Environment and Natural Resources Trust Fund

Research Addendum for Peer Review

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Project Title: Solar Driven Transformation of Pesticides, Pharmaceuticals, Contaminants

Project number: 036-B

1. Abstract

Wastewater, storm water, and agricultural runoff carry pesticides, pharmaceuticals, and nutrients. While these chemicals serve important functions in crop production or treatment of disease in livestock and humans, they become pollutants when discharged into surface waters. When activated by sunlight, dissolved organic matter (DOM) generates reactive species capable of transforming ollutants, and these indirect photolysis reactions may be more important than direct transformation 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 transforming hem. 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 transformation 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 transformation. 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 transformation 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.

2. Background

A variety of processes, including biodegradation, chemical transformation, and photolysis (both direct and indirect) can transform the pollutants carried by wastewater, storm water, and agricultural runoff. Chemicals susceptible to aerobic biodegradation or direct photolysis will be processed rather rapidly in pond/wetland systems. More recalcitrant compounds, however, are often only susciptilble to indirect photolysis, which is mediated by DOM. Thus, it is critical to understand the indirect photolysis processes that occur because their rates will likely dictate the size of pond/wetland necessary to obtain a desired level of treatment. While often thought of as a nuisance, DOM 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. DOM 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. The reactivity relevant to this work is the generation of photochemically produced reactive intermediates (PPRIs) upon solar irradiation of DOM. Organic matter contributes to aquatic photochemistry in three main ways: by attenuating light as it proceeds through the water column, quenching reactive species (both PPRIs and pollutant molecules),

and by sensitizing the production of PPRIs.[1-15] The major PPRIs produced are hydroxyl radical (·OH), singlet oxygen ($^1O_2$), carbonate radical ($CO_3^{·-}$), and triplet excited state organic matter ($^3OM^*$). These PPRIs serve to transform pollutants that may not directly absorb sunlight (Figure 1). In this way, contaminants that do not absorb sunlight and that would ordinarily be considered recalcitrant are susceptible to photochemical reactions. Indirect photolysis pathways involving ·OH, $CO_3^{·-}$, $^1O_2$, and $^3OM^*$ have been shown to be important fate processes for many contaminants in sunlit surface waters.[16-19,36]

The selectivity of the reactions of the PPRIs is also important. While ·OH (E = 2.3 V at pH 7) reacts indiscriminately at essentially diffusion controlled rates with organic compounds, the other PPRIs react more selectively. $^1O_2$ reacts with phenols, electron rich double bonds, and sulfides. $CO_3^{·-}$ (E = 1.59 V) reacts with electron rich amine/N-heterocyclic groups via electron transfer.[20] $^3OM^*$ (E = 1.36-1.95 V) may react via electron transfer, hydrogen abstraction, or energy transfer pathways.[21]
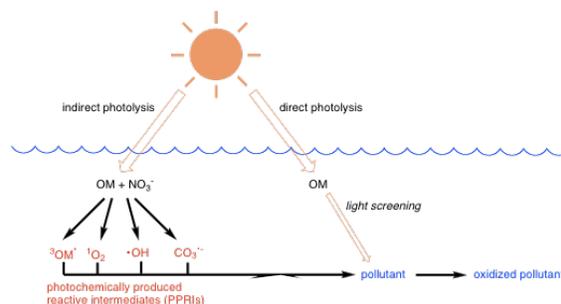

Figure 1. Schematic showing the role of dissolved organic matter in aquatic photochemistry.

The exact chemical structure of aquatic DOM is unknown, because DOM is comprised of a collection of numerous molecules originating from microbial (autochthonous) and terrestrial (allochthonous) precursor materials.[22-26] Allochthonous DOM is characterized by its generally higher molecular weight, more hydrophobic nature, and greater aromaticity relative to autochthonous DOM.[23-26] Autochthonous DOM is noted for its higher sulfur and nitrogen content than found in terrestrial DOM.[27-31] The two major classes of DOM also have quite different spectroscopic properties.[22,25,26,32-35] For example, three-dimensional fluorescence excitation-emission spectra show distinct differences between terrestrial and microbial DOM and have been used to track source material.[22,28,33]

Most studies reporting the photosensitizing ability of DOM tend to focus on allochthonous sources, partly because logic suggests it is present in natural waters and also because of its wider commercial availability. The introduction of wastewater effluent, agricultural runoff, or stormwater flows, however, alters the DOM composition in a system. Given that contaminants entering aquatic systems via agricultural runoff, stormwater runoff, and wastewater effluents are co-located with a specific source of DOM, it is vital that we explore the how the sources of DOM in pollutant-laden water contributes to indirect photodegradation of the contaminants.

