

2014 Project Abstract

For the Period Ending June 30, 2017

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

PROJECT MANAGER: William A. Arnold

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FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2014, Chp. 226, Sec. 2, Subd. 03a

APPROPRIATION AMOUNT: \$291,000

AMOUNT SPENT: \$ 291,000

AMOUNT REMAINING: \$ 0

Overall Project Outcomes and Results

Urban stormwater, agricultural runoff, and municipal wastewater effluent transport pesticides, pharmaceuticals, and other trace organic compounds to aquatic systems. Once in the environment, these compounds are considered pollutants because they may have adverse ecological effects on non-target organisms. It may be possible to use or design wetland systems to take advantage of natural processes to maintain pollutant concentrations below harmful levels. Chemical reactions initiated by sunlight, also called photochemical reactions, are particularly important in degrading these pollutants. The organic matter (produced by the breakdown of plant material or from algae) dissolved in the water absorbs sunlight, and this process reactivates intermediates that breakdown pollutants.

In this work a method was developed to relate the amount of reactive intermediates produced to the source and composition of the organic matter. This allows prediction of how fast pollutants will be broken down by sunlight in surface waters impacted by stormwater runoff or wastewater effluents. Stormwater, wetland surface water, and municipal effluent samples were collected seasonally from Fall 2014 to Spring 2016 throughout the Minneapolis-St. Paul metro area and greater Minnesota. The efficiency of reactive intermediate formation was experimentally measured using chemical probes, and the composition of the organic matter was assessed using light absorbance and fluorescence measurements and high-resolution mass spectrometry. Trends show that organic matter with low capacity to absorb light also has high efficiencies of reactive species formation. The relationship between reactive species formation efficiency and organic matter composition appears to be highly influenced by the content of the organic derived from plants. From this work, a model was developed to aid in the design of treatment wetlands to achieve pollutant removal by allowing an appropriate amount of time for sunlight exposure. In addition, an empirical multiple linear regression model using both chemical information about the organic matter and descriptors of the surrounding landscape was developed to aid in the prediction of reactive species formation in surface waters across regional scales. This will allow prediction of contaminant degradation via sunlight-driven reactions in a broad range of surface waters in Minnesota.

Project Results Use and Dissemination

This work has been presented at two sessions of the Environmental Chemistry Division of the American Chemical Society in March 2017 (both submitted with this report). This work has also been presented at poster sessions of the Minnesota Water Resources Conference (October 2016), the Conference on the Environment (November 2016), and the Year of Water Action Forum (March 2017; poster submitted with this report). One manuscript presenting the results of this work has been accepted for publication (July 2017; manuscript submitted with this report) and additional manuscripts are in preparation.

Additional opportunities are being pursued to develop a pilot-scale treatment wetland to assess the accuracy and applicability of the models developed from this study.



Environment and Natural Resources Trust Fund (ENRTF)

M.L. 2014 Work Plan

Date of Report: August 19, 2017
Date of Next Status Update Report:
Date of Work Plan Approval: June 4, 2014
Project Completion Date: June 30, 2017
Does this submission include an amendment request? Yes

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

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Location: Statewide

Total ENRTF Project Budget: \$291,000

ENRTF Appropriation: \$291,000

Amount Spent: \$291,000

Balance: \$0

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:

Over 40 water samples have been collected in collaboration with metro-area watershed districts and the MPCA and DNR. The samples include both wetland and stormwater runoff samples. All samples have been filter-sterilized. UV-vis absorbance spectra have been collected and some routine analyses have been completed on all samples. The EEM spectrofluorometer has been received and personnel have been trained on its use. Experimental protocols are being developed for chemical probes for steady-state concentrations of reactive intermediates. Finally, environmental box-models are being developed to predict the fate of organic pollutants in treatment wetlands designed to optimize photochemical transformation reactions.

Project Status as of July 1, 2015: Approximately 200 water samples have been collected and processed to date. Photolysis experiments are underway using 2,4,6-trimethylphenol (TMP) in wetland surface waters. These experiments are designed to assess the reactivity of excited triplet states of dissolved natural organic matter.

