Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2014 Work Plan

Date of Report: January 10, 2014

Date of Next Status Update Report: January 1, 2015

Date of Work Plan Approval:

Project Completion Date: June 30 , 2017

Does this submission include an amendment request? No

PROJECT TITLE: Solar Driven Destruction of Pesticides, Pharmaceuticals, Contaminants

Project Manager: William Arnold

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Location: Statewide

Total ENRTF Project Budget: $291,000	**ENRTF Appropriation:**	**$291,000**
	Amount Spent:	**$0**
	Balance:	**$291,000**

Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 03a

Appropriation Language:
$291,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to quantify the solar-driven destruction of contaminants reacting with dissolved organic matter to optimize water treatment methods and guide reuse. This appropriation is available until June 30, 2017, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Solar Driven Destruction of Pesticides, Pharmaceuticals, Contaminants

II. PROJECT STATEMENT:

Wastewater, storm water, and agricultural runoff 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, dissolved organic matter (DOM) generates reactive species capable of destroying pollutants, and these indirect photolysis reactions may be more important than 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. The goals of the proposed research are to 1) characterize the composition and reactivity of organic matter present in waters across Minnesota, 2) develop a rapid screening tool to predict the solar-driven, DOM-mediated destruction of pollutants, and 3) 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. These goals will be met by collecting water samples across broad spatial and temporal scales in Minnesota, characterizing the chemical and spectral features of the DOM, and measuring the production of solar generated oxidants and the destruction of selected pollutants. Using the data collected, design guidelines for treatment wetlands based on organic matter reactivity and recommendations for water reuse will be developed.

III. PROJECT STATUS UPDATES:

Project Status as of January 1, 2015:

Project Status as of July 1, 2015:

Project Status as of January 1, 2016:

Project Status as of July 1, 2016:

Project Status as of January 1, 2017:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Collection of wastewater, storm water, and agricultural runoff samples and characterization of the organic matter they contain

Description: 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. The focus of the work is on the treatment of runoff/effluents via optimization of open water wetlands to facilitate photolysis. Thus, samples will be collected from native wetlands, restored wetlands, agriculturally impacted wetlands, wastewater treatment plant effluents, and storm water ponds. We will seek to generate a spatially distributed, randomized sample set among the open water wetlands and ponds via use of the National Wetlands Inventory (www.fws.gov/wetlands/) and discussions with State agency scientists. Samples will be taken quarterly (when possible) over a wide geographic area, but a majority of samples will be in the Twin Cities area. To obtain enough samples for thorough analysis of the organic matter, we will need approximately 20-25 sites each for storm water, wastewater, and agricultural runoff. Wastewater effluents and pond sampling will be coordinated via contacting the appropriate treatment facility managers. Agricultural runoff and storm water runoff samples will also be collected at Glacial Ridge Refuge, a farm in Tracy, MN, and in collaboration with ongoing sampling efforts of watershed management districts. We will partner with state and local agency scientists (e.g., Department of Natural Resources, Minnesota Pollution Control Agency, local watershed districts) whenever possible with regards to sample collection to ensure a wide range of samples is studied and to avoid duplicative sampling efforts.

In the laboratory, essential water quality parameters including pH, alkalinity, nutrient levels (nitrate, ammonia, dissolved phosphorus), and dissolved organic carbon levels will be measured. Ions, such as chloride and bromide, will be measured via ion chromatography , and ionic strength will be calculated from specific conductance measurements. Filter sterilized water samples for subsequent photolysis experiments will be stored at pH 3 at 4 ^{o}C to minimize biological alteration.

Spectral characterization of the samples will be robust. Specific UV absorbance (SUVA = $UV_{254\ nm}$/DOC) will be determined, because this can give an indication as to whether the organic matter is more “allochthonous-like” or “autochthonous-like” (autochthonous sources generally have lower SUVA values). To further characterize each organic matter sample, spectral slopes and spectral slope ratios will also be evaluated. Excitation-emission matrix (EEM) fluorescence spectroscopy will also be performed on the collected samples. Instrumentation to allow these analyses is requested in the proposed budget. By compiling hundreds of samples and performing EEM spectroscopy, we will be able to build parallel factor analysis (PARAFAC) models for the samples collected.

Additionally, a portion of collected samples (approximately 50 divided among wastewater, storm water, and agricultural runoff) will be extracted using styrene divinyl benzene polymer (e.g., Agilent Bond Elut PPL) cartridges. An advantage of this extraction phase is that the cartridges, while expensive, are re-usable. Selected extracts will be submitted for Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) analysis to the Old Dominion University College of Science Major Instrumentation Cluster. If DOC levels are high enough (and salt levels low enough), it may be possible to analyze the samples without this pre-concentration step. The FT-ICR-MS analysis will provide information about the specific chemical formulas present in each sample, and principal component analysis will be used to determine how similar or different the samples are from one another in this respect. We will obtain FT-ICR-MS spectra for as many samples as possible, but it will not be possible to analyze all of those collected. The first samples to be submitted will be those showing enhanced or suppressed production of PPRIs. The suite will be broadened as the photochemical results are collected.

