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

Project Title: **ENRTF ID: 033-B**

Household Chemicals as Water Pollutants and Toxic Precursors

Category: B. Water Resources

Total Project Budget: $ 236,000

Proposed Project Time Period for the Funding Requested: 2 years, July 2017 – June 2019

Summary:

Environmental levels of household chemical and herbicide ingredients will be quantified in Minnesota rivers and lakes and their potential to form toxic byproducts will be assessed.

Name: William Arnold

Sponsoring Organization: U of MN

Address: 500 Pillsbury Dr SE

Minneapolis MN 55455

Telephone Number: (612) 628-8582

Email arnol032@umn.edu

Web Address www.williamarnold.org

Location

Region: Statewide

County Name: Statewide

City / Township:

Alternate Text for Visual:

Cleaning products, herbicides, and fabric softeners enter lakes and rivers, accumulate in sediments, and may react during water disinfection to form toxic byproducts

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

PROJECT TITLE: Household chemicals as water pollutants and toxic precursors

I. PROJECT STATEMENT

Personal care products, fabric softeners, disinfectants, and herbicides (both those used on land and to control aquatic plants) all have something in common. Each contains a type of chemical known as a quaternary ammonium compound (QAC or "quack"), which can react to form carcinogens in tap water. The overall goal of this project is to improve water quality, protect ecosystem health, and limit the production of carcinogens during tap water disinfection by:

- Quantifying current and historical levels of these pollutants in surface water and sediment samples,
- Evaluating of the persistence of these compounds in surface waters, and
- Determining the levels of carcinogenic nitrosamines produced attributable to these contaminants during drinking water and wastewater disinfection.

Either intentionally or unintentionally, QACs enter the environment. They are biologically active molecules. They kill bacteria, and evidence suggests exposure to these chemicals may affect microbial communities in wastewater treatment and algal communities in surface waters. There is also evidence that exposure to QACs may lead to development of antibiotic resistance. There are also potential effects on plants. Lastly, evidence suggests that if these common chemicals react with the disinfectant used in drinking water and wastewater treatment (chloramines) potent carcinogens known as nitrosamines are produced. *The types and amounts of QACs entering and present in Minnesota's lakes and rivers are unknown.* Our hypotheses are that levels of these chemicals in Minnesota's water and sediment and the carcinogenic nitrosamine formation potential are driven by household uses.

Gathering information about QAC presence and reactivity will reveal the magnitude of any threats to human or ecosystem health posted by these chemicals, which include development of antibiotic resistance, disruption of plant/algal communities, and production of carcinogens in drinking water. This project will also make it possible to evaluate the major sources of these chemicals to Minnesota's waters. This knowledge will be critical in determining if regulations are needed or if risks can be ameliorated via alterations to/improvements in water treatment processes or product usage recommendations.

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: Measurement of quaternary ammonium compound pollutants in river water, sediment cores, and surface sediments **Budget: $ 91,000**

Because QACs stick to particles, the most likely environmental compartment to find them in is sediments. Samples of sediment collected from four lakes and two rivers as part of an ongoing ENTRF project (Antibiotics and Antibiotic Resistance Genes in Minnesota Lakes) will be extracted, and the concentration of the target chemicals will be measured using liquid chromatography tandem mass spectrometry. The sediment cores will provide information about usage over time, and the surface sediments will reveal usage patterns across the state. River water samples to be collected downstream of wastewater treatment plants and elsewhere along the Minnesota and Mississippi Rivers will provide information about current environmental discharges.

Outcome	Completion Date
1. Optimize extraction and analytical methods	12/31/17
2. Measure concentrations in sediment samples	10/31/18
3. Measure concentrations in water samples	4/30/19

Activity 2: Evaluation of environmental persistence in surface waters **Budget: $ 66,000**

The impact of QACs on algal or microbial communities will be a function of both their concentration and persistence. It is known that the compounds will stick to particles and settle to lake bottoms, but the native microbiology in the river may be able to degrade the compounds as well. This will be tested by dosing river water samples with QACs and monitoring their loss over time. It has also been suggested that QACs are associated with the colored organic matter in surface waters. This would make QACs susceptible to reaction with reactive species, such as hydroxyl radicals, produced when organic matter is exposed to sunlight. If these chemicals are associated with the organic matter, their destruction would be enhanced relative to other pollutants. The product will be development of parameters to predict QAC lifetimes in lakes and rivers.

Outcome	Completion Date
1. Measurement of biodegradation rates in river/lake water	9/30/18
2. Quantification of indirect photolysis reaction rate constants	6/30/19

Activity 3: Determination of carcinogen production during water disinfection **Budget: $ 79,000**

When QACs react with the disinfectants used in drinking water and wastewater treatment, it is possible to produce carcinogens known as nitrosamines. Thus, there is the potential for release of carcinogenic nitrosamines to the environment or production in tap water and consumer exposure. Solutions in tap water and wastewater will be exposed to chloramines at various dosages. The formation of nitrosodimethylamine (a known carcinogen) and total nitrosamines will be measured using liquid chromatography and gas chromatography mass spectrometry. Results will demonstrate which compounds have the greatest potential to produce carcinogens.

