Environment and Natural Resources Trust Fund
2014 Request for Proposals (RFP)

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Project Title:

Water: Solar Driven Destruction of Pesticides, Pharmaceuticals, Contaminants

Category: B. Water Resources

Total Project Budget: $ 291,000

Proposed Project Time Period for the Funding Requested: 3 Years, July 2014 - June 2017

Other Non-State Funds: $ 0

Summary:

Solar-driven destruction of contaminants via reaction with dissolved organic matter will be quantified to optimize water treatment and reuse to achieve improved water quality for the benefit of aquatic health.

Name: William Arnold

Sponsoring Organization: U of MN

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Location

Region: Statewide

County Name: Statewide

City / Township:

MP: 0513-2-010-proposa

Budget: 0513-2-010-bud

Qual: 0513-2-010-qualifi

Map: 0513-2-010-map-Ill

Resolution:

List:

_____ Funding Priorities _____ Multiple Benefits _____ Outcomes _____ Knowledge Base

_____ Extent of Impact _____ Innovation _____ Scientific/Tech Basis _____ Urgency

Capacity Readiness Leverage Employment TOTAL

PROJECT TITLE: Water: Solar driven destruction of pesticides, pharmaceuticals, contaminants

I. PROJECT STATEMENT

Dissolved organic matter (DOM) is the material that gives our surface waters their brownish/yellow tint, much like tea. While often thought of as a nuisance, DOM actually plays a critical role in aquatic health because it serves as an important component of the carbon cycle and plays a critical role in the transformation of aquatic contaminants. Dissolved organic matter is usually derived from decaying plant materials or produced by naturally occurring algae. Inputs of water from agricultural fields, storm water, or wastewater effluent affect the quantity and composition of the dissolved organic matter present. As we have changed the hydrological connections in Minnesota via agricultural drainage, storm water collection, or wastewater discharge, we have also changed the dominant sources of DOM, and potentially its reactivity.

Wastewater, storm water, and agricultural runoff also carry pesticides, pharmaceuticals, and nutrients. While these chemicals serve important functions in crop production or treatment of disease, they become pollutants when discharged into surface waters. *When activated by sunlight, DOM destroys pollutants*, and this reaction may be more important that direct destruction of pollutants by sunlight. *Thus, it is critical to understand how the DOM affects the fate of these compounds and whether we can use the reactivity of DOM to destroy them*. In a previous ENTRF project, we found the unexpected result that the dissolved organic matter present in one wastewater effluent played a critical role in solar pharmaceutical destruction. Our work funded by the National Science Foundation revealed that wetland DOM played a major and previously unrecognized role in the solar-mediated destruction of common pesticides. These findings have led to this proposed project, with goals to

- characterize the composition and reactivity of organic matter present in waters across Minnesota,
- develop a rapid screening tool to predict the solar-driven, DOM-mediated destruction of pollutants, and
- optimize wetland/pond technology in terms of residence time and depth for urban storm water, wastewater effluent, and agricultural runoff management to maximize solar pollutant destruction.

The results of this work will allow rapid assessment as to whether specific pollutants will be persistent enough to pose a threat to ecosystems. Solar treatment is a sustainable alternative to highly engineered systems and will improve water quality and ecological health in Minnesota's lakes, streams, and rivers. The direct outcomes are

- A method to quickly evaluate the solar reactivity of the organic matter present in water;
- Optimization of wetland design for solar-driven, DOM-mediated removal of pesticides, pharmaceuticals, and other contaminants; and
- Guidance for wastewater, agricultural runoff, and storm water reuse with respect to solar destruction of pollutants.

II. DESCRIPTION OF PROJECT ACTIVITIES

Activity 1: Collection of wastewater, storm water, and agricultural runoff samples and characterization of the organic matter they contain — Budget: $149,000

Because the quantity and quality of organic matter varies both spatially and temporally, the characterization of hundreds of samples is necessary to relate organic matter properties to reactivity. Samples will be collected from native wetlands, restored wetlands, agriculturally impacted wetlands, wastewater treatment plant effluents, and storm water ponds. Samples will be taken over a wide geographic area and at least quarterly at all sites. Chemical, elemental, and spectral signatures that describe the organic matter in each type of water will be determined and how this signature varies over time and as a function of the surrounding landscape and/or level of water treatment will be evaluated. These properties will be related to the reactivity determined in Activity 2.

