



Environment and Natural Resources Trust Fund

2021 Request for Proposal

General Information

Proposal ID: 2021-142

Proposal Title: Refined Petroleum Leaks: Improving Remediation and Risk Assessment

Project Manager Information

Name: Dalma Martinovic-Weigelt

Organization: University of St. Thomas

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Project Basic Information

Project Summary: Toxicity of fuels and their degradation products common in MN waters is largely unknown. Project will generate knowledge needed for improvement of remediation and risk assessment of fuel spills statewide.

Funds Requested: \$340,000

Proposed Project Completion: 2024-06-30

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.

PETROLEUM SPILLS FROM UNDERGROUND STORAGE TANKS ARE COMMON IN MINNESOTA - Minnesota's water resources (and fish and wildlife) are threatened by petroleum leaks from underground storage tanks. MN Pollution Control Agency-Petroleum Remediation Program is currently monitoring approximately 19,000 leaking tank sites statewide. Some of the known chemical constituents of petroleum have been shown to be very toxic, but the toxicity of most of those chemicals, especially those generated by natural degradation, remains poorly understood.

TOXICITY OF FUELS AND THEIR DEGRADATION PRODUCTS IS POORLY UNDERSTOOD THUS HINDERING RISK ASSESMENT - Recent (ENTRF-funded) peer-reviewed research has shown that the chemical mixtures resulting from natural degradation of crude oil can be toxic (endocrine, liver and developmental effects were indicated). However, comparable comprehensive evaluation of toxicity of degradation products of refined fuels such as diesel fuel, gasoline and heating oil commonly stored in underground tanks is lacking statewide and nationwide.

COMMONLY USED METHODS FOR ASSESSMENT OF PETROLEUM-CONTAMINATED WATERS MAY BE UNDERESTIMATING HAZARD - Particularly concerning are the findings that widely used analytical methods for risk assessment of petroleum-contaminated waters appear to inadvertently remove a portion of toxic chemicals thus likely underestimating the hazard posed by aged (weathered) petroleum spills.

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

This project will generate new knowledge needed for improvement of monitoring, remediation and risk assessment of fuel spills statewide. It will characterize toxicity of fuel spills under variety of conditions that capture diversity of biogeochemical processes in MN waters. It will: 1) identify the types of toxicity associated with refined fuels and the likely regional variation thereof, 2) identify main chemicals of concern, and 3) evaluate the appropriateness of currently prescribed analytical methods for risk assessment of petroleum-contaminated waters.

Novel chemical and molecular methodologies paired with artificial intelligence tools that we developed as a part of the recent ENTRF project allowed us to successfully identify novel hazards and chemicals of emerging concern for crude-oil impacted ecosystems. These proof of concept studies at one of the best characterized petroleum-impacted sites in the nation (near Bemidji, MN) allowed us to assess the toxicity of crude oil-impacted waters faster, cheaper, and more completely. Now that we have road-tested and optimized these novel methodologies, we are uniquely equipped to use those to tackle the issue of the refined fuels in MN waters.

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?

This project will generate data needed to guide protection of the MN water resources. The outcomes are of high importance to the managers and regulators as there is a lack of data regarding toxicity of refined fuels and their degradation products, and there is a lively debate about suitability of the current analytical approaches for the hazard assessment of petroleum-contaminated samples. It will benefit MN agencies; some are currently revisiting/developing guidelines for total petroleum hydrocarbon assessment. It will facilitate essential conversations between public, industry, scientists and regulators about the best practices for risk management of the refined fuel leaks.

Activities and Milestones

Activity 1: Characterize the types of toxicity associated with the refined fuel spills and the regional variation thereof

Activity Budget: \$118,938

Activity Description:

Understanding of fate (including degradation) and transport of fuel/its chemical constituents in the subsurface is critical for water resource protection; fate and transport are influenced by hydrologic and biogeochemical properties of the system. Sediment microcosm experiments will be conducted to simulate degradation under a variety of microbial, geochemical and hydrologic conditions found in MN. Water samples (12) generated by these degradation experiments (and/or field characterized samples) will be assessed for toxicity (including carcinogenesis, endocrine disruption, neurotoxicity). Cutting-edge techniques will be used - living cells will be exposed to “whole” water samples of interest and screened for 90+ types of biological activity indicative of toxic effects. These methods can efficiently screen samples and evaluate the potential of the complex environmental mixtures to pose ecological/health hazards. In addition, assays with aquatic organisms important to ecosystem function (e.g., bacteria, fish) will be conducted; this is important because petroleum products are a common water pollutant. Data will be disseminated to peers, regulators, citizens and educators. If time permits and we can gain access to active fuel leak sites (many are on private property), we will also conduct and consider field sample analyses for toxicity.

