Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2016 Work Plan

Date of Report: December 4, 2015

Date of Next Status Update Report: January 30, 2017

Date of Work Plan Approval:

Project Completion Date: June 30, 2019

Does this submission include an amendment request? No

PROJECT TITLE: Developing a Membrane Filtration System to Treat Lake Superior Ballast Water

Project Manager: Santiago Romero-Vargas Castrillón, Ph. D.

Organization: University of Minnesota, Department of Civil, Environmental, and Geo- Engineering

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Location: Cook, Lake, St. Louis.

Total ENRTF Project Budget:		
	ENRTF Appropriation:	**$151,000**
	Amount Spent:	**$0**
	Balance:	**$151,000**

Legal Citation: M.L. 2016, Chp. xx, Sec. xx, Subd. xx

Appropriation Language: "$151,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop a filtration system utilizing bioactive membrane technologies for use in treating Lake Superior ballast water to remove at least ninety percent of suspended pathogens, invasive species, and contaminants. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2019, by which time the project must be completed and final products delivered."

I. PROJECT TITLE: Developing a Membrane Filtration System to Treat Lake Superior Ballast Water

II. PROJECT STATEMENT: The proliferation of invasive species introduced by ballast water discharge is a major threat to marine ecosystems in Minnesota. In the Port of Duluth the discharge of ballast water introduces invasive species of phyto- and zooplankton, bacteria, mollusks and their eggs and larvae; because of their remarkable adaptability, these organisms threaten the biodiversity and disrupt the ecological balance of their new environment. Processes aimed at minimizing the impact of invasive organisms in ballast waters, such as mid-ocean exchange, fail to remove all organisms, while disinfection-based technologies are costly and may produce toxic disinfection byproducts. Membrane filters, in which a polymer film with small pores allows the separation of water from suspended particulates, has shown promise for treatment of wastewaters. In this project, we aim to provide a proof-of-concept demonstration of membrane microfiltration (MF) as a ballast water treatment technology. The proposed effort is structured along two main goals:

- Phase 1: we will develop microfiltration membranes functionalized with graphene oxide, a hydrophilic and bactericidal nanomaterial that will result in a biofouling resistant MF membrane. Our goal is to develop membranes capable of removing >90% of microorganisms and the larvae of invasive species in surface waters sampled in the Port of Duluth-Superior.
- Phase 2: we will develop a pilot-scale unit with a capacity of ~600 gal/day to treat ballast water.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 30, 2017:

Project Status as of June 30 2017:

Project Status as of January 30, 2018:

Project Status as of June 30 2018:

Project Status as of January 30 2019:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Development of low-fouling MF membranes showing complete microorganism removal. The first expected outcome of our investigation is a novel MF membrane with improved resistance toward organic fouling and biofouling (i.e., the clogging of membrane pores by dissolved and suspended contaminants, particles and microbes). A hydrophilic, bactericidal nanomaterial known as graphene oxide will be deposited on the membrane to create a fouling- and biofouling-resistant coating on the membrane surface. The benefits of operation with the GO-functionalized membranes (hereinafter designated GO-MF) include pumping energy savings and less frequent membrane backwashing stages between filtration cycles; an added benefit is longer membrane useful life. Since membrane replacement due to fouling or biofouling can amount to 50% of the operating costs of membrane filtration, considerable savings could result from the materials herein proposed. We will aim to develop membranes with a water permeability in excess of 1000 L m^{-2} h^{-1} bar^{-1}, showing complete removal of microorganisms with sizes > 1 μm.

Membranes will be fabricated via the phase inversion technique. MF membranes with pores < 1 μm will be prepared using poly(vinylidene fluoride) (PVDF). Surface functionalization of the MF membranes will be accomplished using a wet adhesive known as polydopamine. Polydopamine creates an adhesive coating on the PVDF surface for the robust attachment of graphene oxide nanosheets. The GO-MF membranes fabricated will be tested in a bench-scale dead-end filtration cell (~5 cm^2 membrane area) to characterize their fouling and biofouling

propensity. Ballast waters and Lake Superior water will be used as feed in the fouling experiments. The objective of these small-scale experiments is to identify the membrane fabrication conditions for optimal biofouling resistance and microbe removal.

Summary Budget Information for Activity 1:

ENRTF Budget: $ 58,815
Amount Spent: $ 0
Balance: $ 58,815

Outcome	Completion Date
1. Personnel training, assembly of bench-scale setup	January 31, 2017
2. GO synthesis and membranes fabricated	June 30, 2017
3. Characterization of fouling resistance of GO-MF membranes	January 31, 2018

Activity Status as of January 30, 2017:

Activity Status as of June 30, 2017:

Activity Status as of January 30, 2018:

Activity Status as of June 30, 2018:

Activity Status as of January 30, 2019:

Final Report Summary:

Activity 2: Development of a ~600 gal/day pilot-scale microfiltration unit for the treatment of ballast water. In activity 2, a MF pilot-scale unit will be designed and constructed to demonstrate MF as a viable ballast water treatment technology. PVDF hollow fiber membranes will be functionalized with graphene oxide following the protocol developed in Activity 1. The pilot scale unit will consist of an immersed hollow fiber bundle operating in outside-feed mode. Given that typical MF water fluxes are on the order of 1000 L m^{-2} h^{-1}, and considering that the membrane bundle surface area is typically on the order of 0.1 m^2 for pilot-scale units reported in the literature (see Research Addendum), we expect to develop a filtration apparatus capable of processing 100 L/h = ~ 600 gal/day of ballast discharge.