Project Status as of January 1, 2016: To date, 372 water samples (including stormwater, wetland surface water, and treated wastewater effluent) have been collected. Water chemistry analyses (including dissolved organic and inorganic carbon concentrations, anions, conductivity, and spectroscopic characterization) are underway or nearly complete. Excitation-emission matrix spectra have been collected on approximately 60 samples. Photolysis experiments are underway with a subset of samples using the molecular probe trans,trans-hexadienoic acid. These experiments are designed to assess the reactivity of excited triplet states of dissolved natural organic matter. This probe differs from 2,4,6-trimethylphenol in that it measures triplet states that undergo energy transfer processes instead of electron transfer reactions. TMP are also continuing.

Amendment Request (01/12/2016)

Because the requested fluorometer and supplies have been more costly than anticipated, funds from personnel in activity 1 (\$1,170) are being shifted to cover the overrun in the capital expenditure. Funds from maintenance and repair activity 2 (\$3,000) are being shifted to chemical supplies. This does not affect timelines or project goals. The shift from personnel costs is possible due to internal funding of an undergraduate.

Amendment Approved: January 14, 2016

Project Status as of July 1, 2016:

All water chemistry parameters (anions, pH, conductivity, dissolved organic and inorganic carbon) have been measured on the nearly 400 samples collected to date. Excitation-emission matrix spectra have been collected for all samples and we are in the preliminary stages of building a PARAFAC model. All photochemical experiments for triplet states of dissolved organic matter have been completed and a manuscript is under preparation. A list of samples to be sent for analysis by FTICR MS is being prepared. Finally, experiments examining the change in nitrogen and phosphate under solar irradiation are being conducted.

Project Status as of January 1, 2017:

We are in the process of validating a PARAFAC model for the collected stormwater samples. Once an adequate model has been validated, we will repeat the process with the collected wetland and wastewater samples. Stormwater samples have been analyzed by FTICRMS at the National High Magnetic Field Laboratory (NHMFL) at Florida State University. We have processed the data and are analyzing trends in photochemical properties. We are conducting photolysis experiments with the contaminant list below to determine the contribution of triplet states of dissolved natural organic matter to the photochemical loss of these contaminants. We are continuing to examine nitrogen processing in sunlight. 62 wastewater samples have been analyzed for anions, pH, conductivity, dissolved organic and inorganic carbons, as well as spectral properties analyzed using both UV-Vis and EEMS. 17 more samples are currently being analyzed. 2,4,6-trimethylphenol photolysis experiments have been completed on 62 wastewater samples and their triplet DOM production analyzed. Possible correlations between spectral and/or water chemistry properties with triplet production have been analyzed.

Overall Project Outcomes and Results:

Urban stormwater, agricultural runoff, and municipal wastewater effluent transport pesticides, pharmaceuticals, and other trace organic compounds to aquatic systems. Once in the environment, these compounds are considered pollutants because they may have adverse ecological effects on non-target organisms. Natural processes that transport and transform these compounds are critical in maintaining environmental concentrations below harmful levels. Chemical reactions initiated by sunlight, also called photochemical reactions, are particularly important in attenuating these pollutants because they have the capacity to degrade the pollutants into less harmful products. Dissolved natural organic matter (DOM) that originates from plants and algae is extremely important in controlling photochemical reactions because DOM absorbs most of the light in a water column and when DOM absorbs light, reactive species form (such as excited state molecules and radicals) that can promote pollutant degradation. The composition of DOM varies depending on the source and type of water system, and these compositional differences directly influence efficiencies of photochemical reactions. The objectives of this project were to relate the composition of DOM to the production of reactive species that are known to be important in pollutant degradation in surface waters and to use these relationships to develop prediction tools for sunlight-driven production of reactive species. Stormwater, wetland surface water, and municipal effluent samples were collected seasonally from Fall 2014 to Spring 2016 throughout the Minneapolis-St. Paul metro area and greater Minnesota. The efficiency of reactive species formation was experimentally measured using steady-state chemical probes, and the composition of DOM was assessed using absorbance and fluorescence spectrophotometries and high-resolution mass spectrometry. Trends show that DOM with low capacities to absorb light also have high efficiencies of reactive species formation. The relationship between reactive species formation efficiency and DOM composition appears to be highly influenced by the content of the DOM derived from plants. From this work, a model was developed to aid in the design of treatment wetlands with specific water residence times to achieve desired pollutant removal efficiencies via photochemical reactions. In addition, an empirical multiple linear regression model using landscape descriptors and DOM composition descriptors was developed to aid in the prediction of reactive species formation efficiencies on regional and global scales. Results from this project are included in a peer-reviewed publication, two presentations, and one poster submitted with this report.