Outcome	Completion Date
1. Collect water samples and perform routine analyses (pH, carbon/nutrient levels, etc.)	4/30/16
2. Measure and analyze excitation emission spectra to build spectral library	9/30/16
3. Mass spectrometric analysis of organic matter to build composition library	12/31/16

Activity 2: Measurement of sunlight-generated oxidants and solar destruction of pesticides and pharmaceuticals — Budget: $110,000

Sunlight can destroy pesticides, pharmaceuticals, and other contaminants of emerging concern. Our recent work suggests that highly reactive species (such as radicals) that are generated when the light interacts with dissolved organic matter in water are more important than direct destruction by light. Using waters collected in Activity 1, we will quantify production of the organic matter-derived reactants that destroy contaminants. We will also evaluate the destruction of approximately twenty pesticides and pharmaceuticals. This will allow determination of the solar processes that dictate contaminant removal and how to optimize these processes through wetland design. We will also evaluate any nitrogen and phosphorus release from organic matter that occurs during light exposure.

Outcome	Completion Date
1. Determine concentrations of radicals generated in sunlight that are responsible for contaminant destruction	4/30/16
2. Measure nutrient release to evaluate any potential for biological growth	6/30/16
3. Determine pesticide removal rates in the waters collected in Activity 1	4/30/16
4. Determine pharmaceutical removal rates in the waters collected in Activity 1	6/30/16

Activity 3: Produce design guidelines for pollutant destruction in wetlands and recommendations for water reuse **Budget: $32,000**

Using the data collected in Activity 1 with regards to organic matter composition and in Activity 2 with regards to organic matter reactivity, a protocol will be developed to assess the solar reactivity of pollutants in a given water. This will allow reactivity of wastewater, storm water, or agricultural runoff samples collected in the future to be evaluated easily. This tool will allow us to provide

- assessment of organic matter composition/quality that leads to maximum pollutant destruction,
- design parameters for wetlands for treatment of agricultural runoff, wastewater or storm water based on the reactivity of the organic matter,
- assessment of potential benefits of solar treatment to allow wastewater or storm water reuse for irrigation, or if reuse leads to enhanced pollutant destruction via introduction of more reactive organic matter.

Key design parameters will be wetland area and depth, which dictate the amount of water exposed to light and light penetration efficiency, coupled with DOM reactivity.

Outcome	Completion Date
1. Develop organic matter parallel factor analysis models to predict radical production	9/30/16
2. Quantify organic matter characteristics leading to pollutant destruction	3/30/17
3. Determine wetland depths/areas to optimize pharmaceutical destruction for wastewater systems	6/30/17
4. Optimize pesticide destruction in storm water and agricultural systems	6/30/17

III. PROJECT STRATEGY

A. Project Team/Partners : The project will be led by the Principal Investigator William Arnold (U of MN, Department of Civil Engineering). The team will consist of one graduate and two undergraduate student researchers. Arnold has extensive experience in studying the solar destruction of pollutants and the detection of the dissolved reactive species responsible. We will partner with state and local agency scientists whenever possible with regards to sample collection to ensure as wide of a range samples as possible is studied and to avoid duplicative sampling efforts. The UMN team will share data with the appropriate partners.

B. Timeline Requirements: The proposed project will be completed in a three-year period. The project requires two full years of water sampling to ensure spatial and temporal dynamics in organic matter quality and quantity are observed.

C. Long-Term Strategy and Future Funding Needs: This project will provide an understanding of how human activities are changing organic matter in our waters, how these changes affects pollutant cycling, and how we can use these changes to our benefit in terms of the protection of human and aquatic health. The project will lead to a sustainable, solar driven treatment system for a variety of aquatic contaminants. The results will be disseminated via a manual that provides a method to evaluate organic matter reactivity and using this information for design of treatment wetlands based on the water flows, the water quality, the pollutant levels, and desired removal rate.

