

**Environment and Natural Resources Trust Fund  
2017 Request for Proposals (RFP)**

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**Project Title:**

**ENRTF ID: 048-B**

Reassessing Toxicity of Petroleum Spills with New Technologies

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**Category:** B. Water Resources

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**Total Project Budget:** \$ 423,189

**Proposed Project Time Period for the Funding Requested:** 3.5 years, July 2017 - August 2020

**Summary:**

Reassess the toxicology of groundwater and associated surface water impacted by petroleum spills using new technologies. Past toxicity assessments are based on incomplete chemical knowledge and inadequate biological effects data.

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**Name:** Dalma Martinovic-Weigelt

**Sponsoring Organization:** University of St. Thomas

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**Web Address** http://www.stthomas.edu/biology/research/environmental-toxicology.html

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**Location**

**Region:** Northwest

**County Name:** Beltrami

**City / Township:**

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**Alternate Text for Visual:**

Petroleum Toxicity Project-Conceptual Model

_____ Funding Priorities	_____ Multiple Benefits	_____ Outcomes	_____ Knowledge Base
_____ Extent of Impact	_____ Innovation	_____ Scientific/Tech Basis	_____ Urgency
_____ Capacity Readiness	_____ Leverage	_____ TOTAL	_____ %



**PROJECT TITLE:**

Reassessing toxicity of petroleum spills with new technologies

**I. PROJECT STATEMENT**

**Threat:** Minnesota’s water resources (and wildlife and fish that use those) are threatened by petroleum spills from leaking underground storage tanks, oil refineries, and spills from the transnational pipeline that crosses our state. For example, at this time MN Pollution Control Agency-Petroleum Remediation Program (MPCA-PRP) is monitoring more than 19,000 leaking tank sites. Many of the known chemical constituents of petroleum are very toxic to the fish and wildlife, and the toxicity of many of these constituents has not been evaluated.

**Major Knowledge Gaps:**

We do not know the chemical identity, quantity and toxicity of many chemicals present in petroleum-impacted groundwater and surface water, particularly the chemicals that result as the petroleum degrades over time (i.e., degradation products). **Past toxicity assessments of petroleum-impacted surface and groundwater are: 1. Incomplete** – because only a small subset of known chemicals have been assessed for toxicity, and **2. Inadequate** for identification of many sublethal effects (including those on endocrine, immune and nervous systems) – which are important determinants of organism’s survival and population health.

Below we frame our contribution in a well-known context communicated by the **former Secretary of Defense Donald Rumsfeld:**

1. *“There are known knowns. These are things we know that we know” - this is what we already regulate for and what we monitor in MN.*
2. *“There are known unknowns. That is to say, there are things that we know we don't know.” – we know that past toxicity assessment omitted analyses of many biologically important effects and propose to evaluate those (e.g., endocrine, immune, neurotoxic effects).*
3. *“But there are also unknown unknowns. There are things we don't know we don't know” – new technologies allow us to look for unknown toxic chemicals and to detect toxicity in the whole samples that we could not have predicted based on our past knowledge.*

**Opportunity:** Over the past two years exciting new technologies emerged that will allow us to investigate the toxicity of petroleum-impacted waters **faster, cheaper, and far more completely.** For the first time in the history of science, we have tools to analyze whole-water samples (waters containing both original petroleum compounds and degradation products) for over 100 toxicity indicators in a time- and cost-effective manner and develop new, cutting-edge water chemistry analyses that can help us identify unknown pollutants.

The work proposed here would improve our understanding of the lasting effects of oil spills on groundwater and associated surface water, and allow regulators to better prioritize clean-up efforts to mitigate risk to ecological health given limited funds.

**Activity 1:** More completely characterize the chemistry of waters impacted by petroleum.

**Budget: \$ 221,308**

Water samples will be collected from environments impacted by petroleum release and will include impacted **groundwater, as well as water from a lake and wetland.** We plan to analyze at least **12 sites for ~90 chemical parameters.** We will analyze the current and historical water chemistry of these locations using well established methods within the PI’s expertise as well as developing new techniques to quantify the extractable organic compounds within the real, “whole water” samples. To capitalize on more than 30 years of investments



**Environment and Natural Resources Trust Fund (ENRTF)**

**2017 Main Proposal**

**Project Title:** Reassessing toxicity of petroleum spills with new technologies

in data and infrastructure already made, we propose to complete this study at the national crude oil research site located near Bemidji, MN; however, this novel approach could be applied to any well-characterized site.

