Environment and Natural Resources Trust Fund
2016 Request for Proposals (RFP)

Project Title: **ENRTF ID: 122-D**

Using Membranes to Treat Lake Superior Ballast Water

Category: D. Aquatic and Terrestrial Invasive Species

Total Project Budget: $ 151,091

Proposed Project Time Period for the Funding Requested: 2 years, July 2016 to June 2018

Summary:

We will develop a filtration system to treat Lake Superior ballast water. The filtration system will remove >90% of suspended pathogens, invasive species, and contaminants.

Name: Santiago Romero-Vargas Castrillón

Sponsoring Organization: U of MN

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Minneapolis MN 55455

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Location

Region: NE

County Name: Cook, Lake, St. Louis

City / Township:

Alternate Text for Visual:

The problem: pollutants and invasive species discharged in ballast water. The solution: a membrane-based filtration system that removes >90% of pathogens and contaminants.

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

I. PROJECT STATEMENT

Ballast water is used in shipping to stabilize large vessels. When a ship uploads cargo, it discharges ballast water into the surrounding waters; when cargo is offloaded, ballast water reservoirs are filled to compensate for the change in the ship's tonnage. Ballast water contains small fish, microorganisms (bacteria, zooplankton, and phytoplankton), in addition to dissolved and suspended organic contaminants. **In Lake Superior, the discharge of ballast water is a source of water pollution and introduces invasive organisms into the new aquatic ecosystem, both of which threaten biodiversity and may lead to water-borne illness.** Each year, 1,000 vessels discharge ballast water in the Port of Duluth-Superior. There is, therefore, a **clear need to develop technologies to efficiently and economically treat ballast water**, in order to minimize its environmental impact. Mid-ocean exchange, a common practice to dispose of vessel ballast water by replacing it multiple times *en route*, does not completely eliminate microorganisms, while using biocides (e.g., chlorine and ozone) to kill microorganisms in ballast water could also release harmful chemicals into the environment, and may also lead to corrosion of ballast tanks. **We propose to develop a filtration system specifically designed for the treatment of ballast water.** In this system, a **bioactive polymer membrane** (a plastic film with pores that allow passage of clean water while retaining large microorganisms and dissolved organic pollutants) will be fabricated and its surface modified **with graphene oxide, a nanomaterial that kills water-borne pathogens**. The goals of this project are to:

- Fabricate filtration membranes for ballast water treatment functionalized with antibacterial graphene oxide.
- Characterize the biocidal activity of the membranes (their ability to kill pathogens in ballast water), their filtration properties (their ability to reject microorganisms and dissolved or suspended particles).
- Provide a pilot-scale demonstration of the filtration unit using real ballast waters as feed.

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: Fabricate membranes for ballast water filtration, showing >90% rejection of suspended pathogens and contaminants. **Budget: $65,119**

Activity 1 is focused on formulating a "recipe" for the microfiltration membranes. These will be prepared following well-studied methods for the fabrication of porous polymeric filters. The resulting materials will comprise a finely porous selective layer (known as the "skin") overlaying a substrate of larger pores that provides structural support. By adjusting the synthesis conditions it is possible to tune the pore size of the "skin" to achieve high rejection of microorganisms and contaminants. Commercially available raw materials will be used to fabricate the membranes. Unlike conventional microfilters, the surface of our filtration membranes will be modified with graphene oxide, a biocidal nanomaterial that inactivates microorganisms by a combination of oxidation and physical damage to the microorganism cell membranes. Graphene oxide will be immobilized on the membrane surface by polydopamine, a water-proof polymeric adhesive that will prevent leaching of the nanomaterial. In addition, graphene oxide functionalization will yield a more wettable and clogging-resistant membrane surface.

In activity 1, we will fabricate small membrane coupons (~4 in x 4 in) to facilitate lab-scale investigations. The materials developed will be characterized in terms of water permeability, rejection of organic matter, bacteria and microorganisms (phytoplankton and zooplankton), biocidal activity (i.e., their ability to kill microorganisms) and clogging resistance. All experiments and measurements performed with membranes functionalized with graphene oxide will be compared to control experiments using graphene-free membranes. The outcome of activity 1 is a set of optimal membrane fabrication conditions. The membrane properties to be optimized are the

average pore size to ensure high microorganism rejection (to meet US Coast Guard-recommended standards) while maintaining acceptable water permeability, and the graphene oxide surface loading necessary to achieve biocidal activity and clogging resistance.