Summary Budget Information for Activity 1: **ENRTF Budget: $ 149,000**
Amount Spent: $ 0
Balance: $ 149,000

Activity Completion Date:

Outcome	**Completion Date**	**Budget**
1. Collect water samples and perform routine analyses (pH, carbon/nutrient levels, etc.)	4/30/16	$ 40,000
2. Measure and analyze excitation emission spectra to build spectral library	9/30/16	$ 60,000
3. Mass spectrometric analysis of organic matter to build composition library	12/31/16	$ 49,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017

Final Report Summary:

ACTIVITY 2:

Activity 2: Measurement of sunlight-generated oxidants and solar transformation of pesticides and pharmaceuticals

Description: Based on the results of the characterization described above, we will select a subset of water samples for detailed photochemical experiments. Once trends are identified based on the EEM and FT-ICR-MS analyses, we will verify these observations by conducting photochemical experiments with additional water samples.

A solar simulator (Atlas Suntest CPS) equipped with broadband Xe lamps and 295 nm long pass filters will be used as the light source for most photolysis experiments. Having the ability to set the light intensity and using simulators with known spectral profiles offers the experimental advantage of being able to compare results from day to day. Experiments will also be conducted using natural solar light to better place in context our laboratory work conducted with artificial light sources. Chemical actinometry experiments will also be performed to monitor the irradiation intensity. All experiments will be conducted using quartz test tubes and results will be compared to dark controls to account for any non-photolysis losses.

Our studies will primarily focus on measuring the photoproduction of triplet excited state organic matter ($^3OM^*$), but will also measure the downstream products ·OH, $^1O_2$, and $CO_3^{\cdot-}$, when necessary. Because the DOM composition is likely to vary from site to site and because $^3OM^*$ is particularly important for contaminant transformation and generation of other PPRIs, this is a logical starting point. If the studies described below reveal that another PPRI is responsible for contaminant degradation, measurements of other PPRI steady state concentrations will be performed. It is noted here that ·OH is also produced via nitrate irradiation. Nitrate will likely be present in wastewater effluents (if they are nitrified) and agricultural/storm water runoff. For the compounds to be studied (see below), however, reaction with ·OH is not expected to be the dominant indirect photolysis pathway. Should nitrate be found to be a major contributor of ·OH, its role will be determined by comparing photochemical results of whole water samples to the organic matter isolated via solid phase extraction by drying a portion of the extract, re-dissolving it in pH buffered distilled water, and quantifying the production of hydroxyl radical.

The efficiency by which DOM produces specific PPRIs will be monitored indirectly using well-established molecular probe techniques. A probe molecule that has been chosen for its selectivity for a given PPRI is spiked into the sample solution. Steady-state PPRI concentrations are calculated from the bimolecular rate constant for reaction of the given PPRI and probe combination and either the probe loss rate or product formation rate. Should our $[PPRI]_{SS}$ results show interesting trends, apparent quantum yields of PPRI production can be calculated following literature precedent.

In parallel to the studies described above, we will also determine the photolysis process(es) responsible for transformation of pollutants expected to be present in agricultural runoff, storm water runoff, or wastewater effluents. Experiments will be conducted in the appropriate matrix (e.g., agricultural pesticides in agricultural runoff samples). All of these compounds have been detected in the appropriate matrix, and preliminary results suggest indirect photolysis processes are important in their fate. Additional compounds may be added as the work progresses. The preliminary list of compounds is as follows:

Agricultural: atrazine, metolachlor, mesotrione, pyraclostrobin, genistein, estrone
Wastewater: sulfmethoxazole, carbamazepine, propranolol, DEET, sucralose
Storm water: prometon, mecoprop, chlorpyrifos, bifenthrin

Target compounds will be spiked into the appropriate water sample and a distilled water sample (to quantify any loss due to direct photolysis) such that the initial concentration will be ≤10 μM to ensure optically dilute solutions. In all experiments, reaction solutions will be irradiated in UV transparent quartz test tubes. Samples will be withdrawn as a function of time and analyzed using chromatographic methods. To verify the PPRI or PPRIs responsible for contaminant degradation, quenching experiments will be used. We will also evaluate any nitrogen and phosphorus release from organic matter that occurs during light exposure.