Though evidence is scarce, a set of recent studies suggests that autochthonous DOM may be a more efficient producer of $^3OM^*$ (or that autochthonous $^3OM^*$ is more reactive) than is allochthonous DOM.[16,17] For example, Guerard et al.[17] demonstrated that the autochthonous DOM in an aquaculture pond produced $^3OM^*$ capable of transforming the antibiotic sulfadimethoxine. The same effect was observed with *autochthonous* fulvic acid derived from Pony Lake in Antarctica, but *allochthonous* DOM from a surface water near the aquaculture pond was unable to sensitize the same reaction.[17] This is an important finding that merits further study, not only because it suggests that the reactivity and/or rate of production of $^3OM^*$ from autochthonous and allochthonous sources differ, but also because $^3OM^*$ is responsible for the production of other "downstream" PPRIs such as $^1O_2$, $O_2^{·-}$, H_2O_2, and ·OH.[2-12,14,15]. For these reasons, it is hypothesized that effluents/runoff may lead to higher steady state concentrations of PPRIs than would be predicted based on studies using allochthonous reference materials, which has the potential to 1) alter the dominant photochemical pathway for pollutants and 2) accelerate pollutant processing, which could be exploited by allowing passive solar treatment to occur in engineered open-water systems (e.g., ponds or wetlands). Because $^3OM^*$, $^1O_2$, ·OH,

and CO_3^- have been implicated in indirect photochemical reactions with myriad organic substrates in natural waters, sensitizers that lead to the production of these PPRIs merit study as potential controls on pollutant fate.

The impetus for this project is recent work from the Arnold group that has shown that $^3OM^*$, $^1O_2$, and CO_3^-, may be more important than previously thought in the indirect photolysis of various pesticides and pharmaceuticals.[36,37] Using quenchers, the overall fraction of photolytic loss due to $^3OM^*$, CO_3^-, $^1O_2$, and $\cdot OH$ was determined for a water sample collected from a wetland with little anthropogenic impact (i.e., no nitrate inputs). As shown in Figure 2, $^3OM^*$ and $^1O_2$ are important contributors, with CO_3^- also playing a role.[36] The Arnold laboratory has also found that photolysis of two antibiotic compounds, trimethoprim and sulfamethoxazole, proceeds via different mechanisms in wastewater effluent as compared to a natural water.[37] In effluent, ~25% and ~75% of the indirect photochemical loss of these compounds was due to $^3OM^*$ and $\cdot OH$ respectively. For both drugs, however, transformation rate enhancements due to

Figure 2. Percent contributions of direct photolysis, $CO_3^{\cdot-}$, $\cdot OH$, $^1O_2$, $^3DOM^*$ and other processes to the photodegradation of pesticides in wetland water under simulated sunlight. The major role of $^3DOM^*$ was unexpected.[36]

$^3OM^*$ in river water were minimal. This again indicates that the DOM in the effluent/runoff may drive the indirect photolysis, and it is necessary to understand the photoreactivity of DOM to engineer systems to take advantage of this reactivity.
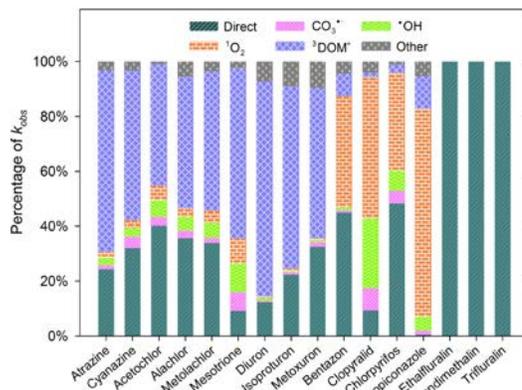
3. Hypothesis

The central hypothesis is that the production PPRIs will be dependent on chemical and spectral features of the dissolved organic matter. In particular, it is hypothesized that steady state level of $^3OM^*$ will be higher in systems displaying characteristics of autochthonous DOM. Thus, it is also hypothesized that the production of PPRIs will vary in stormwater, agricultural and wastewater runoff and that there will be variations in production depending on the surrounding landscape and season. Ultimately, the potential for using passive solar treatment to treat contaminants in various situations will depend on the photoreactivity of DOM.