Amendment Request (08/19/2017)

To complete the goals of the project and continue payment of personnel until the project end date, unused funds for travel and sampling were used for personnel in activities 1 and 2 and additional supplies in activity 2. This led to slight changes (<\$700) changes in the activity 1 and 2 overall budgets.

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 °C to minimize biological alteration.

Spectral characterization of the samples will be robust. Specific UV absorbance ($SUVA = UV_{254\text{ nm}}/DOC$) 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: \$ 148,388

Amount Spent: \$ 148,388

Balance: \$ 0

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	\$ 48,388

Activity Status as of January 1, 2015:

Approximately 40 water samples have been collected in collaboration with metro-area watershed districts as well as the Minnesota Pollution Control Agency and the Department of Natural Resources. These samples include both stormwater runoff samples and wetland surface water samples. All samples have been filter sterilized and some routine analyses have been performed (pH and conductivity/TDS). In addition, UV-vis absorbance spectra have been collected for all samples. In the coming weeks, routine analyses will be completed. In addition, the EEM fluorometer has been received and training has been completed.

Activity Status as of July 1, 2015:

Approximately 200 water samples have been collected and processed to date. Samples include stormflow, baseflow, snowmelt, wetland surface water, and wastewater effluent. Conductivity, pH, and UV-vis absorbance spectra have been measured for all samples. Anions, including nitrate, nitrite, and phosphate, have been measured on half the samples. Alkalinity measurements will be completed in the next three weeks. Total organic carbon and excitation emission matrix spectra will be completed in the coming weeks.

Activity Status as of January 1, 2016:

372 water samples (including stormwater, wetland surface water, and treated wastewater effluent) have been collected. Water chemistry analyses (including dissolved organic and inorganic carbon concentrations, anions, conductivity, and spectroscopic characterization) are underway or nearly complete. Excitation-emission matrix spectra (EEMs) have been collected on approximately 60 samples. Upon completion of EEMs characterization, a PARAFAC model will be constructed and select samples will undergo DOM extraction for NMR and high resolution mass spectroscopy analysis.

In addition, work is underway to characterize the land cover (e.g., percent impervious, agriculture, urban or suburban) of the watersheds from which stormwater samples have been collected. Once these analyses are complete, correspondences between land cover and DOM characteristics will be used to predict photochemical behavior of CECs based on watershed land use.

Activity Status as of July 1, 2016:

All water chemistry analyses (pH, DOC, alkalinity/inorganic carbon, conductivity, ion chromatography) have been completed on all samples collected. Excitation-emission matrix spectra have been collected on all samples and we are in the preliminary stages of building a PARAFAC model to identify the principle fluorescent components in our samples.

We are in the processes of submitting samples to the Florida State University's (FSU) National High Magnetic Field Laboratory for FTICR MS analysis. A subset of ~24 samples will initially be sent. Pending the results, we will determine if further samples should be sent for analysis. We decided to send samples to the FSU facility instead of Woods Hole because the FTICR instrument at Florida State is more powerful and because of the FSU has more competitive analysis costs.

Finally, watershed land cover, percent impervious, and percent tree canopy analyses are 95% complete. This data will be used to develop pollutant lifetime predictive tools for watershed managers.

Activity Status as of January 1, 2017

We are building and validating PARAFAC models for the collected stormwater, wetland surface water and wastewater samples. Dissolved organic matter was extracted using PPL SPE cartridges from 24 stormwater and analyzed at NHMFL in November 2016. Plans are underway to send wastewater and wetland samples for FTICR MS analysis, as well. Trends between DOM quality, land cover, and photochemical reactivity are being developed. Water chemistry analyses on wastewater samples collected in summer of 2016 has been completed and is underway for samples collected in fall 2016.