Outcome	Completion Date
1. Nitrosamine formation potential in drinking water	1/31/19
2. Nitrosamine formation potential in wastewater	6/30/19

III. PROJECT STRATEGY

A. Project Team/Partners

The project will be led by William Arnold (University of Minnesota, Department of Civil, Environmental, and Geo-Engineering) who has extensive experience in quantifying pollutants in environmental matrices and studying the degradation of environmental contaminants. The team will consist of a postdoctoral researcher and one graduate student research assistant.

B. Project Impact and Long-Term Strategy

This project will provide information regarding the usage of QACs in Minnesota and their distribution in the environment. Knowing the environmental fate of these pollutants will aid in assessment of environmental impacts, which include disruption of plant or algal function and development of antibiotic resistance. There potential for carcinogenic nitrosamines to be present in river and drinking water from the reaction of the target chemicals has important implications for the protection of human health. This study will reveal if action needs to be taken with regards to QACs in Minnesota's natural and engineered water systems. The results will be disseminated via the scientific literature and a publically available final report.

C. Timeline Requirements

The proposed project will be completed in a two-year period. Because the sediment samples have already been collected and preserved as part of the ENTRF project Antibiotics and Antibiotic Resistance Genes in Minnesota Lakes and because we expect the analytical protocols to be similar to those already in use, extraction and analyses of environmental samples will commence at the start of the project.