Outcome	Completion Date
1. Characterize the current and historical chemistry of contaminated water samples using existing and new analytical techniques. Water chemistry will include both <i>in-situ</i> field chemistry and laboratory analyses and measurements for circa 100 chemical parameters.	August 2019
2. Identify areas of greatest risk and communicate results to regulators (MPCA, MDH)	June 2020

**Activity 2:** Determine the toxicity of petroleum-impacted waters

**Budget: \$ 201,881**

**Samples will be analyzed for approximately 100 different toxicity types** (including carcinogenesis, DNA damage, endocrine disruption, neurotoxicity) using cutting-edge techniques where living cells/proteins are exposed to “whole” water samples of interest and screened for changes in biological activity that are indicative of potential toxic effects. Unlike past approaches, these novel methods can quickly and efficiently screen samples for many toxicity responses and evaluate the potential of the **complex environmental mixtures** to pose health hazards. In addition, assays with aquatic animals important to ecosystem function (*Daphnia sp.* and/or native fish) will be conducted. Direct assessments of impacts on aquatic organisms is important as petroleum products are a common water pollutant. The effects on the health of exposed animals will be evaluated by measuring gene responses that are important for maintenance of normal reproductive and metabolic function.

**Outreach and Dissemination of project data** will be used to enhance Minnesota’s STEM education via a) direct training of students, b) undergraduate classroom activities, and c) dissemination of educational materials through extracurricular academic routes such as SEAK. The SEAK (“Scientists Eagerly Acquiring Knowledge”) program is a partnership between Wolf Ridge Environmental Learning Center, the Boys & Girls Clubs, and several schools to give urban students an opportunity to explore careers in science.

Outcome	Completion Date
1. Analyze whole waters for 100 toxicity outcomes using high-throughput techniques.	August 2019
2. Characterize the resulting water chemistry, toxicity and hazard to native aquatic species (invertebrates and fish) using recently developed modeling tools.	December 2019
3. Communicate findings to interested parties as in Activity 1	June 2020
4. Outreach activities via UST courses and extracurricular venues such as SEAK	May 2020

**III. PROJECT STRATEGY**

**A. Project Team/Partners**

This project will be carried out under the supervision of Dr. Martinovic-Weigelt and Dr. McGuire (University of St. Thomas), with a collaborator Dr. Cozzarelli (United States Geological Survey). Information transfer and study design will be conducted with contacts at the MN Dept. of Health and MPCA-Petroleum Remediation Program.

**B. Project Impact and Long-Term Strategy**

Data collected will improve understanding of the longer term effects of oil spills on ecological and human health for use by regulatory agencies, such as the MPCA and MDH, to manage contaminated sites safely.

**C. Timeline Requirements**

3 years

## 2017 Detailed Project Budget

Project Title: *Reassessing toxicity of petroleum spills with new technologies*

### IV. TOTAL ENRTF REQUEST BUDGET 3 years

BUDGET ITEM	AMOUNT
<b>University of Saint Thomas Personnel: Prof. Dr. Dalma Martinovic-Weigelt, Principal Investigator (PI)</b> , 1 month summer salary (8.33% effort) per year (totaling \$27,260 for 3 yrs) plus 7.65% fringe (\$2,085.37 for 3 years). Duties: Responsible for high throughput assay assessment, analyses and interpretation of those assays, compiling reports and disseminating results. <b>Prof. Dr. Jennifer T. McGuire, Co-Principal Investigator (Co-PI)</b> , 2 months summer salary (16.6% effort) per year (totaling \$59,070 for 3 yrs) plus 7.65% fringe (\$ 4,519) for 3 years). Duties: Responsible for coordinating project, conducting field experiments & chemistry analyses, and compiling reports and disseminating results. <b>Undergraduate students</b> , Assist with field sampling and lab analyses. One student during the academic year, 10 hrs for 32 weeks each year @ \$10/hr, totaling \$9,600 for three years, no fringe (0%). 2 students during each summer, 40 hrs/week for 10 weeks @ \$10/hour totaling \$24,000 plus 7.65% fringe (\$1,836). <b>Postdoctoral Researcher</b> , assist with field sampling and lab analyses, full time (100% effort) per year for 2 years (totaling \$91,350 for 2 years) plus 25% fringe (\$22,838),	\$232,089
<b>Contracts:</b> Water chemistry not conducted at UST (aprox. 60 analyses at a minimum of 12 site locations), including development of new analytical techniques to quantify metabolites of crude oil in natural waters, will be conducted by USGS laboratories supervised by Dr. Cozzarelli.	\$ 94,000
<b>Equipment/Tools/Supplies:</b> \$57,200 - High Throughput toxicity assay runs - ca \$4,400 per sample. \$6,900 Field sampling supplies (bottles, tubing, filters, reagents): \$13,400 Miscellaneous lab supplies (capillaries, reagents, filters, buffer solutions) and sample processing supplies (disposable plastic sampling containers, chemicals, extraction supplies etc.); \$4,900 Lab animal microcosm setups and microbiology supplies	\$ 82,400
<b>Travel:</b> Travel to conduct field sampling and field experiments, 1 week field campaign - team of 4 x 5 days x 100 (lodging and food)x 3 yrs = \$6,000; Mileage for travel to field sites in MN @ \$0.50/mile = \$5,100; Present findings of the study at the annual conference of Society of Env Toxicology and Chemistry (McGuire), \$3,000.	\$ 14,100
<b>Additional Budget Items:</b> Computer Software for TOXcalcs (\$600)	\$ 600
<b>TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND \$ REQUEST =</b>	<b>\$ 423,189</b>