The pilot-scale unit will be demonstrated with waters sampled from Port of Duluth. Permeate quality will be analyzed by total organic carbon and dissolved organic carbon analyses, turbidity, and total suspended solids. Considering that the pore size of the PVDF membranes that will be used in this work is < 1 μm, we expect that the MF pilot-scale unit will achieve >90% removal of suspended pathogens and microscopic larvae.

Summary Budget Information for Activity 2:

ENRTF Budget: $ 92,185
Amount Spent: $ 0
Balance: $ 92,185

Outcome	Completion Date
1. Pilot-scale construction	June 30, 2018
2. Pilot-scale testing	June 30, 2019

V. DISSEMINATION:

Description: Results will be disseminated via publication in peer-reviewed journals such as The Journal of Membrane Science, Water Research, and Environmental Science & Technology. Results will also be communicated through oral and poster presentations at local, regional and national conferences on water technology.

Status as of January 30, 2017:

Status as of June 30 2017:

Status as of January 30, 2018:

Status as of June 30 2018:

Status as of January 30 2019:

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
Personnel: Graduate student support	$ 87,395	Graduate research assistant (50% time per year for two years, salary 57% of cost, tuition 33% of cost, fringe benefits 10% of cost)
Professional/Technical/Service Contracts:	$ N/A	
Equipment/Tools/Supplies: reagents, chemicals, consumables.	$ 28,105	Reagents and laboratory consumables including, but not limited to, polymers for membrane fabrication (polysulfone, polyethersulfone, pvdf), solvents for membrane fabrication (NMP, DMF, acetone, isopropanol), reagents to synthesize graphene oxide, membrane casting equipment (PET fabric, thin film applicator, glass plates), hollow fibers and chemicals to modify hollow fiber membranes, foulants (humic acids, proteins, polysaccharides), supplies for membrane characterization (SEM and AFM sample holders and AFM probes), analytical equipment user fees. Stirred filtration cell with data logger.
Capital Expenditures over $5,000: MF pilot-scale unit	$ 34,500	Construction of a pilot-scale MF unit.
Travel Expenses in MN:	$ 1,000	Travel in Minnesota for ballast and surface water collection from Lake Superior. Mileage will be reimbursed at $0.55 per mile or current UMN compensation plan.
TOTAL ENRTF BUDGET:	**$ 151,000**	

Explanation of Use of Classified Staff:

Explanation of Capital Expenditures Greater Than $5,000:

MF pilot scale unit: custom-made hollow fiber membrane module, pump and motor assembly, valves, fittings, tubing, flow meters and pressure gauges, data acquisition and logging computer, heater/chiller.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: A full-time graduate student researcher will be employed with this appropriation for 2 years (for 2 FTE over the entire 3-year project period). This results in a total of 2 FTE for the total project.

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

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state	N/A	N/A	N/A
	N/A	N/A	N/A
State	N/A	N/A	N/A
	$	$	
TOTAL OTHER FUNDS:	**$N/A**	**$N/A**	

VII. PROJECT STRATEGY:

A. Project Partners:

The project manager will be Professor Santiago Romero-Vargas Castrillón (U. of Minnesota), who will supervise a graduate student in the execution of the proposed work. Romero-Vargas has expertise in the development, characterization, and testing of membrane materials for water purification, and membrane-based processes for water production.

B. Project Impact and Long-Term Strategy:

The proposed work will result in membrane materials and processes for the treatment of ballast water discharges in Minnesota. This project therefore directly addresses one of the main vectors for invasive species in the State. We expect this project to lead to further applications in drinking water treatment and, also, to patentable technology.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount
United States Geological Survey. Project title: "Improving the (Bio)fouling and Mechanical Resistance of Ultrafiltration Membranes for Drinking Water Production". The project proposed in this work plan partially builds on results and expertise developed during the USGS-sponsored project.	3/1/2015 – 2/28/2016	$30,000
Matching funds from UMN for the abovementioned USGS project.	3/1/2015 – 2/28/2016	$60,000

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:

A. Parcel List: N/A

B. Acquisition/Restoration Information: N/A

IX. VISUAL COMPONENT or MAP(S):

See attached graphic.

X. RESEARCH ADDENDUM:

See attached research addendum.

XI. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted no later than January 30, 2017, June 30, 2017, January 30, 2018, June 30, 2018, January 30, 2019. A final report and associated products will be submitted between June 30 and August 15, 2019.