Final Report Summary:

In total, 186 stormwater samples (with 29 baseflow and 18 snowmelt samples), 113 wetland surface water samples, and 95 wastewater samples were collected from 85 sites. Dissolved organic matter composition and source was evaluated using three different techniques: (1) ultraviolet-visible (UV-vis) absorbance spectrophotometry, (2) fluorescence spectroscopy, and (3) high-resolution mass spectrometry. UV-vis absorbance and fluorescence spectroscopies give robust proxy information about DOM composition and source, whereas high-resolution mass spectrometry gives detailed molecular level information about DOM composition. Based on the proxy information derived from UV-vis absorbance and fluorescence spectroscopies, several trends were observed:

- DOM from watersheds with relatively large open water systems, such as lakes or wetlands with unconsolidated bottoms, tended to have low molecular weight and low aromaticity;
- The samples from watershed with high intensity development and open water compared to samples from vegetated watersheds tended to have high content of algae-derived and recently produced organic matter;
- Samples from highly vegetated watersheds tended to have DOM with a higher content of soil organic matter (often described as *humified* organic matter) in comparison to samples from watersheds with high development and open water;
- Wastewater samples contained DOM with high microbial content with moderate to moderately-low molecular weight and aromaticity;
- DOM with low molecular weight, low aromaticity, and high content of algae-derived DOM tended to have low rates of light absorption;

High resolution mass spectrometry was performed on a subset of 21 stormwater and 2 baseflow samples. From this analysis, we observed that samples from high and low intensity developed watersheds have a higher content of biologically labile molecular compositions (5–19%) compared to samples from watersheds with high vegetation and open water (2–6%). Samples from developed watersheds were enriched in aliphatics and unsaturated compositions, samples from both vegetated and developed watersheds were enriched in polyphenolic and polyaromatic compositions (such as combustion derived aromatic compounds), and samples from watersheds dominated by open water were enriched in aliphatic compositions. We are continuing work to analyze treated wastewater effluent samples using high-resolution mass spectrometry.

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 ($^3\text{OM}^*$), but will also measure the downstream products $\cdot\text{OH}$, $^1\text{O}_2$, and $\text{CO}_3^{\cdot-}$, when necessary. Because the DOM composition is likely to vary from site to site and because $^3\text{OM}^*$ is particularly important for contaminant transformation and generation of other PPRI, 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 $\cdot\text{OH}$ 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 $\cdot\text{OH}$ is not expected to be the dominant indirect photolysis pathway. Should nitrate be found to be a major contributor of $\cdot\text{OH}$, 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 PPRI 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 $[\text{PPRI}]_{\text{ss}}$ 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 $\leq 10 \mu\text{M}$ 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 PPRI 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: \$ 110,612
Amount Spent: \$ 110,612
Balance: \$ 0

Activity Completion Date:

Outcome	Completion Date	Budget
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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	\$ 30,612
4. Determine pharmaceutical removal rates in the waters collected in Activity 1	6/30/16	\$ 30,000

Activity Status as of January 1, 2015:

Work on this activity has focused on developing 2,4,6-trimethylphenol (TMP) into a quantitative probe for the steady-state concentration of triplet excited state natural organic matter that undergoes charge-transfer reactions. An analytical HPLC method has been developed. In the coming weeks, preliminary experiments will be performed to measure the half-life of TMP in collected water samples and assess the involvement of other reactive intermediates (hydroxyl radical, singlet oxygen, and carbonate radical) in the observed loss of TMP.

Activity Status as of July 1, 2015:

Photolysis experiments have been conducted using 2,4,6-trimethylphenol (TMP) in wetland surface waters. These experiments are designed to assess the reactivity of excited triplet states of dissolved natural organic matter. Trends are being developed between organic matter quality (assessed with UV-vis absorbance spectroscopy) and reactivity of excited triplet states.

In addition, experiments using model triplet photosensitizers and phenol quenchers are being conducted for two reasons: (1) ensure our photosimulator produces similar trends as those reported in the literature and (2) estimate a second order rate constant for the reaction between excited triplet states and TMP.

Activity Status as of January 1, 2016:

We are continuing experiments with the TMP probe. Photolysis experiments are also underway with a subset of samples using the molecular probe trans,trans-hexadienoic acid. These experiments are designed to assess the reactivity of excited triplet states of dissolved natural organic matter. This probe differs from 2,4,6-trimethylphenol in that it measures triplet states that undergo energy transfer processes instead of electron transfer reactions.

