	December 31, 2026

### Activity 3: Quantify microbial responses to fluorinated pesticides and pharmaceuticals

**Activity Budget:** \$168,000

#### Activity Description:

Biological degradation of fluorinated chemicals is particularly complicated in soils or wastewater, with multiple microorganisms potentially participating and making different fluorinated byproducts. To understand the diverse responses of environmental microorganisms to the presence to bio-transformable fluorinated pharmaceuticals and pesticides, it is important to determine when and under which conditions the microorganisms are active. By using fluorescent labels, cells that are actively degrading compounds can be detected, sorted, and then identified by sequencing. co-PI Behrens has recently developed a protocol to track protein synthesis (i.e., biological activity) in wastewater activated sludge. Here we will apply the technique to label active subpopulations that show high fluoride release. Cell suspensions derived from wastewater activated sludge and soils will be incubated with selected fluorinated pharmaceuticals and pesticides. Cells will be disaggregated, stained, and sorted on a cell sorter calibrated to detect the fluorescence signal. We will extract DNA from the sorted cell fractions, to identify which microorganisms best degrade fluorinated pesticides and pharmaceuticals. This will provide a means to identify microorganisms present in various environments that can degrade the compounds, and it will also provide opportunities to develop bioremediation systems for fluorinated compounds if needed.

#### Activity Milestones:

Description	Approximate Completion Date
Set up microcosms and quantify fluorine release from pollutants	June 30, 2025
Identify conditions for microorganisms to actively degrade fluorinated compounds	June 30, 2026
Stain and sort active microbial populations	December 31, 2026
DNA sequencing and data analysis	June 30, 2027
Publicaiton/disseminaiton	June 30, 2027

## Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
William Pomerantz	University of Minnesota, Department of Chemistry	co-Investigator. Dr. Pomerantz is an expert in the synthesis and characterization of fluorochemicals. He will oversee the NMR analyses to obtain fluorine balances and interpret degradation pathways.	Yes
Sebastian Behrens	University of Minnesota, Civil, Environmental, and Geo-Engineering	co-Investigator: Dr. Behrens will lead the biodegradation studies and evaluate the microbial responses to organofluorine biotransformation.	Yes

## 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 laboratories, agencies, stakeholders (including wastewater and drinking water plant operators) and practitioners through open access publications, direct meetings, and conference presentations. 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
Mapping Antibiotic Resistance in Minnesota to Help Protect Environmental, Animal, and Human Health	M.L. 2018, Chp. 214, Art. 4, Sec. 2, Subd. 04h	\$750,000
Determining Influence of Insecticides on Algal Blooms	M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04a	\$350,000
Benign Design: Environmental Studies Leading to Sustainable Pharmaceuticals	M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04b	\$415,000
Improving Drinking Water for Minnesotans through Pollution Prevention	M.L. 2019, First Special Session, Chp. 4, Art. 2, Sec. 2, Subd. 04f	\$345,000
Technology For Energy-Generating Onsite Industrial Wastewater Treatment	M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 04b	\$450,000
Monitoring Emerging Viruses in Minnesota's Urban Water Cycles	M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 04c	\$416,000
Microgeographic Impact of Antibiotics Released from Identified Hotspots	M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 04d	\$508,000

## 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.**

Dr. William Arnold has been studying the fate of pharmaceutical and pesticide 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, including antibiotics and neonicotinoid insecticides. His past work on the detection and fate of the antibacterial triclosan led to Minnesota being the first state to remove this compound from consumer products. He

has published over thirty peer-reviewed papers on the presence of pesticide and pharmaceutical in the environment and their degradation reactions in the past 10 years. His recent work has focused on fluorinated pesticides and pharmaceuticals that form this basis for this proposal. He is the co-author of a textbook on water chemistry published in 2011 (1st edition) and 2022 (2nd edition). He has advised over 40 graduate students whose current work is having a positive impact on the environment in Minnesota and across the country.