Environment and Natural Resources Trust Fund
M.L. 2016 Project Budget

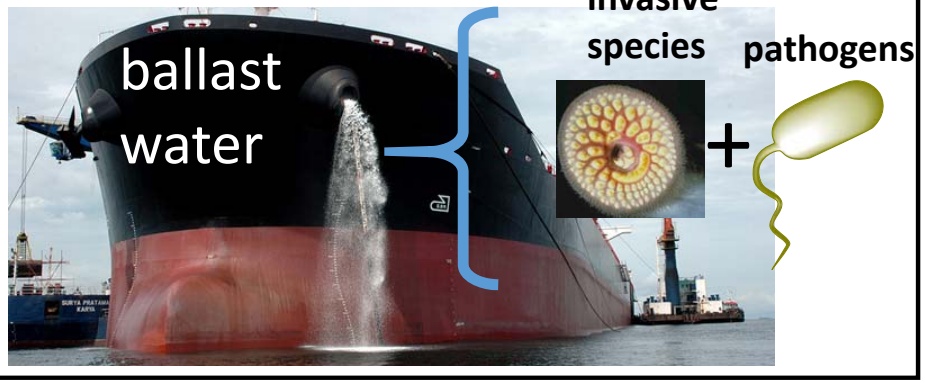
Project Title: Developing a Membrane Filtration System to Treat Lake Superior Ballast Water
Legal Citation:
Project Manager: Santiago Romero-Vargas Castrillón
Organization: University of Minnesota - Twin Cities
M.L. 2016 ENRTF Appropriation: $151,000
Project Length and Completion Date: 3 years, June 30, 2019
Date of Report: January 30, 2017

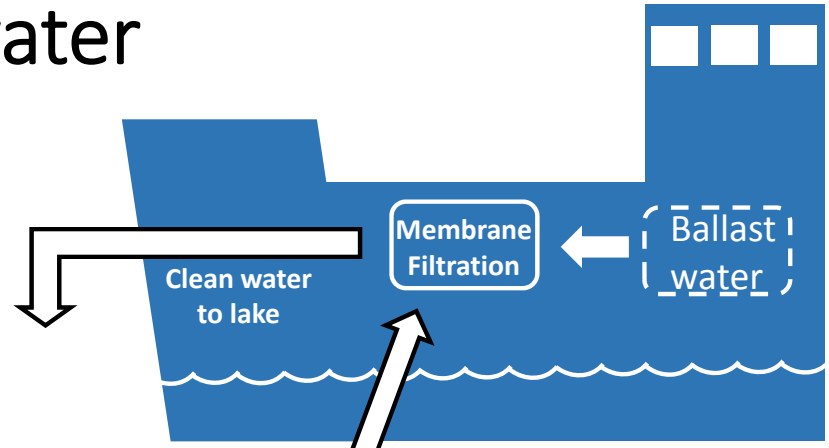
ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	***MF Membrane Fabrication and Characterization***			***Development of a MF Pilot-Scale Unit for Ballast Water Treatment***				
Personnel (Wages and Benefits)								
Graduate research assistant (50% time per year for two years, salary 57% of cost, tuition 33% of cost, fringe benefits 10% of cost)	$43,263	$0	$43,263	$44,132	$0	$44,132	$87,395	$87,395
Equipment/Tools/Supplies								
Reagents and laboratory consumables including, but not limited to, Polymers for membrane fabrication (polysulfone, polyethersulfone, pvdf), solvents for membrane fabrication (NMP, DMF, acetone, isopropanol), reagents to synthesize graphene oxide, membrane casting equipment (PET fabric, thin film applicator, glass plates), hollow fibers and chemicals to modify hollow fiber membranes, foulants (humic acids, proteins, polysaccharides, supplies for membrane characterization (SEM and AFM sample holders and AFM probes), analytical equipment user fees.	$12,552	$0	$12,552	$12,553	$0	$12,553	$25,105	$25,105
Stirred cell for membrane characterization with data logger (scale and computer)	$3,000	$0	$3,000	$0	$0	$0	$3,000	$3,000
Capital Expenditures Over $5,000								

Construction of a pilot-scale MF unit: custom-made hollow fiber membrane module, pump and motor assembly, valves, fittings, tubing, flow meters and pressure gauges, data acquisition and logging computer, heater/chiller.	$0	$0	$0	$34,500	$0	$34,500	$34,500	$34,500
Travel expenses in Minnesota								
Mileage and lodging. To collect water samples within Minnesota. Mileage will be reimbursed @ $0.55 per mile or current U of M compensation plan.	$0	$0	$0	$1,000	$0	$1,000	$1,000	$1,000
COLUMN TOTAL	**$58,815**	**$0**	**$58,815**	**$92,185**	**$0**	**$92,185**	**$151,000**	**$151,000**

Using membranes to treat **Lake Superior** ballast water

The problem:





pollutants, invasive
Microorganisms are rejected

Ballast water

Ballast
water

**Clean water
(to Lake
Superior)**

Hollow-fiber
membranes

Bio-active microfiltration membrane

- Removes pollutants
- Kills pathogens

Clean water

**Clean water
(to Lake
Superior)**