Outcome	Completion Date
1. Initial membranes fabricated in the lab	12/31/2016
2. Optimization of the water permeability, contaminant rejection (>90%), and biocidal activity (>65% microorganism inactivation)	6/30/2017
3. Lab-scale filtration tests demonstrating biocidal activity and microorganism rejection	12/31/2017

Activity 2: >30,000 Liter/hour ballast water pilot-scale filtration unit **Budget: $85,972**

Once a suitable "recipe" for material fabrication has been identified, we will proceed to up-scale the membranes into hollow fiber modules, which comprise bundles of thin membrane tubes, each with a diameter of ~5 mm. Fabrication of the hollow fibers will be carried out using a custom-made spinneret machine. The main advantage of the hollow fiber configuration is that high membrane packing fractions, around ~300-3000 m^2 of membrane per m^3 of module, can be achieved, resulting in compact filtration units that can be easily carried aboard a ship. Assuming a conservative estimate of the water permeability of the membranes (~50 L of water per m^2 of membrane/bar-hour) operating at an applied pressure of 2 bar, and considering a conservative packing fraction of 300 m^2 of membrane packed in a 1-m^3 module, we expect that the pilot-scale will process ~30,000 L of ballast water per hour. The pilot-scale unit will also be fitted with a sieving wire screen to remove sea lamprey and fish before the feed ballast water reaches the membrane.

Outcome	Completion Date
1. 30,000 liter/hour pilot-scale unit completed showing removal (>90%) and inactivation (>65%) of microorganisms and pollutants from ballast water	6/30/18

III. PROJECT STRATEGY

A. Project Team/Partners
The project manager will be 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 and membrane-based processes for water purification.

B. Project Impact and Long-Term Strategy
The envisioned filtration system will be capable of producing microorganism- and invasive species-free ballast water, thereby minimizing the environmental impact of ballast water discharge in Lake Superior.
This work is expected to contribute towards reducing the spread of aquatic invasive species found in ballast water. In addition, the graphene-based antibacterial coatings that would result from the proposed work could find applications as membranes for drinking water treatment across Minnesota, as well as in antibacterial coatings for biomedical devices such as catheters and bandages. We expect that the work herein proposed will lead to patentable technology. Given the interest in graphene-based environmental applications, the technology developed in this work may lead to applications well beyond the one herein proposed.

C. Timeline Requirements
The proposed project will be completed in the allotted two-year period.

2016 Detailed Project Budget

Project Title: Using membranes to treat Lake Superior ballast water

IV. TOTAL ENRTF REQUEST BUDGET 2 years

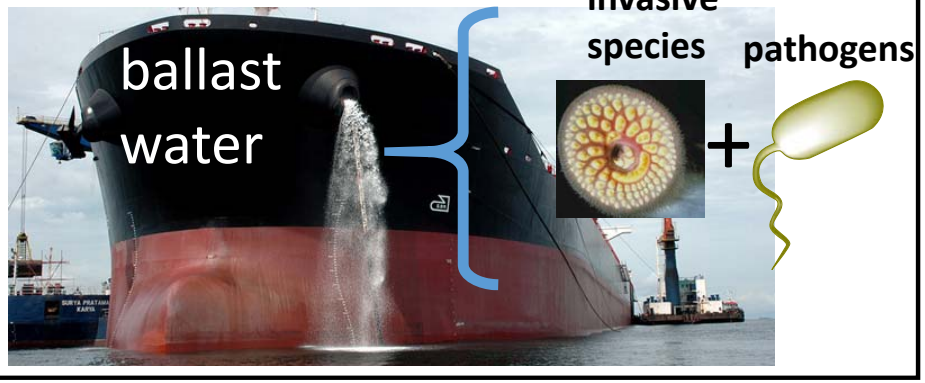
BUDGET ITEM	AMOUNT
Personnel: Support for a 50% appointment for 1 graduate student for 2 years.	$ 89,459
Personnel: Romero-Vargas (PI), two weeks of summer salary per year and 5% AY.	$ 25,376
Tools/Supplies: Polymers for membrane fabrication (1000 grams, total: $671), solvents for membrane fabrication (36 liters, total: $2131), reagents needed for the synthesis of graphene oxide (bulk graphite, sulphuric acid, potassium permanganate, dopamine, 1600 grams, total: $1310), membrane casting supplies (non-woven fabric, glass plates, total: $1548), chemicals to simulate natural organic matter (humic acids, polysaccharides, proteins, 1150 grams, total: $763), supplies for membrane characterization (microscopy sample holders and cantilevers for force spectroscopy, colloidal probes, total: 100 units, $1613), characterization facility user fees (for use of microscopes and spectrometers at the U. Minnesota Characterization Facility, 80 hours, total: $2800).	$ 10,836
Travel: Travel from Minneapolis to Duluth, MN, for ballast water sample collection. Mileage and lodging per University regulations.	$ 1,000
Additional budget items: Stirred filtration cell for membrane testing ($1,300) and computer for data logging ($1,120). Custom-made hollow fiber fabrication setup with spinneret ($15,000). Pilot-scale ballast water filtration unit: electrical motor and pump ($2000), unit instrumentation (flow meters, valves, total: $5000)	$ 24,420
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$ 151,091