In addition, we plan to revise the original list of CECs to prioritize contaminants that are expected to have notably different photoreactivity with DOM collected from the different source waters. Specifically, we plan to conduct photochemical experiments with multiple contaminants in *selected water samples* that vary widely in reactive species production and conduct experiments with *selected contaminants* that react predominantly via a specific pathway in a broad range collected water samples. The specific matrix will be developed and begun in the next reporting period as the data from the TMP and trans,trans-hexadienoic acid is collected.

Activity Status as of July 1, 2016:

We have narrowed our list of pollutants to focus on those that are anticipated to be found in agricultural and urban stormwater and wastewater effluent that will have reactivity with ³OM*:

Agriculture: Acetochlor, Mesotrione, Isoproturon, Genistein (plant hormone), Estrone (hormone)

Wastewater: Sulfamethoxazole, Carbamazepine, Propranolol

Urban: Prometon (industrial/right-of-way), 2,4-D (lawn), Mecoprop (lawn)

We have concluded our experiments with the probes for excited triplet states of dissolved organic matter (³OM*), 2,4,6-trimethylphenol and trans,trans-hexadienoic acid. We also developed a novel method to measure the second order rate constants for reaction between ³OM* and target pollutants using competition kinetics.

We are in the preliminary stages of writing the manuscript for this data. In the coming weeks we plan to apply this novel competition kinetics method to other pollutants listed above.

Finally, experiments are underway to understand the speciation of nitrogen under solar irradiation. To do this, we have developed and adapted analytical methods to accurately measure nitrate, nitrite, ammonium, and dissolved organic nitrogen. Our preliminary experiments showed us that there is some production of ammonium under solar irradiation and possibly some loss of total nitrogen. The process of ammonium production is known as photoammonification and we are conducting follow-up studies to determine which pool of nitrogen contributes to ammonium production.

Activity Status as of January 1, 2017

We are currently conducting photolysis experiments with the contaminants listed above under Activity Status as of July 1, 2016. 2,4,6-trimethylphenol and trans,trans-hexadienoic acid are being used as traps for excited triplet states of dissolved organic matter ($^3\text{DOM}^*$) to determine the relative contribution of $^3\text{DOM}^*$ to the overall photochemical loss of the contaminants. Additionally, experiments are being conducted with the model ketone triplet sensitizer, 4-carboxybenzophenone, to determine (1) if bimolecular rate constants between the contaminants and $^3\text{DOM}^*$ or 4-carboxybenzophenone agree, and (2) to determine the capacity of the natural DOM to act as an antioxidant, inhibiting triplet sensitized oxidation of the contaminants.

We are continuing experiments to understand the speciation of nitrogen under solar irradiation. Preliminary experiments showed there is production of ammonium under solar irradiation and possibly some loss of total nitrogen. Long-term, outdoor (~days to weeks) follow-up studies showed that photoammonification does occur in addition to increasing in total dissolved nitrogen, primarily dissolved organic nitrogen. This suggests that nitrogen fixation (e.g., by cyanobacteria) is possible in these systems. The relevance of this process has yet to be determined because literature sources suggest that denitrification also occurs in constructed photolysis wetlands. Short-term (hours) follow-up studies using a solar simulator will be conducted to minimize potential growth of cyanobacteria and examine only the light-driven processes.

Final Report Summary:

We measured the rate of triplet excited state of dissolved natural organic matter ($^3\text{DOM}^*$) formation in all collected water samples using the electron-transfer probe, 2,4,6-trimethylphenol (TMP). $^3\text{DOM}^*$ is arguably one of the most important reactive species formed in sunlit surface waters because it reacts at near-diffusion controlled rates with several organic pollutants and it forms secondary reactive species, such as singlet oxygen. We observed a direct link between the concentration of dissolved organic carbon and the rates of both light absorption and formation of $^3\text{DOM}^*$. In contrast, the efficiency of $^3\text{DOM}^*$ formation was independent of DOC concentration. In stormwater, the efficiency of $^3\text{DOM}^*$ varied with DOM source: developed land cover (4 – 6%) \approx open water > vegetated land cover (3%). In wetland surface water, relatively high efficiencies of $^3\text{DOM}^*$ formation ($\sim 7\%$) were observed in wetlands with long hydroperiods and >50% cropland watershed land cover as compared to wetlands with >50% vegetative watershed land cover (<1%–4%). In treated wastewater effluent, the average efficiency of $^3\text{DOM}^*$ formation was moderate ($\sim 4\%$) and no consistent trends were observed with the specific treatment train. In relation to DOM composition and source, the efficiency of $^3\text{DOM}^*$ formation was positively related to an index for microbial/algal DOM content and negatively related to DOM molecular weight, DOM aromaticity, and the content of polyphenols (plant-derived structural molecules). The outcomes of this work demonstrated that TMP is an effective probe for the determination of the rate and efficiency of $^3\text{DOM}^*$ formation in whole water samples.