Summary Budget Information for Activity 2: **ENRTF Budget: $ 110,000**
Amount Spent: $ 0
Balance: $ 110,000

Activity Completion Date:

Outcome	**Completion Date**	**Budget**
1. Determine concentrations of radicals generated in sunlight that are responsible for contaminant transformation	4/30/16	$ 35,000
2. Measure nutrient release to evaluate any potential for biological growth	6/30/16	$ 15,000
3. Determine pesticide removal rates in the waters collected in Activity 1	4/30/16	$ 30,000
4. Determine pharmaceutical removal rates in the waters collected in Activity 1	6/30/16	$ 30,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017

Final Report Summary:

ACTIVITY 3: Produce design guidelines for pollutant transformation in wetlands and recommendations for water reuse
Description: Using the data collected with regards to DOM composition and reactivity, a protocol will be developed to assess the solar reactivity of pollutants. The spectral and composition analysis will be combined with the photolysis results and used to evaluate any trends that give rise to the reactivity observed in the photolysis experiments. Statistical tools such as principal component analysis and non-metric multidimensional scaling analysis will be used.

The goal is to develop a method that will allow simple characterization of the organic matter in wastewater, storm water, or agricultural runoff samples to be used to predict the potential of a given water to attenuate pollutants contained within it. This tool will allow us to provide 1) an assessment of organic matter composition/quality that leads to maximum pollutant transformation, 2) design parameters for wetlands for treatment of agricultural runoff, wastewater or storm water based on the reactivity of the organic matter, and 3) assessment of potential benefits of solar treatment to allow wastewater or storm water reuse for irrigation, or if reuse leads to enhanced pollutant transformation 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.

Summary Budget Information for Activity 3: **ENRTF Budget: $ 32,000**
Amount Spent: $ 0
Balance: $ 32,000

Activity Completion Date:

Outcome	Completion Date	Budget
1. Develop organic matter parallel factor analysis models to predict radical production	9/30/16	$ 10,000
2. Quantify organic matter characteristics leading to pollutant transformation	3/30/17	$ 10,000
3. Determine wetland depths/areas to optimize pharmaceutical transformation for wastewater systems	6/30/17	$ 6,000
4. Optimize pesticide transformation in storm water and agricultural systems	6/30/17	$ 6,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017

Final Report Summary:

V. DISSEMINATION:

Description: The results will be disseminated via peer reviewed publications in scientific journals, presentations at local/regional conferences, and 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.

Status as of January 1, 2015:

Status as of July 1, 2015:

Status as of January 1, 2016:

Status as of July 1, 2016:

Status as of January 1, 2017

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Explanation
Personnel:	$ 222,000	PI at 8% time per year. One graduate student at 50% time per year. Two undergraduate students at 100% time in the summer, 12.5% in the academic year. Costs include fringe benefits for all and tuition for the graduate student.

Equipment/Tools/Supplies:	$ 22,000	Chemical standards, instrument/analytical time, solvents, consumable supplies, notebooks, software licenses
Capital Expenditures over $5,000:	$ 40,000	Horiba Aqualog benchtop fluorometer for organic matter characterization.
Travel Expenses in MN:	$ 5,000	Mileage charges and univeristy vehicle rental charges for trips to collect water samples. Hotel/meal charges if overnight stay required.
Other:	$ 2,000	Shipping costs for samples collected by others.
TOTAL ENRTF BUDGET:	**$ 291,000**	

Explanation of Use of Classified Staff: not applicable

Explanation of Capital Expenditures Greater Than $5,000: The instrument to be purchased allows spectral characterization of organic matter. By processing hundreds of samples, we plan to build a parallel factor analysis model to relate reactivity to spectral features. The item requested is a Horiba Aqualog. This instrument performs the analysis in minutes (compared to hours for other instruments) and exports the data in a format in which appropriate corrections are made for ready analysis in appropriate software. This instrument is not currently available at the University of Minnesota. The instrument will continue to be used for the same types of purposes at the University of Minnesota throughout its useful life. If its use changes or it is otherwise sold, the Environment and Natural Resources Trust Fund will be paid back an amount equal to the cash value received or a residual value approved by the LCCMR director.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 2.0

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			
	$ 110,000	$ 0	Arnold will also devote 1% time per year in kind ($6900). Because the project is overhead free, laboratory space, electricity, and other facilities/administrative costs (52% of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind ($103,100)
State			
	$ 0	$ 0	
TOTAL OTHER FUNDS:	**$ 110,00**	**$ 0**	

VII. PROJECT STRATEGY:

A. Project 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 transformation 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. Project Impact and Long-term Strategy:
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.