Activity Milestones:

Description	Completion Date
1. Conduct fuel degradation experiments under variety of hydro-biogeochemical processes typical of MN ecosystems	2022-06-30
2. Characterize toxicity types (90+ tests) in samples generated in Milestone-1.1.	2022-09-30
3. Characterize toxicity of samples from Milestone-1.1 to aquatic organisms (bacteria and fish behavior/physiology)	2023-06-30
4. Collect field samples (if access granted) and characterize toxicity/chemistry and compare to lab	2024-06-30

Activity 2: Identify main chemicals and toxicities of concern

Activity Budget: \$221,062

Activity Description:

We will analyze the chemistry of the fuel contaminated samples (using established methods within the researchers' expertise) and develop new techniques to quantify the extractable organic compounds within the real, “whole water” samples, as well as the specific fractions of samples. Particular attention will be given to the isolation of chemicals of emerging concern (oxygen-containing hydrocarbon metabolites in the form of acids versus non-acids). Recent research indicates that these are common by-products of petroleum degradation and that they can be toxic. Data analytics methods including artificial intelligence will be used to integrate toxicity and chemistry data to identify chemicals of concern.

We will also investigate whether widely used sample preparation/analytical methods for risk assessment of petroleum-contaminated waters might inadvertently remove a portion of the toxic chemicals thus likely underestimating the hazard posed by the aged refined fuel spills.

New data about toxicity of degraded fuels paired with the analysis of suitability of the current analytical approaches for the hazard assessment will improve managers' ability to cost-effectively remediate and monitor fuel impacted sites. A

variety of outreach activities will be executed including annual event at the State Fair (opportunity to interact with Minnesotans from all over the state).

Activity Milestones:

Description	Completion Date
1. Separate samples from Milestone-1.1. into fractions using three methods used for risk assesment	2022-10-31
2. Separate fuel-contaminated samples from Milestone-1.1. into fractions based on chemical characteristics	2023-02-28
3. Complete toxicity analyses of fractions generated in Milestones 2.1 and 2.2.	2023-06-30
4. Complete chemical analyses of toxic fractions generated in Milestones 2.1. and 2.2	2024-03-31
5. Integrate toxicity and chemistry data to identify main chemical drivers of toxicity	2024-06-30

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Chih Lai	University of St. Thomas	Computer Scientist - Professor (Ph.D. - Oregon State U, 1999). Recipient of more than \$920,000 in research funding from federal (National Science Foundation), state (MN), and industry (Amazon). Co-authored 20+ peer-reviewed publications and 5 patents. Recipient of Medtronic, Multimedia Data Mining and Aerospace Industry awards.	Yes
Jennifer McGuire Illig	University of St. Thomas	Geologist- Professor - U of St. Thomas, MN (2008-present); Texas A&M (2002-08, tenured). Ph.D.- Environmental Geoscience-Toxicology (Michigan State U, 2002). Co-authored 20+ research manuscripts that address chemical fate & transport and biogeochemistry. Managed \$1.8 million of projects that address toxicity, bioremediation (petroleum) in aquifers and wetlands.	Yes
Phoebe Zito	University of New Orleans	Environmental Chemist – (Ph.D. 2014, U of New Orleans) – development/application of analytical methods to measure compositional and optical changes after petroleum compounds are photodissolved and/or biodegraded in aquatic systems. Dr. Zito has co-authored over 30 peer-reviewed scientific papers and was involved in a photochemistry panel regarding the Deepwater Horizon oil spill.	Yes
David Podgorski	University of New Orleans; Pontchartrain Institute for Environmental Sciences and Department of Chemistry	Chemist - Assistant Professor (Ph.D. - Florida State U); Researches production, transport and fate of dissolved organic compounds and contaminants in aquatic ecosystems. Principal investigator on several externally funded studies of of biotic and abiotic degradation processes in petroleum-contaminated environments. Co-authored 50 peer-reviewed scientific papers.	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 be funded?