2017 Detailed Project Budget

Project Title: Household chemicals as water pollutants and toxic precursors

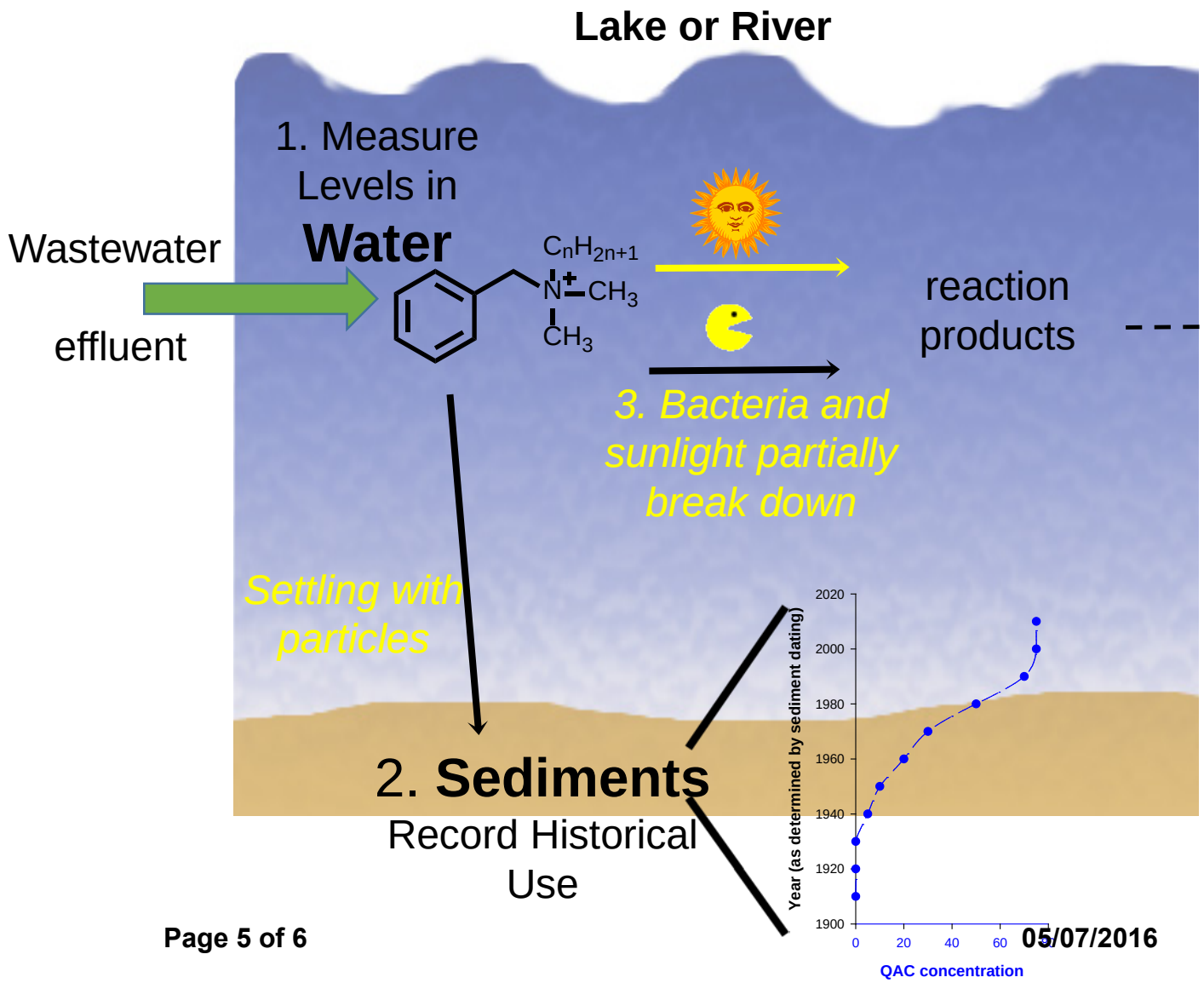
IV. TOTAL ENRTF REQUEST BUDGET 2 years

BUDGET ITEM	AMOUNT
Personnel: William Arnold, Project Manager (75% salary, 25% fringe benefits). 8% FTE for year 1 and year 2	$ 38,800
Personnel: Postdoctoral Researcher, sediment and water extractions and analyses (82% salary, 18% fringe benefits). 75% FTE for year 1 and50% year 2	$ 71,200
Personnel: Graduate student Research assistant, photochemical and drinking water oxidation experiments (57% salary, 43% fringe benefits) 50% FTE for year 1 and year 2	$ 91,000
Equipment/Tools/Supplies: Supplies (chemical and isotopically labelled standards, chemical reagents for fate experiments , necessary glassware, instrument/analytical time for product identification, solvents, consumable supplies, laboratory notebooks, software licenses; $19,000 total). Analytical time for compound quantification is a major portion of supply costs ($4,000 per year). Operating costs for laboratory instruments required for analyses and experiments; costs portioned based on usage by project ($3,000 total)	$ 30,000
Travel:charges and univeristy vehicle rental charges for trips to water samples. Hotel/meal charges if overnight stay required. Attendence for students at local conferneces to disseminate project	$ 2,000
Additional Budget Items: Publication charges to make published journal articles (2-3) immediately available via open access to maximize data availability and dissemination	$ 3,000
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$ 236,000

V. OTHER FUNDS

SOURCE OF FUNDS	AMOUNT	Status
Other Non-State $ To Be Applied To Project During Project Period: N/A	$ -	
Other State $ To Be Applied To Project During Project Period: N/A	$ -	
In-kind Services To Be Applied To Project During Project Period: Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (53% in Y1 and 54% in Y2 of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind	$ 103,000	Secured
Funding History: This project leverages samples and knowledge obtained from ENTRF project Antibiotics and antibiotic resistance genes in Minnesota lakes (2014-2017)	$ 300,000	
Remaining $ From Current ENRTF Appropriation: Antibiotics and antibiotic resistance genes in Minnesota lakes (2014-2017). Samples and techniques developed in this ongoing project will be used in proposed project. All funds from current ENRTF appropriation will be spent by June 30, 2017.	$ 125,000	obligated to current students/analyses

Ingredients in Fabric Softeners, Disinfectants, and Herbicides (known as QACs) May Contaminate Minnesota Waters And Generate Carcinogens



4. Water Treatment with Chloramine

5. Formation of ***carcinogenic nitrosamines***

Outcomes

1. Understand current and historical use
2. Quantify degradation rates
3. Evaluate carcinogen formation
4. Inform use and treatment

Project Manager Qualifications and Organization Description

William A. Arnold
Joseph T. and Rose S. Ling Professor and Associate Head
Department of Civil, Environmental, and Geo- Engineering, University of Minnesota

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

Dr. William Arnold will be responsible for overall project coordination and supervision and design of the field sampling and reactivity studies. He has been studying the fate of pharmaceutical and pesticide compounds in aquatic environments for seventeen years. As part of these studies, he has determined the transformation rates and identified reaction products of numerous compounds. Work has focused on the phototransformation of pesticides in prairie wetlands, pesticides losses in soils, and antibiotic fate in surface waters. He has published over twenty peer-reviewed papers on pesticide and pharmaceutical fate since 2003, and he is the co-author of a textbook on water chemistry published in 2011. Dr. Arnold is a Resident Fellow of the University of Minnesota Institute on the Environment, an Associate Fellow of the Minnesota Supercomputing Institute, and a member of the graduate faculty in Water Resources Science. He won the *Arcadis/Association of Environmental Engineering and Science Professors Frontier in Research Award* in 2012 and the University of Minnesota College of Science and Engineering *George W. Taylor Award for Distinguished Research* in 2011.

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 laboratories and offices of the PI contain the necessary fixed and moveable equipment and facilities needed for the proposed studies.