Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2017 LCCMR Work Plan

Date of Submission: September 14, 2016

Date of Next Status Update Report: January 2018

Date of Work Plan Approval: 06/07/2017

Project Completion Date: June 30, 2019

Does this submission include an amendment request? No

PROJECT TITLE: Assessment of Household Chemicals and Herbicides in Rivers and Lakes

Project Manager: William Arnold

Organization: University of Minnesota

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Location: Statewide

Total ENRTF Project Budget:		
	ENRTF Appropriation:	**$236,000**
	Amount Spent:	**$0**
	Balance:	**$236,000**

Legal Citation: M.L. 2017, Chp. 96, Sec. 2, Subd. 04a

Appropriation Language:
$236,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota to quantify environmental levels of household chemical and herbicide ingredients in rivers and lakes and assess their potential to form toxic by-products.

I. PROJECT TITLE: Household chemicals as water pollutants and toxic precursors

II. 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 1) Quantifying current and historical levels of these pollutants by measuring concentrations in surface water and sediment samples, 2) Evaluating of the persistence of these compounds in surface waters through studies of biological degradation and indirect photolysis, and 3) Determining the levels of carcinogenic nitrosamines produced attributable to these contaminants during drinking water and wastewater disinfection.

Either intentionally (in use as herbicides as active or inactive ingredients) or unintentionally (via release in wastewater effluent due to incomplete removal in the treatment process), 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, because there are herbicides that contain this moiety. 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.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 1, 2018:

Project Status as of July 1, 2018:

Project Status as of January 1, 2019:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Measurement of quaternary ammonium compound pollutants in river water, sediment cores, and surface sediments
Description: Because QACs stick to particles, the most likely environmental compartment to find them in is sediments. The target compounds will be selected based on 1) previous reports of QACs in the literature, 2) an evaluation of consumer products available in the Twin-Cities area, and 3) agricultural QAC sales data from the Minnesota Department of Agriculture. The Arnold lab has 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)

stored in freezers. We will evaluate previously reported methods using an accelerated solvent system to extract both wet and freeze-dried samples. We anticipate a clean-up step using solid phase extraction will be required. We will use a spike and recovery method to evaluate extraction efficiency of the QACs, and isotopically labelled surrogates to determine recovery.

Once extracted, 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. The different QACs found will allow assessment of the loadings of these compounds to surface waters in Minnesota, as well as attribution to different sources/uses.

We will also collect wastewater effluents from several wastewater treatment plants and river water samples downstream of wastewater treatment plants and elsewhere along the Minnesota and Mississippi Rivers. These samples will be extracted using the solid phase extraction method developed for clean-up of the sediment samples and analyzed using the same mass spectrometry methods. The water samples will provide information about current environmental discharges. We will also attempt untargeted analysis to determine if any unanticipated quaternary ammonium compounds are present.

Summary Budget Information for Activity 1:

ENRTF Budget: $ 91,000
Amount Spent: $ 0
Balance: $ 91,000

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 1 Status as of January 1, 2018:

Activity 1 Status as of July 1, 2018:

Activity 1 Status as of January 1, 2019:

Final Report Summary:

ACTIVITY 2: Evaluation of environmental persistence in surface waters
Description: The impact of QACs on algal or microbial communities will be a function of both their concentration and persistence. The persistence will be dictated by the (bio)availability as well as their reaction with reactive species produced by sunlight.

QACs, being positively charged, may associate with negatively charged dissolved organic matter. If associated with organic matter, the compounds may be less available to bacteria to degrade. Alternatively, because organic matter produces reactive species, such as hydroxyl radical, this association may enhance degradation via indirect photolysis. Using an established solid-phase microextraction method, the partitioning coefficients of the target QACs to dissolved organic matter (using standard materials, river water, and wastewater effluent) will be measured. By comparing how the chemical structure affects this partitioning, the potential effects on the susceptibility to degradation processes for various QACs will be evaluated.

The native microbiology in the river may be able to degrade the compounds. This will be tested by dosing river water samples collected from the Mississippi River with QACs and monitoring their loss over time using liquid chromatography. The detection methods will depend on the dosed concentration. The reactors will be 1-L

Erlenmeyer flasks with a foam plug to allow air exchange. The reactor will be stirred and sampled as function of time. Biomass will be estimated via measurement of optical density and volatile suspended solids.