### V. OTHER FUNDS

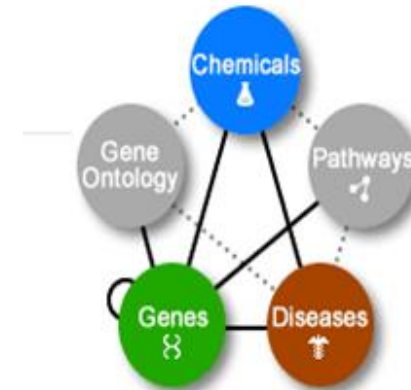
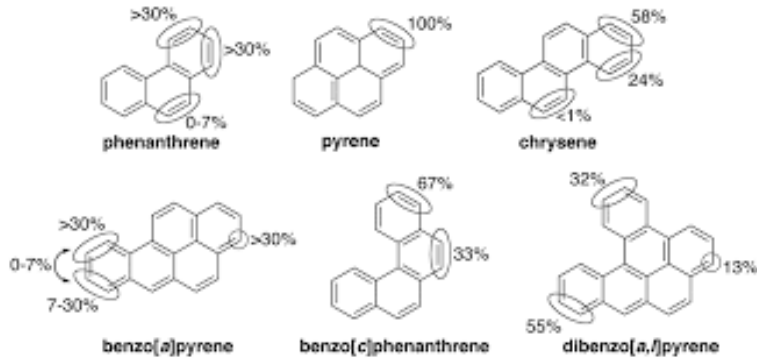
SOURCE OF FUNDS	AMOUNT	Status
<b>Other Non-State \$ Being Applied to Project During Project Period:</b> <i>Indirect costs to Univesity of St. Thomas-waived</i>	\$ 173,507	<i>Indicate: Secured or Pending</i>
<b>Other State \$ Being Applied to Project During Project Period:</b>	\$ -	<i>Indicate: Secured or Pending</i>
<b>In-kind Services During Project Period:</b> <i>Dr. Cozzarelli, US Geological Survey, will contribute 1 month per year of her salary for 3 years (\$16252 per year, \$48,756 total) and \$2000 per year in field travel funds (total \$6000)</i>	\$ 54,756	<i>Indicate: Secured or Pending</i>
<b>Remaining \$ from Current ENRTF Appropriation (if applicable):</b>	\$ -	<i>Indicate: Unspent? Not Legally Obligated? Other?</i>
<b>Funding History:</b>	\$ -	

# PROJECT TITLE: Reassessing toxicity of petroleum spills with new technologies

## ACTIVITY 1

Collect petroleum contaminated groundwater, lake and wetland samples

Identify and quantify circa 100 chemicals (known and new) in these samples



Integrate data from Activities 1 and 2 with historical chemistry data and publically available toxicity data to:

- 1) Identify main contaminants of concern
- 2) Identify animal health hazards

OUTREACH &  
DISSEMINATION

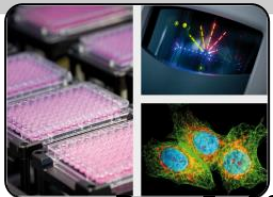
STEM Education  
MN Regulatory  
Agencies