4. Methodology

Water Collection and Characterization

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. Wastewater effluents and pond sampling will be coordinated via contacting the appropriate treatment facility managers. Agricultural runoff and storm water runoff samples will be collected by taking advantage of ongoing sampling efforts of watershed districts (stormwater) and state agencies

(agriculture). Established relationships with two agriculturally impacted sites (near Crookston and Tracy, MN) are also in place. Agricultural runoff and storm water runoff samples will also be collected when opportunities allow. 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 are studied and to avoid duplicative sampling efforts.

Samples will be grab samples unless we are able to obtain composites from sampling efforts already in place (e.g., at wastewater treatment plants). Wetland samples will be dip/grab samples from the waters' edge. Samples will be taken quarterly (when possible) over a wide geographic area, but a majority of samples will be in the Twin Cities area. We have ongoing efforts allowing samples to be collected in Crookston and Tracy, MN. We will also seek partners in Duluth. To obtain enough samples for thorough analysis of the organic matter, we will need approximately 20-25 sites each for stormwater, wastewater, and agricultural runoff. Samples will be collected in clean glass or polycarbonate bottles. The bottles will be stored in coolers on ice, transported back to the laboratory, and filter sterilized upon arrival (0.2 μm Waters Omnipore membranes). Essential water quality parameters including pH, alkalinity, nutrient levels (nitrate, ammonia, dissolved phosphorus), and dissolved organic carbon levels will be measured in the laboratory. Ions, such as chloride and bromide, will be measured via ion chromatography , and ionic strength will be calculated from specific conductance measurements. All necessary equipment for these analyses is present in the Department of Civil Engineering. Filter sterilized water samples for subsequent photolysis experiments will be stored at pH 3 at 4 ^{o}C to minimize biological alteration. The pH will be readjusted to the native value prior to conducting the photolysis studies.

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).[32] To further characterize each organic matter sample, spectral slopes and spectral slope ratios will also be evaluated.[32] 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[38] for the samples collected. It is possible that separate models will be required for different sources of water (i.e., wastewater effluent versus storm water) and that spatial or temporal separation may also arise.

Additionally, a portion of collected samples (at least 50, divided among wastewater, stormwater, and agricultural runoff) will be will extracted using styrene divinyl benzene polymer (e.g., Agilent Bond Elut PPL) cartridges as described by Dittmar et al.[39] An advantage of this extraction phase is that the cartridges, while expensive, are re-usable. These 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. A selection of 50 or more samples will allow the variation in chemical composition to be seen and enough samples for robust statistical analysis. The 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 due to budget constraints. 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.

Measurement of PPRI production and solar transformation of pesticides and pharmaceuticals

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 conducted 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 $^3OM^*$, but will also measure the downstream products $\cdot OH$, $^1O_2$, and CO_3^- in some samples. 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 in that specific sample. It is not possible to measure all of the PPRIs in all samples, but we will measure all PPRIs in a selection of samples (3 to 5) from wastewater, storm water, and agricultural runoff. In the end, the most important parameter for wetland design is the overall first order rate constant. It is noted here that $\cdot OH$ is also produced via nitrate irradiation. Nitrate will be present in wastewater effluents (even if they are denitrified) and agricultural/storm water runoff. For the compounds to be studied (see below), however, reaction with $\cdot OH$ is not expected to be the dominant indirect photolysis pathway. Should nitrate be found to be a major contributor of $\cdot OH$, 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.[9,40-47] 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.[15]

Sorbic acid (*trans,trans*-hexadienoic acid, HDA) will be the probe used for $^3OM^*$.[41] Water samples will be amended with HDA at various concentrations and photolysed. An aliquot of sample will be removed from each reaction solution at selected time intervals and quenched with 50 µL glacial acetic acid. The isomerization rate constant of HDA is converted to the steady-state concentration of $^3OM^*$ concentration using the method described by Grebel et al.[105] We will correct the result for any isomerization of HDA observed in DI water. The Arnold lab has recently used this method to measure [$^3OM^*$]$_{ss}$ in prairie pothole wetlands.[36] The role of $^3OM^*$ will be verified via deoxygenation to enhance $^3OM^*$ or adding isoprene as a quencher. The role of dissolved oxygen is critical in these experiments. The HDA isomerization method measures the [$^3OM^*$]$_{ss}$ with oxygen present. Conducting experiments in the absence of oxygen will reveal the maximum [$^3OM^*$]$_{ss}$.