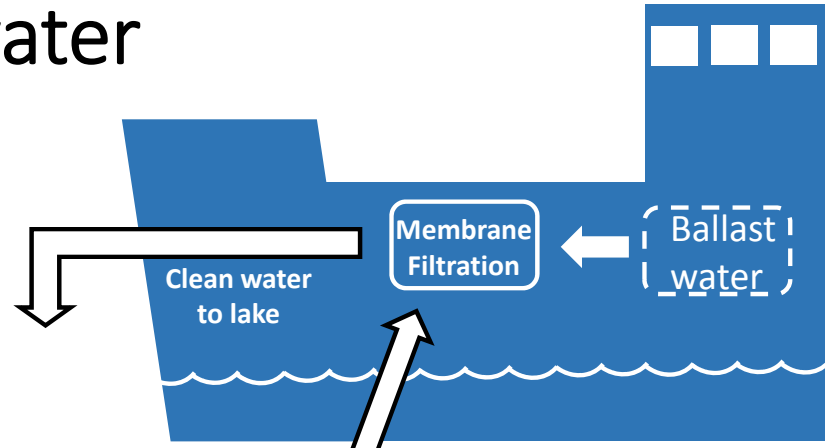
V. OTHER FUNDS *(This entire section must be filled out. Do not delete rows. Indicate "N/A" if row is not applicable.)*

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:	$ -	*N/A*
Funding History: United States Geological Survey (ultrafiltration membrane for drinking water production)	$ 30,000	awarded
Remaining $ From Current ENRTF Appropriation:	$ -	*N/A*

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

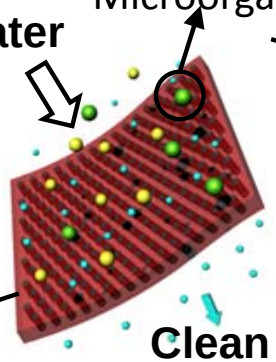
The problem:





pollutants, invasive
Microorganisms are rejected

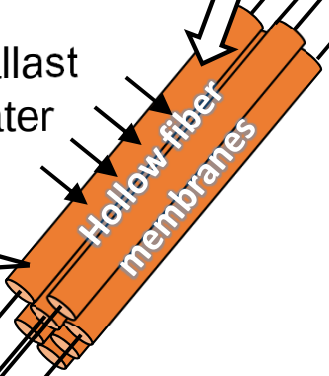
Ballast water



Bio-active microfiltration membrane
- Removes pollutants
- Kills pathogens

Clean water

Ballast
water



Clean water (to Lake Superior)

Clean water (to Lake Superior)

Investigator's qualifications

Santiago Romero-Vargas Castrillón

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Education:

2012 Ph.D. Princeton University, Princeton, NJ (Chemical Engineering)
2007 Diploma of the Imperial College, Imperial College, U. K. (Chemical Engineering)
2005 M. Eng. Sci., University of Western Ontario, London, ON (Chemical Engineering)
2002 B. Eng. (Distinction), McGill University, Montreal, QC (Chemical Engineering)

Professional Experience:

October 2014 – Assistant Professor, CEGE Department, University of Minnesota
2012 – 2014 Postdoctoral Associate, Yale University (Environmental Engineering)
2006 – 2011 Research Assistant, Department of Chemical Engineering, Princeton University
2005 – 2006 Research Engineer, RECAT Technologies, London, Canada
2003 – 2005 Research Assistant, Department of Chemical and Biochemical Engineering, UWO
2002 – 2003 Research Assistant, Department of Chemical Engineering, Imperial College

Selected Publications (of 15 total):

S. Romero-Vargas Castrillón, F. Perreault, A. F. Faria, M. Elimelech, Interaction of graphene oxide with bacterial cell membranes: Insights from force spectroscopy, *Environ. Sci. Technol. Lett.* **2015**, *2*, 112-117

S. Romero-Vargas Castrillón, X. Lu, D. L. Shaffer, M. Elimelech, Amine enrichment and poly(ethylene glycol) (PEG) surface modification of thin-film composite forward osmosis membranes for organic fouling control, *J. Membr. Sci.* **2014**, *450*, 331-339

X. Lu, S. Romero-Vargas Castrillón, D. L. Shaffer, M. Elimelech, In situ surface chemical modification of thin-film composite forward osmosis membranes for enhanced organic fouling resistance, *Environ. Sci. Technol.* **2013**, *47*, 12219-12228

S. Romero-Vargas Castrillón, S. R. Matysiak, F. H. Stillinger, P. J. Rossky, P. G. Debenedetti, Phase behavior of a lattice hydrophobic oligomer in explicit water, *J. Phys. Chem. B* **2012**, *116*, 9540-9548

S. Romero-Vargas Castrillón, N. Giovambattista, I. A. Aksay, P. G. Debenedetti, Structure and energetics of thin film water, *J. Phys. Chem. C* **2011**, *115*, 4624-4635

Organization description. The University of Minnesota is a public, land-grant, sea-grant, and space-grant research university located in Minneapolis and Saint Paul, Minnesota.