ENRTF ID: 048-B

## ACTIVITY 2

Test water samples from Activity 1 for approximately 100 toxicity indicators using high-efficiency, low-cost cell assays

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



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Cell assays

Animal assays

05/07/2016

## **Project Managers Qualifications and Organization Description**

### **The University of St. Thomas (UST) – Dalma Martinović-Weigelt, PhD –Principal Investigator**

Dalma Martinović-Weigelt completed her Ph.D. in Fisheries Science and Water Resources at the U of MN (2005), and served as National Academies Research Associate at the U.S. Environmental Protection Agency (USEPA) from 2006-09. Dr. Martinovic is an associate professor at University of St. Thomas in St. Paul, MN (2009-present). Dr. Martinovic-Weigelt's research interests include: 1) Characterization of proximate mechanisms that underlie behavior and reproduction in fish, 2) Assessment of effects of environmental stressors and contaminants (e.g., hypoxia, nitrates, chemicals of emerging concern) to inform adverse outcome pathway development for small fish models, 3) Optimization and development of approaches for bioeffects-based monitoring (using high-content, omic-based approaches). Dr. Martinovic has co-authored two reports to MN Legislature (Endocrine Disrupting Compounds, Irp-ei-15yo8; Wastewater Treatment Plant Endocrine Disrupting Chemical Monitoring Study, Irp-ei-15y11) and circa 40 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 received external-funding from a variety of state and federal agencies including MN Pollution Control Agency, USEPA and National Science Foundation.

**The University of St. Thomas (UST) - Jennifer McGuire, Ph.D. , Co-Principal Investigator –** Dr. McGuire is a Professor at UST, St. Paul, MN (2008-present). From 2002-2008 she served as an Assistant Professor at Texas A&M University where she was tenured. She completed her Ph.D. in Environmental Geoscience-Environmental Toxicology, at Michigan State University, 2002. Dr. McGuire has co-authored circa 20 research manuscripts that address chemical fate and transport and environmental biogeochemistry. Her research focuses on understanding the controls on the spatial and temporal variability of microbial metabolism which is necessary to evaluate health and safety concerns such as: chemical routes of exposure (risk assessment), natural attenuation and bioremediation capabilities, and the management of redox sensitive environments such as lakes, wetlands and estuaries. Dr. McGuire has been awarded, and has managed several externally-funded projects at UST (ca \$1,550,000) including MN PCA's Field Studies of Chemical and Microbiological Controls on Biodegradation Rates of Crude Oil in Aquifer and Wetland Systems and NSF's Biocomplexity in the Environment: Quantifying the Role of Mixing Interfaces in Biogeochemical Cycling in a Contaminated Aquifer-Wetland System: Linking Hydrogeological, Microbiological, and Geochemical Processes Grants.

### **The University of St. Thomas (UST) – Institution 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 \$5.7 million of capital equipment, nearly half of which is owned/ maintained by Biology.

**PROJECT TITLE:** Evaluating oil's toxic effects on water resources

**Contract-United States Geological Survey- Dr. Isabelle Cozzarelli**

Isabelle Cozzarelli is a Research Hydrologist in the USGS National Research Program. She holds a Ph.D. (1993) and M.S. (1986) from the University of Virginia in Environmental Sciences-Geochemistry. As a Lead Scientist in USGS, Dr. Cozzarelli conducts interdisciplinary long-term research on the fate and geochemical effect of organic contaminants in surface and subsurface environments. Her research focuses on the coupled hydrogeological, microbiological, and geochemical processes that control the redox potential of subsurface systems and are a fundamental issue in understanding nutrient and contaminant biogeochemical cycles and in protecting drinking water and ecosystem health. She is currently PI of studies of aquifers and wetlands contaminated with hydrocarbon, oil and gas wastewaters, and landfill leachate, with an emphasis on understanding the long-term natural attenuation of contaminants. Dr. Cozzarelli has co-authored over 100 peer-reviewed scientific papers and served as Associate Editor, *Water Resources Research*, *Ground Water*, and currently for *Journal of Contaminant Hydrology*. In 2005 she was Elected GSA Fellow. She serves on the International Advisory Board for the Danish GEOCON Project (<http://www.geocon.env.dtu.dk/People-and-Institutions>) and has served as technical advisor to US EPA on oil spills response.