Furfuryl alcohol (FFA; 10 μM) will be used to measure steady-state concentrations of $^1O_2$.[40] Samples (~500 μL) will be removed at various times and analyzed using reverse phase HPLC with UV detection. L-histidine a quencher of $^1O_2$, can be added to decrease $[^1O_2]_{ss}$ in a predictable way to verify that FFA loss is indeed due to reaction with $^1O_2$.[48,49] The loss of the FFA probe molecule is expected to be inversely related to the amount of quencher added with an asymptote of zero if $^1O_2$ is the only contributor to its reactivity. Any non-zero asymptote will be due to other transformation pathways and will be taken into account when determining $[^1O_2]_{ss}$.[44] Recent work has suggested that reaction with $^3OM^*$ must be accounted for in FFA degradation in some waters, and we will explore this effect in any waters displaying anomalous quenching behavior.[50]

Experiments to determine the apparent $CO_3^{\bullet-}$ steady state concentration will use N,N-dimethylaniline (DMA) as a probe.[47] It is recognized that DMA is not a perfect probe/quencher for $CO_3^{\bullet-}$ because it also interacts with $^3OM^*$. Other possibilities will be sought, but none is currently available. Similarly to FFA, the loss of DMA is monitored as a function of time, and the steady state concentration is calculated using the known second-order rate constant of DMA with $CO_3^{\bullet-}$. The values are corrected for any DMA losses in irradiated DI water samples at the same pH.

Terephthalate (TPA; 10 μM) is the probe for $\cdot$OH. Methods for using this probe in aquatic systems have been developed in part by a graduate student co-advised by Dr. Arnold.[43,44] This is an example of a fluorescent "turn-on" probe, as the TPA probe is non-fluorescent while the fluorescent hTPA product can be sensitively detected by fluorescence spectroscopy.[43,44] As such, to sensitively and selectively detect $\cdot$OH, we will monitor the formation of the fluorescent hTPA product by HPLC with fluorescence detection. The steady-state concentration of $\cdot$OH is determined from the measured hTPA production rate, the known bimolecular rate constant of reaction between TPA and $\cdot$OH, and the initial concentration of TPA.

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, usage data suggests high or increasing use, 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 and that the levels are well above background concentrations. For each group of compounds, we will spike them in a mixture to reduce the number of experiments necessary, if preliminary experiments show there are no synergistic photochemical effects. 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. The contaminant photolyses will be conducted alongside tubes containing the water sampling containing the introduced contaminant and spiked with isopropyl alcohol (IPA, an $\cdot$OH quencher), N,N-dimethylaniline (a $CO_3^{\cdot-}$ quencher), histidine (a $^1O_2$ quencher), or HDA ($^3OM^*$ quencher).[1-5] Additionally, deoxygenated experiments will be performed. For these experiments, the test tubes will have a septum seal to prevent introduction of oxygen when sampling (the volume sampled through the septum will be replaced by introduction of N_2 gas). If $^3OM^*$ is important, removal of oxygen should accelerate the reaction and if $^1O_2$ oxygen is responsible, removal of oxygen will halt the reaction.[51] Similarly, increased dissolved oxygen levels will be used to look for the opposite effects.

One potential concern of using passive solar treatment in ponds or wetlands to transform pesticides or pharmaceuticals is the potential release of nitrogen or phosphorus as the DOM is photolyzed. During the experiments described above, nitrate, ammonia, and dissolved phosphorus levels will be measured at the beginning and end of the photolysis to evaluate if any such release occurs using an autoanalyzer. We recognized that the changes may not be able to be seen over the background levels of the nutrients, but this it is important to attempt to quantify these changes.

Design guidelines for wetlands and recommendations for water reuse

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 via indirect photolysis. 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.