VIII. ACQUISITION/RESTORATION LIST: not applicable

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

X. ACQUISITION/RESTORATION REQUIREMENTS WORKSHEET: not applicable

XI. RESEARCH ADDENDUM: to be inserted upon completion of peer review

XII. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted not later than January 1, 2015; July 1, 2015; January 1, 2016; July 1, 2016, and January 1, 2017. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund
M.L. 2014 Project Budget

Project Title: Solar Driven Destruction of Pesticides, Pharmaceuticals, Contaminants
Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 03a
Project Manager: William Arnold
Organization: University of Minnesota
M.L. 2014 ENRTF Appropriation: $ 291,000
Project Length and Completion Date: 3 Years, June 30, 2017
Date of Report: January 10, 2014

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	**Collection of wastewater, storm water, and**			**Measurement of sunlight-generated oxidants**			**Produce design guidelines for pollutant**				
Personnel (Wages and Benefits)	$95,000	$0	$95,000	$95,000	$0	$95,000	$32,000	$0	$32,000	$222,000	$222,000
Arnold (PI, 8% time per year, salary 74.8% of cost, fringe benefits 25.2% of cost. Estimated total: $54,300). Project supervision, supervision of graduate and undergraduate students and project reporting. Development of tool to predict microcontaminant photodestruction potential.											
Graduate student (50% time during academic year, 50% time in summer; 56% salary, 33% tuition, 11% fringe benefits. Estimated total: $131,700). Conducting solar pesticide removal evalutions, water collection and characterization. Quantify links between organic matter quality and quantity with reactivity.											
Undergraduate student #1 (100% time during summer, 12.5% time in academic year; 93.3% salary, 6.7% fringe benefits. Estimated total: $18,000). Water sample collection and characterization.											
Undergraduate student #2 (100% time during summer, 12.5% time in academic year; 93.3% salary, 6.7% fringe benefits. Estimated total: $18,000). Water sample collection, assist graduate student with photolysis experiments.											
Equipment/Tools/Supplies											
Chemical standards, instrument/analytical time, solvents, consumable supplies, notebooks, software licenses;	$10,000	$0	$10,000	$6,000	$0	$6,000				$16,000	$16,000
Maintenance and repair of liquid and gas chromatographs and solar simulator required for analyses and experiments				$6,000	$0	$6,000				$6,000	$6,000
Capital Expenditures Over $5,000											
Horiba Aqualog benchtop fluorometer for organic matter characterization.	$40,000	$0	$40,000							$40,000	$40,000
Travel expenses in Minnesota											
Mileage charges and univeristy vehicle rental charges for trips to collect water samples. Hotel/meal charges if overnight stay required.	$3,000	$0	$3,000	$2,000	$0	$2,000				$5,000	$5,000
Other											
Shipping costs for samples collected by others.	$1,000	$0	$1,000	$1,000	$0	$1,000				$2,000	$2,000
COLUMN TOTAL	**$149,000**	**$0**	**$149,000**	**$110,000**	**$0**	**$110,000**	**$32,000**	**$0**	**$32,000**	**$291,000**	**$291,000**

Sunlight activated organic matter can destroy pollutants

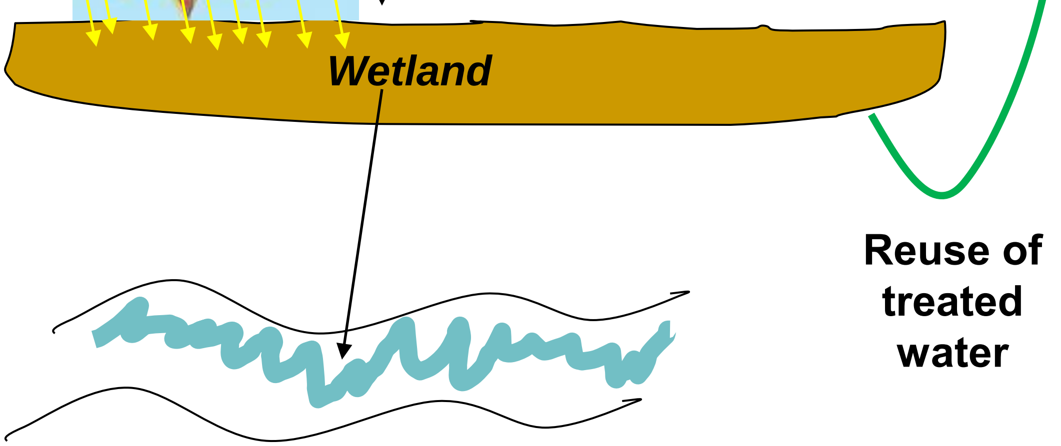
Organic matter gives water its brown/yellow color

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