The novel toxicity assessment toolbox we develop as part of this project will be transferable to variety of sites in MN and broader, and its findings will continue to inform risk assessment, remediation and regulatory efforts statewide. Our work will be widely disseminated via peer-reviewed literature and via conferences attended by industry, government and academic representatives to promote tripartite, collaborative advancement of risk assessment of petroleum impacted site. Finally, the data generated by this project will give rise to new questions and solutions; we plan to seek funds from state and federal entities to address those.

Other ENRTF Appropriations Awarded in the Last Six Years

Name	Appropriation	Amount Awarded
Reassessing Toxicity of Petroleum Spills on Groundwater and Surface Water	M.L. 2017, Chp. 96, Sec. 2, Subd. 04e	\$300,000

Project Manager and Organization Qualifications

Project Manager Name: Dalma Martinovic-Weigelt

Job Title: Professor- Toxicologist

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

Dalma Martinović-Weigelt completed her Ph.D. in Fisheries Science and Water Resources at the U of MN – Twin Cities (2005). She served as National Academies Research Associate at the U.S. Environmental Protection Agency (U.S. EPA) from 2006-09. She is a professor at the University of St. Thomas in St. Paul, MN (2009-present). Dr. Martinović-Weigelt’s research interests include: 1) Assessment of effects of environmental stressors and contaminants (e.g., chemicals of emerging concern, hypoxia) that informs risk assessment, 2) Development of chemical hazard evaluation approaches that use modern molecular biology tools to increase efficiency of toxicity testing in complex environmental scenarios. Dr. Martinovic has co-authored three reports to MN Legislature (Pharmaceuticals and Chemicals of Concern in Rivers: Occurrence and Biological Effects (2017), tdr-g1-20; Wastewater Treatment Plant Endocrine Disrupting Chemical Monitoring Study (2011), lrp-ei-1sy11; Endocrine Disrupting Compounds (2008), lrp-ei-1syo8;) and circa 50 research manuscripts that assess occurrence and the effects of chemicals of emerging concern and other stressors on fish and aquatic ecosystems. Dr. Martinovic is a recipient of several US EPA’s Scientific and Technological Achievement Awards. She has served on the Editorial Board of the Environmental Toxicology and Chemistry Journal, as a member of The Contaminant Screening Criteria and Prioritization Development Task Group for MN Dept. of Health, and as a president of Midwest Chapter of Society of Environmental Toxicology and Chemistry. Since her arrival to UST in 2009 Dr. Martinović-Weigelt has been awarded and has managed several externally-funded projects (ca \$1,300,000) funded by a variety of state and federal agencies including ENTRF, MN Pollution Control Agency, U.S. EPA and National Science Foundation (NSF).

Organization: University of St. Thomas

Organization Description:

UST was founded in 1885 and emphasizes values-based education and career preparation, it helps solve community problems through education and service-learning programs. 56% of UST students receive need-based scholarship or grant aid. The largest private university in Minnesota (11,000 students, 461 full-time faculty), it offers bachelor's degrees in 85 major fields of study and 45 graduate degree programs, and is ranked as a National University. UST’s Biology Department views -faculty research as essential - over the past 10 years, the faculty in Biology Department have received research grants from the NSF, NIH, USDA, USEPA, USGS, and multiple MN agencies (DNR, MPCA). Currently, the UST’s Science Division has ca \$5.95 million of capital equipment, nearly half of which is owned/ maintained by Biology Dept.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	\$ Amount
Personnel								
Project Manager/Toxicologist		Manage and oversee project, conduct toxicity analyses, disseminate data			8%	0.51		\$68,400
Co-principal Investigator/Bigeochemist		Conduct biogeochemistry lab experiments, oversee students and field work			8%	0.51		\$72,994
Co-principal Investigator/Data Analytics Specialist		Use advanced statistical and artificial intelligence methods to integrate chemistry and toxicity data			8%	0.09		\$13,740
Undergraduate Research Assistant		Conduct lab experiments during academic year			0%	0.27		\$7,200
Undergraduate Research Assistant		Conduct lab and field experiments during summers (June 1-Aug 31)			8%	0.51		\$15,552
							Sub Total	\$177,886
Contracts and Services								
University of New Orleans	Sub award	Drs. Zito and Podgorski will provide excitation-emission matrix spectroscopy, and ultrahigh resolution mass spectrometry data - 48 samples in duplicate analyzed for 60 chemicals; \$16 per analysis. Unique qualifications: 1) extensive experience with weathered petroleum/novel chemistry methods for complex mixtures, 2) experience with supporting our specific toxicology/data analyses.				0.99		\$92,400
							Sub Total	\$92,400
Equipment, Tools, and Supplies								
	Tools and Supplies	High throughput toxicity assay supplies, Attagene assay runs and assay setup - 6480 analyses at \$8.33 each totaling \$54,000 (i.e., 36 samples tested in duplicate for 90 toxicity parameters)	To conduct comprehensive molecular toxicity evaluation					\$54,000
	Tools and Supplies	Miscellaneous disposable lab supplies - microcosms, capillaries, reagents, filters,	Used to set up fuel degradation experiments, to conduct					\$11,314