5. Results and Deliverables

The work is divided into the three parts: 1) the collection and characterization of water samples, 2) the photolysis experiments, and 3) the assessment of organic matter reactivity and evaluation of passive solar treatment for contaminant transformation. For the first result, the deliverable is a database of organic matter and water quality properties relative to photochemistry in a spatially and temporally rich set of Minnesota waters. The deliverables for the second task are measurement of PPRI levels in these waters and an evaluation of the importance of triplet excited state organic matter in the transformation of a variety of pollutants. The deliverables for the final part of the work are quantification of factors that lead to enhanced reactivity of the organic matter and development of design guidelines that can use this reactivity to transform the pollutants. To this end, we will seek to modify the recently published APEX model[52] for the prediction of photolysis in surface waters such that it can be used as a design tool for wetland surface area/depth.

This will be the first work to compare the solar reactivity of agricultural runoff, storm water runoff, and wastewater effluent. The work will also demonstrate whether it is advisable to retain the water (and its associated pollutants) to affect treatment in a wetland or pond prior to discharge into the receiving water. We note that the results may also be useful in the evaluation of photochemical pollutant processing in streams, but this will require future research beyond the scope of this study. The direct outcomes will be 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 transformation of pollutants. 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.

6. Timetable

The research tasks outlined above will be accomplished according to the following schedule. Shaded regions are continuous efforts and X's mark discreet events.

	Year 1				Year 2							
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Result 1: Water sample collection, organic matter characterization												
Sample collection	▓	▓	▓	▓	▓	▓	▓					
pH, nutrient, DOC meas.	▓	▓										
Spectral analysis			▓	▓	▓	▓	▓					
Mass spectrometric analysis												
Data Analysis	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	
Product Delivery								X		X		
Result 2: Measurement of PPRIs and pollutant photolysis												
PPRI measurements	▓	▓	▓	▓	▓	▓	▓					
N and P release measurement	▓	▓				▓	▓					
Pesticide photolysis			▓	▓	▓	▓	▓	▓				
Pharmaceutical photolysis		▓	▓	▓					▓	▓		
Data analysis		▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
Product delivery								X		X		
Result 3: Wetland design/reuse guidelines												
PARAFAC analysis				▓	▓	▓	▓	▓	▓	▓		
Evaluate DOM characteristics								▓	▓	▓	▓	
Optimize wetland design for solar treatment/water reuse										▓	▓	▓
Product delivery												X
Reporting		X		X		X		X		X		X

7. Budget

The requested funds from LCCMR total $291,000. See attached sheets for cost breakdown. The justificaiton is as follows.

Staff or Contract Services. Over the two year project, Dr. Arnold will devote 8% (1 month per year) of time to the project (total salary and fringe benefits of $54,300). The responsibilities of the principal investigator include experimental design, product coordination, data analysis, student guidance, and report/product preparation. One graduate student researcher pursuing a Ph.D. degree will conduct the day-to-day experiments described above. A 50% appointment is considered full time for students (and includes tuition payment and health insurance), and funds for three academic years and three summers ($131,700). Two undergraduate students will also be supported by the project full time in each summer and for up to 10 hours per week during the academic year ($18,000). The undergradate researchers will assist with water sample collection, characterization of the organic matter, and running photolysis experiments.

Equipment. A sum of $40,000 is budgeted for the purchase of a compact benchtop fluorometer for the characterization of dissolved organic matter. This essential piece of equipment is needed to generate the excitation-emission spectra and will also allow simultaneous collection of UV-Visible absorbance spectra. This instrument allows rapid collection of spectra (minutes), and thus will allow the processing of hundreds of samples. Given the number of samples to develop the PARAFAC models, this efficiency is needed. In the future, the equipment would be used for additional organic matter characterization and potentially instructional purposes. Equipment able to rapidly process samples with customized software for PARAFAC modeling is currently not available at the University of Minnesota. Given the number of samples expected to generated by the project, it is more economical to purchase an instrument rather than pay fees to an outside contractor to process the samples to be analyzed.

Supplies and Maintenance. A total of $16,000 is requested for laboratory supplies (glassware, chemicals, analytical reagents/consumables, extraction cartridges gloves, data storage media, laboratory notebooks, laboratory safety equipment) and for fourier transform-ion cylctron resonance mass spectrmetric analysis of up to fifty extracted organic matter samples at the Old Dominion Univervisty COSMIC facilty ($40 per sample). Additionally, $6,000 is requested for maintenance and repair of the liquid chromatograph, gas chromatograph, and solar simulator that will be used by the project.