If associated with the dissolved organic matter in surface waters, QACs would be especially susceptible to reaction with reactive species, such as hydroxyl radicals. Because these reactive species are produced when organic matter is exposed to sunlight, the concentration of such species is elevated near the organic matter. The rate constants of the QACs with hydroxyl radical and singlet oxygen will be measured by generating these species in the laboratory. Experiments will then be performed in river water and wastewater effluent to measure 1) the concentrations of singlet oxygen and hydroxyl radical produced using chemical probes and 2) the loss rate of QACs due to indirect photolysis. Indirect photolysis will be quantified as the difference between direct photolysis (measured in distilled water) and that in the organic matter-containing water. Specific indirect photolysis processes will be confirmed with quenchers. Because the chemical probes measure the concentration of hydroxyl radical and singlet oxygen in bulk solution, a comparison between the predicted and actual QAC loss rates will reveal if the QACs experience higher than expected concentrations due to their association with organic matter.

The product of this activity will be rate constant and sorption parameters that will be of use to predict QAC lifetimes in lakes and rivers.

Summary Budget Information for Activity 2:

ENRTF Budget: $ 66,000
Amount Spent: $ 0
Balance: $ 66,000

Outcome	Completion Date
1. Measurement of partitioning to river water and wastewater dissolved organic carbon	6/30/18
2. Measurement of biodegradation rates in river/lake water	9/30/18
3. Quantification of indirect photolysis reaction rate constants	6/30/19

Activity 2 Status as of January 1, 2018:

Activity 2 Status as of July 1, 2018:

Activity 2 Status as of January 1, 2019:

Final Report Summary:

ACTIVITY 3: Determination of carcinogen production during water disinfection
Description: 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 of QACs in tap water and wastewater will be exposed to chloramines at various dosages. Waters will be collected from five drinking water systems and five wastewater systems to obtain a variety of water sources/chemistries.

The formation of nitrosodimethylamine (a known carcinogen) and total nitrosamines will be measured using liquid chromatography and gas chromatography mass spectrometry and a chemiluminescence method, respectively. Samples that are not dosed with QACs will be measured as well to measure background QAC production. The background QAC levels in these samples will be measured using the methods developed in activity 1 to determine the total nitrosamine production attributable to QACs. Results will demonstrate which QACs have the greatest potential to produce carcinogens.

Summary Budget Information for Activity 3:

ENRTF Budget: $ 79,000

Amount Spent: $ 0
Balance: $ 79,000

Outcome	Completion Date
1. Validation of analytical methods	9/30/18
2. Nitrosamine formation potential in drinking water	3/31/19
3. Nitrosamine formation potential in wastewater	6/30/19

Activity 3 Status as of January 1, 2018:

Activity 3 Status as of July 1, 2018:

Activity 3 Status as of January 1, 2019:

Final Report Summary:

V. DISSEMINATION:

Description: The results will be disseminated via peer reviewed publications in scientific journals, presentations at local/regional conferences, and via a publically available final report. Funds have been requested to pay fees for open access, so the articles will be available to the public and stakeholders without an embargo period.

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:
A. Preliminary ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
Personnel:	$ 201,000	Arnold Project Manager (75% salary, 25% fringe benefits 7% FTE per year; $38,800). Postdoctoral Researcher, (82% salary, 18% fringe benefits, 75% FTE for year 1 and 50% year 2; %71,200). Graduate student Research Assistant and/or Temporary Casual Employee, (57% salary, 43% fringe benefits; 50% FTE for year 1 and year 2; $91,000). Costs include fringe benefits for all and tuition for the graduate student.
Equipment/Tools/Supplies:	$ 30,000	Chemical standards and reagents, instrument consumables ($18,000) and analytical time for quantification of target compounds and detection of reaction products ($9,000).

		Equipment operating and maintenance costs ($3,000)
Travel Expenses in MN:	$ 2,000	Sample collection and presentations at local conferences/workshops
Other:	$ 3,000	Publication fees for open access
TOTAL ENRTF BUDGET:	**$ 236,000**	

Explanation of Use of Classified Staff: not applicable

Explanation of Capital Expenditures Greater Than $5,000: not applicable

Total Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 3.25

Total Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
	$ 103,000	$ 0	Because the project is overhead free, laboratory space, electricity, and other facilities/administrative costs (53-54% of direct costs, depending on FY, excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind by the University of Minnesota
State			
	$	$	
TOTAL OTHER FUNDS:	**$ 103,000**	**$ 0**	

VII. PROJECT STRATEGY:

A. Project 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. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount

This project leverages samples and knowledge obtained from ENTRF project Antibiotics and antibiotic resistance genes in Minnesota lakes M.L. 2014, Chp. 226, Sec. 2, Subd. 03e	2014-2017	$ 300,000

VIII. REPORTING REQUIREMENTS:

- **The project is for 2 years, will begin on 07/01/2017, and end on 06/30/2019.**
- **Periodic project status update reports will be submitted 01/15 and 07/15 of each year.**
- **A final report and associated products will be submitted between June 30 and August 15, 2019**.