		buffers, sample processing supplies (disposable sampling containers, pipette tips, chemicals, extraction columns), animal microcosm setups, and microbiology supplies.	extractions and fractionations and to conduct traditional toxicity analyses					
							Sub Total	\$65,314
Capital Expenditures								
							Sub Total	-
Acquisitions and Stewardship								
							Sub Total	-
Travel In Minnesota								
	Miles/ Meals/ Lodging	Travel for project staff to conduct field sampling/experiments, team of 4 x 2 days per location x 5 locations x \$100 (cost of daily lodging and food) x 1 years = \$4,000	Collect contaminated fuel samples form MN sites					\$4,000
							Sub Total	\$4,000
Travel Outside Minnesota								
							Sub Total	-
Printing and Publication								
							Sub Total	-
Other Expenses								
		Shipping	Shipping of samples for chemistry and toxicity analyses					\$400
							Sub Total	\$400
							Grand Total	\$340,000

Classified Staff or Generally Ineligible Expenses

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

Category	Specific Source	Use	Status	Amount
State				
			State Sub Total	-
Non-State				
In-Kind	Unrecoverable Indirect Cost	Indirect facilities and administrative costs including maintenance and use of variety of specialized lab spaces and equipment, and servers and workstations for computing.	Secured	\$102,506
			Non State Sub Total	\$102,506
			Funds Total	\$102,506

Attachments

Required Attachments

Visual Component

File: [fd0ff5d7-f61.pdf](#)

Alternate Text for Visual Component

Figure 1. Project Methodology and Petroleum Cleanup Sites in MN -

Petroleum spills from underground storage tanks are very common in MN. This project will: 1) identify the types of toxicity associated with refined fuels and the likely regional variation thereof, 2) identify main chemicals of concern, and 3) evaluate the appropriateness of currently prescribed analytical methods for risk assessment of petroleum-contaminated waters.

Financial Capacity

File: [68125a71-095.pdf](#)

Administrative Use

Does your project include restoration or acquisition of land rights?

No

Does your project have patent, royalties, or revenue potential?