Travel expenses: A total of $5,000 is requested for in-state travel to collect water samples .

Shipping: A total of $2,000 is requested for shipping costs for samples collected by others.

Other. In-kind contributions total $110,000. These funds include in-kind effort of the PI (1%; $6,900) and the facilities/administrative costs that are waived on State of Minnesota funded research (52% of direct costs excluding permanent equipment and graduate student academic year fringe benefits; $103,100).

8. Credentials

Dr. Arnold is a nationally-known researcher with expertise on the fate and transport of anthropognic organic chemicals (including solvents, pesticides, and pharmaceuticals). 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 transformation 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.

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Professional Preparation
Massachusetts Institute of Technology, Chemical Engineering, Minor in Chemistry, S.B., 1994
Yale University, Chemical Engineering, M.S., 1995
The Johns Hopkins University, Environmental Engineering, Ph.D., 1999

Appointments
2010-present	**Joseph T. and Rose S. Ling Professor**, Department of Civil Engineering, University of Minnesota and member of the graduate faculty in Water Resources Science and Stream Restoration Science and Engineering
2013-2014	**Visiting Researcher**, Woods Hole Oceanographic Institution, Department of Marine Chemistry & Geochemistry
2005-2010	**Associate Professor**, Department of Civil Engineering, University of Minnesota and member of the graduate faculty in Water Resources Science and Stream Restoration Science and Engineering
2006-2007	**Visiting Researcher**, Eawag, The Swiss Federal Institute of Aquatic Science and Technology
1999-2005	**Assistant Professor**, Department of Civil Engineering, University of Minnesota and member of the graduate faculty in Water Resources Science

Selected Honors and Awards
Super Reviewer Award from the journal *Environmental Science and Technology*, 2013
Arcadis/AEESP Frontier in Research Award 2012
George W. Taylor Award for Distinguished Research, 2011
Joseph T. and Rose S. Ling Professorship in Civil Engineering, 2009-present
CH2M Hill/AEESP Outstanding Doctoral Dissertation Award, 2000

Professional Societies
American Chemical Society, Environmental Chemistry Division (ACS), American Geophysical Union, Hydrology Section (AGU), American Society of Civil Engineers (ASCE), Association for the Sciences of Limnology and Oceanography (ASLO), Association of Environmental Engineering and Science Professors (AEESP)

Selected Peer-Reviewed Publications
Five most closely related to the proposed project:
1. Zeng, T.; **Arnold**, **W.A.** 2013. Pesticide photolysis in prairie potholes: Probing photosensitized processes. *Environmental Science and Technology,* 47, 6735-6745.
2. Kelly, M.M.; **Arnold, W.A.**, 2012. Direct and Indirect Photolysis of the Phytoestrogens Genistein and Daidzein. *Environmental Science and Technology*, 46, 5396-5403.
3. Page, S.E.; **Arnold, W.A.**; McNeill, K. 2011. Assessing the contribution of free hydroxyl radical in organic matter-sensitized photo-hydroxylation reactions. *Environmental Science and Technology,* 45(11) 2818-2825.
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Synergistic Activities
- National Research Council's Committee on Future Options for Management in the Nation's Subsurface Remediation Effort (Water Science and Technology Board; 2010-2012)
- Multicultural Center for Academic Excellence, Office of Equity and Diversity President's Distinguished Faculty Mentor Program Participant (named an Outstanding Mentor)
- President (2011-2012) and Member of the Board of Directors, Minnesota Section of ASCE
- Resident Fellow of University of Minnesota Institute on the Environment and Associate Fellow of the Minnesota Supercomputing Institute
- Associate Editor of *Environmental Science and Technology Letters* (2013-)

9. Dissemination and Use

Findings will be disseminated and archived via reports to LCCMR, peer-reviewed publications, and presentations at conferences. We will also, when appropriate, disseminate results via the media. The audience is not only the scientific community, but also the public, policymakers, and practitioners. We will produce an archive that contains the DOM characteristics for the waters samples during the study. The information derived from this research will be used to develop guidelines for wetland design based on the pollutants to be treated, the quality of the organic matter, and the expected levels of reactive intermediates. To this end, we will seek to modify the recently published APEX model[52] for the prediction of photolysis in surface waters such that it can be used as a design tool for wetland surface area/depth.

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