**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 PIs 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
<b>Personnel</b>								
Principal Investigator - Arnold		Lead project, supervise students			27%	0.18		\$56,198
co-Principal Investigator - Pomerantz		supervise students, lead fluorochemical identification work			27%	0.12		\$26,969
co-Principal Investigator - Behrens		supervise students, lead enzymatic and biodegradation studies			27%	0.12		\$27,452
Graduate Student #1		Perform chemical degradation experiments and product analyses, build database			44.4%	1.5		\$163,541
Graduate Student #2		Perform microbiological experiments, develop fluoride assay			44.4%	1.5		\$163,541
Undergraduate researcher		assist graduate students			0%	0.57		\$18,000
							<b>Sub Total</b>	<b>\$455,701</b>
<b>Contracts and Services</b>								
Core facilities at the University of Minnesota	Internal services or fees (uncommon)	Fees for NMR instrument time and microbial sequencing analyses				-		\$28,299
							<b>Sub Total</b>	<b>\$28,299</b>
<b>Equipment, Tools, and Supplies</b>								
	Tools and Supplies	Laboratory supplies	necessary chemicals, solvents, reagents, analytical supplies, and laboratory consumables needed for the experiments					\$40,000
	Tools and Supplies	Equipment maintenance	Parts and service to keep necessary instruments functioning					\$15,000
							<b>Sub Total</b>	<b>\$55,000</b>

<b>Capital Expenditures</b>								
							<b>Sub Total</b>	-
<b>Acquisitions and Stewardship</b>								
							<b>Sub Total</b>	-
<b>Travel In Minnesota</b>								
	Conference Registration Miles/ Meals/ Lodging	Project team to attend MN Water Conference	disseminate results to Minnesota audience					\$1,500
							<b>Sub Total</b>	<b>\$1,500</b>
<b>Travel Outside Minnesota</b>								
	Conference Registration Miles/ Meals/ Lodging	one trip for each graduate student to a national professional society meeting, includes airfare, registration, lodging and meals	Present project results to scientific peers and obtain feedback	X				\$3,500
							<b>Sub Total</b>	<b>\$3,500</b>
<b>Printing and Publication</b>								
	Publication	Open access fees for journal articles	Open access maximized availability of results to the public and stakeholders					\$16,000
							<b>Sub Total</b>	<b>\$16,000</b>
<b>Other Expenses</b>								
							<b>Sub Total</b>	-
							<b>Grand Total</b>	<b>\$560,000</b>



## Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
<b>Travel Outside Minnesota</b>	Conference Registration Miles/Meals/Lodging	one trip for each graduate student to a national professional society meeting, includes airfare, registration, lodging and meals	It is important for the students to be able present their work at a national meeting for their professional development

Non ENRTF Funds

Category	Specific Source	Use	Status	Amount
<b>State</b>				
			<b>State Sub Total</b>	-
<b>Non-State</b>				
In-Kind	Indirection costs not charged	U of MN facilities and administrative support	Secured	\$252,170
			<b>Non State Sub Total</b>	<b>\$252,170</b>
			<b>Funds Total</b>	<b>\$252,170</b>

## Attachments

### Required Attachments

#### *Visual Component*

File: [172f360d-25c.pdf](#)

#### *Alternate Text for Visual Component*

Fluorinated pesticides enter surface waters from (sub)urban and agricultural land. Fluorinated pharmaceuticals enter the environment via wastewater treatment. Biological, sunlight-driven, and other reactions can convert these pollutants into PFAS or fluoride. This work will assess which chemicals can form PFAS and provide options to minimize this process....

### Optional Attachments

#### *Support Letter, Photos, Media, Other*

Title	File
UMN authorization to submit	<a href="#">f42b53d0-d0a.pdf</a>

## 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?**

No

**Does your project include the design, construction, or renovation of a building, trail, campground, or other capital asset costing \$10,000 or more?**

No

**Do you propose using an appropriation from the Environment and Natural Resources Trust Fund to conduct a project that provides children's services, as defined in Minnesota Statutes section 299C.61 Subd.7?**

No