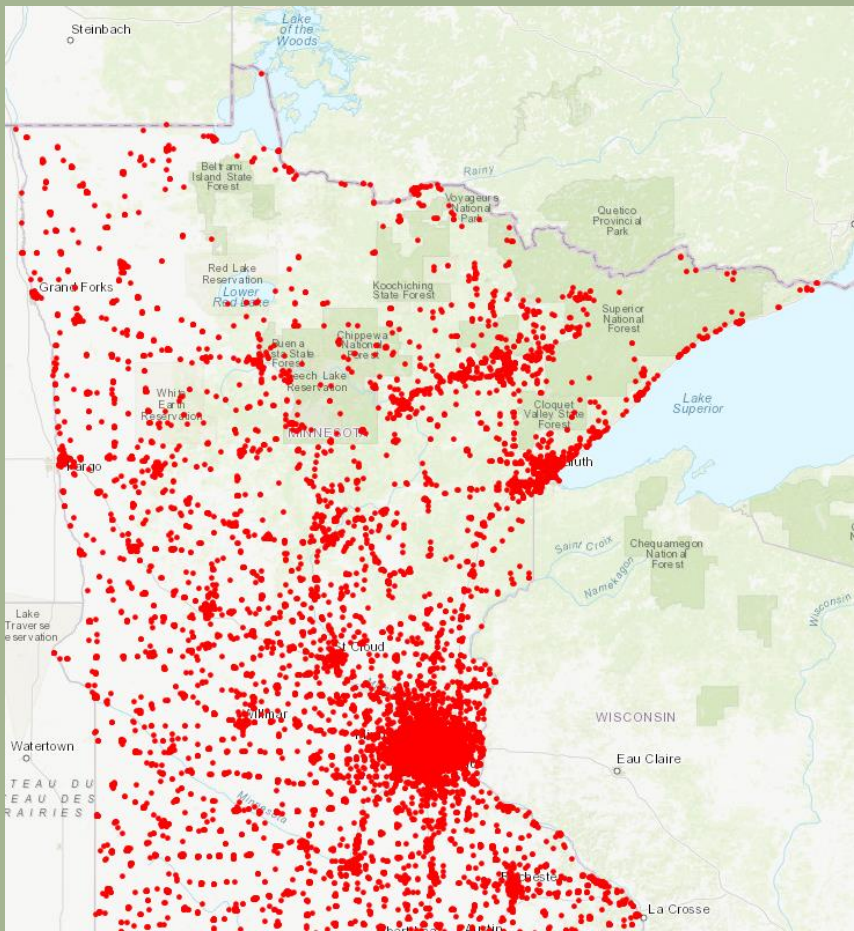
No

Does your project include research?

Yes

Does the organization have a fiscal agent for this project?

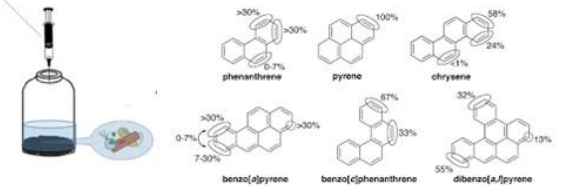
No



Chemistry

Collect and generate fuel contaminated samples

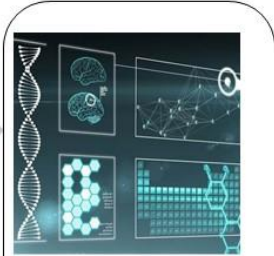
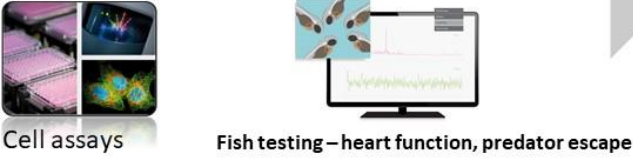
Identify and quantify chemicals (known and new) in these samples



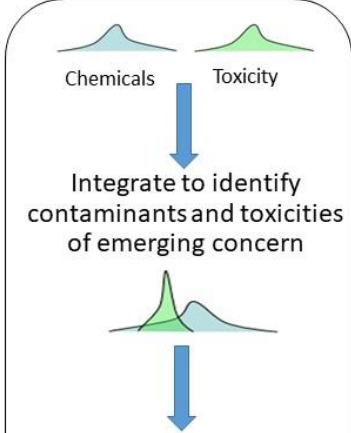
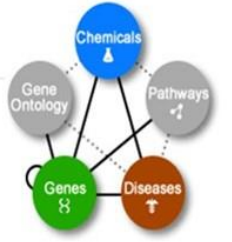
Toxicology

Test above water samples for 90 toxicity indicators using cell assays

Identify toxic outcomes of concern and confirm those in live animal tests with bacteria and fish



Integrate
data with historical chemistry data and toxicity data in public domain



St. Thomas students and faculty discussing past ENTRF funded project with public at the State Fair

Image sources: <https://www.noldus.com/darioscope> and <https://www.americanaf.org/future-medical-technology.html>

Still image of an interactive map showing petroleum cleanup sites in MN - MN PCA maps
<https://mpca.maps.arcgis.com/apps/webappviewer/index.html?id=8cb48bd1696e4426834b80aaa18be468>

Overview of the Project Methodology