IX. VISUAL COMPONENT or MAP(S): See attached

X. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS: Not applicable

Environment and Natural Resources Trust Fund
M.L. 2017 Project Budget

Project Title: Assessment of Household Chemicals and Herbicides in Rivers and Lakes
Legal Citation: M.L. 2017, Chp. 96, Sec. 2, Subd.04a
Project Manager: William Arnold
Organization: University of Minnesota
M.L. 2017 ENRTF Appropriation: $236,000
Project Length and Completion Date: 2 Years, June 30, 2019
Date of Report: September 14, 2016

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Activity 3 Budget	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	**Measurement of quaternary ammonium compound pollutants**			**Evaluation of environmental persistance in surface waters**			**Determination of carcinogen production during water disinfection**				
Personnel (Wages and Benefits)	$76,000		$76,000	$56,000		$56,000	$69,000		$69,000	$201,000	$201,000
William Arnold, Project Manager (75% salary, 25% fringe benefits 7% FTE per year). Project supervision, design of experiments and data analysis of Activities 1 &2, supervision of postdoctoral researcher and graduate students and project reporting.	$13,800		$13,800	$13,000		$13,000	$12,000		$12,000	$38,800	$38,800
Postdoctoral Researcher, (82% salary, 18% fringe benefits, 75% FTE for year 1 and 50% year 2). Extraction and analysis of water and sediment samples, development of analytical methods, photolysis experiments, initation of disinfection experiments with chloramines, data analysis and interpretation.	$42,720		$42,720	$17,800		$17,800	$10,680		$10,680	$71,200	$71,200
Graduate student Research Assistant and/or Temporary Casual Employee, (57% salary, 43% fringe benefits; 50% FTE for year 1 and year 2) Assist with extraction and analysis of water and sediment samples and method development, photolysis experiments, sorption to organic matter experiments, biodegradation experiments, disinfection experiments with chloramines, data analysis and interpretation.	$20,020		$20,020	$25,480		$25,480	$45,500		$45,500	$91,000	$91,000
Equipment/Tools/Supplies											

Supplies $18,000 (chemical standards - $3500, isotopically labelled internal standards - $3000, chemical reagents for perisistence experiments and carinogen formation assays-$2500, necessary glassware-$2000, solvents - $1500, consumable supplies (autosampler vials, syringes, SPE cartridges, gloves)- $5000, laboratory notebooks-$250, software licenses-$250)	$10,000		$10,000	$4,000		$4,000	$4,000		$4,000	$18,000	$18,000
Analytical time in mass spectrometry facility for QAC detection in sediment and water (250 analyses for method development, calibration standards, and samplse from sediment cores x $20 per sample = $5,000; appromiately 200 samples from product identification studies in Activity 2 and 3 x $20 per sample = $4	$5,000		$5,000	$2,000		$2,000	$2,000		$2,000	$9,000	$9,000
Operating and maintenance costs for laboratory instruments required for analyses and experiments; costs portioned based on usage by project $3,000. Anticipated contributions to maintence costs include: seals and filters for HPLC pumps ($500, twice during project), HPLC detector replacement ($500), lamp replacement ($500), water purificaiton cartridges ($500), injector replacement ($500)	$1,000		$1,000	$1,000		$1,000	$1,000		$1,000	$3,000	$3,000
Travel expenses in Minnesota											
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 findings to stakeholders and the public.	$1,000		$1,000	$500		$500	$500		$500	$2,000	$2,000
Other											
Publication charges to make published journal articles (four) immediately available via open access to maximize data availability and dissemination	$1,000		$1,000	$1,000		$1,000	$1,000		$1,000	$3,000	$3,000
COLUMN TOTAL	**$94,000**		**$94,000**	**$64,500**		**$64,500**	**$77,500**		**$77,500**	$236,000	**$236,000**