2014 Detailed Project Budget

Project Title: Water: Solar driven destruction of pesticides, pharmaceuticals, contaminants

IV. TOTAL ENRTF REQUEST BUDGET *3* years

BUDGET ITEM *(See "Guidance on Allowable Expenses", p. 13)*	**AMOUNT**
Personnel: Arnold (PI, 8% time per year, salary 74.8% of cost, fringe benefits 25.2% of cost). Project supervision, supervision of graduate and undergraduate students and project reporting. Development of tool to predict microcontaminant photodestruction potential.	$ 54,300
Personnel: Graduate student (50% time during academic year, 50% time in summer; 56% salary, 33% tuition, 11% fringe benefits). Conducting solar pesticide removal evalutions, water collection and characterization. Quantify links between organic matter quality and quantity with reactivity.	$ 131,700
Personnel: Undergraduate student #1 (100% time during summer, 12.5% time in academic year; 93.3% salary, 6.7% fringe benefits). Water sample collection and characterization.	$ 18,000
Personnel: Undergraduate student #2 (100% time during summer, 12.5% time in academic year; 93.3% salary, 6.7% fringe benefits). Water sample collection, assist graduate student with photolysis experiments.	$ 18,000
Equipment: Horiba Aqualog benchtop fluorometer for organic matter characterization. Equipment is not available at UMN and critical to fast processing of hundreds of samples.	$ 40,000
Supplies: Supplies (chemical standards, instrument/analytical time, solvents, consumable supplies, notebooks, software licenses; $16,000 total).Maintenance and repair of liquid and gas chromatographs and solar simulator required for analyses and experiments ($6,000 total)	$ 22,000
Travel: Mileage charges and univeristy vehicle rental charges for trips to collect water samples. Hotel/meal charges if overnight stay required.	$ 5,000
Additional Budget Items: Shipping costs for samples collected by others.	$ 2,000
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$ 291,000

V. OTHER FUNDS

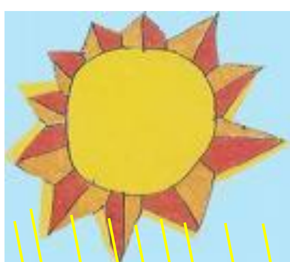
SOURCE OF FUNDS	**AMOUNT**	**Status**
Other Non-State $ Being Applied to Project During Project Period: none	$ -	
Other State $ Being Applied to Project During Project Period: none	$ -	
In-kind Services During Project Period: Arnold will also devote 1% time per year in kind ($6900). Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (52% of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind ($103,100)	$ 110,000	secured
Remaining $ from Current ENRTF Appropriation (if applicable): no current project directly applicable	$ -	
Funding History: Proposed project is a result of unexpected findngs of FY 2007 ENTRF funding and past National Science Foundation project	$~200,000	past funding

Sunlight activated organic matter can destroy pollutants

Organic matter gives water its brown/yellow color

Each source of organic matter has different solar-driven reactivity with pollutants

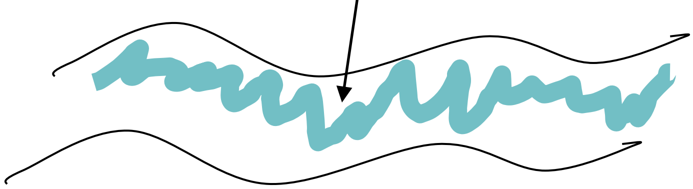
wastewater **agricultural runoff** **storm water**



Solar activated organic matter destroys pollutants (more efficiently than sunlight alone)

Wetlands used to collect pesticides, pharmaceuticals and contaminants

Reuse of treated water



Stream receiving clean water

Benefits

- Reduced toxicity to fish and animals
- Better water clarity
- Restored habitat
- Water reuse

Project Manager Qualifications and Organization Description

William A. Arnold

Joseph T. and Rose S. Ling Professor and Associate Head, Environmental Engineering, Department of Civil 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. He has been studying the fate of pharmaceutical and pesticide compounds in aquatic environments for fourteen years. The main focus has been the photolysis rates of pharmaceuticals and personal care products in surface water to determine the persistence of these compounds in the environment. As part of these efforts, reaction products have been identified to determine if photolysis leads to a loss of biological activity of the compounds and/or if reaction products are of additional environmental concern. Recent work in Dr. Arnold's group funded by the National Science Foundation has shown that photo-excited dissolved organic matter is much more important than previously thought in the destruction of various pesticides. He has published over twenty peer-reviewed papers on photolysis 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://www1.umn.edu/twincities/about/index.html). The laboratories and offices of the PI contain the necessary fixed and moveable equipment and facilities needed for the proposed studies.