To date, we have measured the photochemical transformation rates of isoproturon (herbicide), genistein (plant hormone), estrone (animal hormone), and pyraclostrobin (fungicide; included in initial proposal). Based on sensitizer and quencher experiments, the phototransformations of isoproturon and genistein appear to be dominated by reactions with $^3\text{DOM}^*$ (second order rate constants $2.8(\pm 0.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $1.3(\pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively). In contrast, the photodegradation of estrone and pyraclostrobin largely proceed through direct

photolysis mechanisms. The half-lives of these compounds under midday sunlight are approximately 60 min and 5 min, respectively. Because the quencher experiments that we had proposed yielded complicated and unexpected results and because the analyses of DOM composition that we proposed were far more involved than we anticipated, we are continuing work to assess the contribution of ³DOM* to the phototransformation rates of the other compounds.

Inorganic nitrogen in the form of ammonium is released upon UVA and UVB light exposure. In a subset of stormwater samples, we have quantified both the initial rate of ammonium released (that is, the concentration of ammonium released per time or unit light dose) and the capacity of the samples to release inorganic nitrogen (that is, the fraction of organic nitrogen that is photochemically available). The initial rate of ammonium production was estimated to be 4.2(±2.0) µg-N L⁻¹ h⁻¹ in the solar simulator, which is 13.5(±6.5) µg-N m² L⁻¹ MJ⁻¹ in per unit UVA+UVB light dose. From 72-h exposure experiments, it was estimated that 23% of the organic nitrogen is photochemically available. No detectable change was observed in the inorganic phosphorous (orthophosphate) concentration during these experiments. Currently we are seeking additional funding opportunities to understand if the photochemically-released ammonium is more biologically available than the precursor organic nitrogen moieties and to understand molecular-level composition of the photochemically labile organic nitrogen.

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: \$ 32,000
Balance: \$ 0

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:

Effort is being made to develop appropriate models for stormwater detention ponds and treatment wetlands to achieve water quality and pollutant level goals. A literature review has revealed that there are few examples of the phototransformation rates of organic contaminants in stormwater detention ponds or wetlands. There is evidence, however, that treatment wetlands designed to treat municipal wastewater operates under a plug-flow type reactor.

Activity Status as of July 1, 2015: Further progress on this activity is awaiting additional experimental data.

Activity Status as of January 1, 2016: Further progress on this activity is awaiting additional experimental data.

Activity Status as of July 1, 2016: We are actively trying to identify a modeling platform that would be amenable to integration of our photochemical parameters as well as useful to watershed managers throughout Minnesota. The EPA maintained program, AquaTox with the GIS-based extension BASINS, has been identified as a potential candidate.

Activity Status as of January 1, 2017

We are continuing to identify a modeling platform. An alternative program maintained by the EPA, EXAMS (Exposure Analysis Modeling System), is a potential candidate. It has been applied in the literature to simulate the impact of sensitized photolysis of contaminants (e.g., pesticides) in the literature.

Our intent is you use EXAMS to determine depth and hydraulic retention times necessary to achieve desired dissipation (e.g., 90 % influent concentration) and pair this with a simple plug-flow/contactor type reactor model to determine design specifications (depth and area requirements) to achieve dissipation.

Final Report Summary:

Our initial intent in fulfilling the objectives of this portion of the project was to use an existing pollutant modeling platform (see previous activity status reports above) to estimate half-lives of the pollutants with the inclusion of photochemical reactions and other loss process, for example, sorption to particles or biological transformation. The challenge with sunlight-driven photochemical reactions, however, is that rates continuously change with sunlight conditions. Seasonal changes, diurnal cycling, and cloud cover all influence sunlight intensity at the Earth's surface. Because existing modeling platforms cannot account this high-frequency variation in rate constants, we wrote a simple program in MATLAB (Mathworks, Natick, MA) that numerically estimates the change in concentration of a pollutant through a treatment wetland over a user-defined period of time assuming the only loss mechanism is through a reaction with photochemically-produced triplet excited states of dissolved organic matter. The wetland is treated as a series of completely mixed flow reactors, and at each discreet time step, a new reaction rate constant is calculated to account for the change in sunlight conditions over a 24-h period. As the program stands, the user defines the water residence time and the number of tank-in-series and the effluent concentration of the pollutant is estimated. Future improvements to the model will include an alternative version where the user can define a desired treatment efficiency (90% removal, for example) and a characteristic water residence time will be computed as well as to implement ways to assess the impact of variable depths on the treatment efficiency given a specific wetland area. The MATLAB program was submitted with this report.

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:

Further work on activities 1 through 3 is required prior to disseminating results or completing manuals on treatment wetlands.

Status as of July 1, 2015:

Further work on activities 1 through 3 is required prior to disseminating results or completing manuals on treatment wetlands. Results of experiments using the probe 2,4,6-trimethylphenol in wetland surface water to probe reactivity of excited triplet state organic matter have been presented at an undergraduate research symposium at the University of Minnesota.

Status as of January 1, 2016: Further work on activities 1 through 3 is required prior to disseminating results or completing manuals on treatment wetlands.

Status as of July 1, 2016: A manuscript presenting the results of results assessing the formation of triplet excited states of dissolved natural organic matter is under preparation for submission to a peer-reviewed journal. In addition, an abstract has been submitted to present results at the Minnesota Water Resources Conference.

Status as of January 1, 2017

Two manuscripts (one for the results of the stormwater analysis and one for the wetland analysis) are under preparation for submission to peer-reviewed journals. Two poster presentations have been given, one at the 2016 Minnesota Water Resources Conference and one at the 2016 CSWEA Conference on the Environment. In addition, abstracts have been submitted for presentation at the 253rd American Chemical Society National Meeting.

Final Report Summary:

This work has been presented at two sessions of the 253rd American Chemical Society in March 2017. This work has also been presented at poster sessions of the Minnesota Water Resources Conference (October 2016), the Conference on the Environment (November 2016), and the Year of Water Action Forum (March 2017). One manuscript presenting the results of this work has been accepted for publication in the journal *Environmental Science and Technology* (July 2017) and additional manuscripts are in preparation.

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 university 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 Equivalent (FTE) Directly Funded with this ENRTF Appropriation: 2.0

Number of Full-time Equivalent (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	\$ 110,000	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:	\$ 110,000	\$ 110,000	

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: August 4, 2017

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Revised Activity 1 Budget 8/4/17	Amount Spent	Activity 1 Balance	Activity 2 Budget	Revised Activity 2 Budget 8/4/17	Amount Spent	Activity 2 Balance	Activity 3 Budget	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM									Produce design guidelines for pollutant				
Personnel (Wages and Benefits)	\$93,830	\$96,024	\$96,024	\$0	\$95,000	\$96,023	\$96,023	\$0	\$32,000	\$32,000	\$0	\$224,047	\$0
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 evaluations, 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	\$10,000	\$10,000	\$0	\$9,000	\$11,589	\$11,589	\$0				\$21,589	\$0
Maintenance and repair of liquid and gas chromatographs and solar simulator required for analyses and experiments					\$3,000	\$3,000	\$3,000	\$0				\$3,000	\$0
Capital Expenditures Over \$5,000													
Horiba Aqualog benchtop fluorometer for organic matter characterization.	\$41,170	\$41,170	\$41,170	\$0								\$41,170	\$0
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	\$1,194	\$1,194	\$0	\$2,000	\$0	\$0	\$0				\$1,194	\$0
Other													
Shipping costs for samples collected by others.	\$1,000	\$0	\$0	\$0	\$1,000	\$0	\$0	\$0				\$0	\$0
COLUMN TOTAL	\$149,000	\$148,388	\$148,388	\$0	\$110,000	\$110,612	\$110,612	\$0	\$32,000	\$32,000	\$0	\$291,000	\$0

Sunlight-driven transformation of contaminants of emerging concern in stormwater

Andrew J. McCabe and William A. Arnold

University of Minnesota, Department of Civil, Environmental, and Geo- Engineering, 500 Pillsbury Drive SE, Minneapolis MN 55455

Why are we studying this?

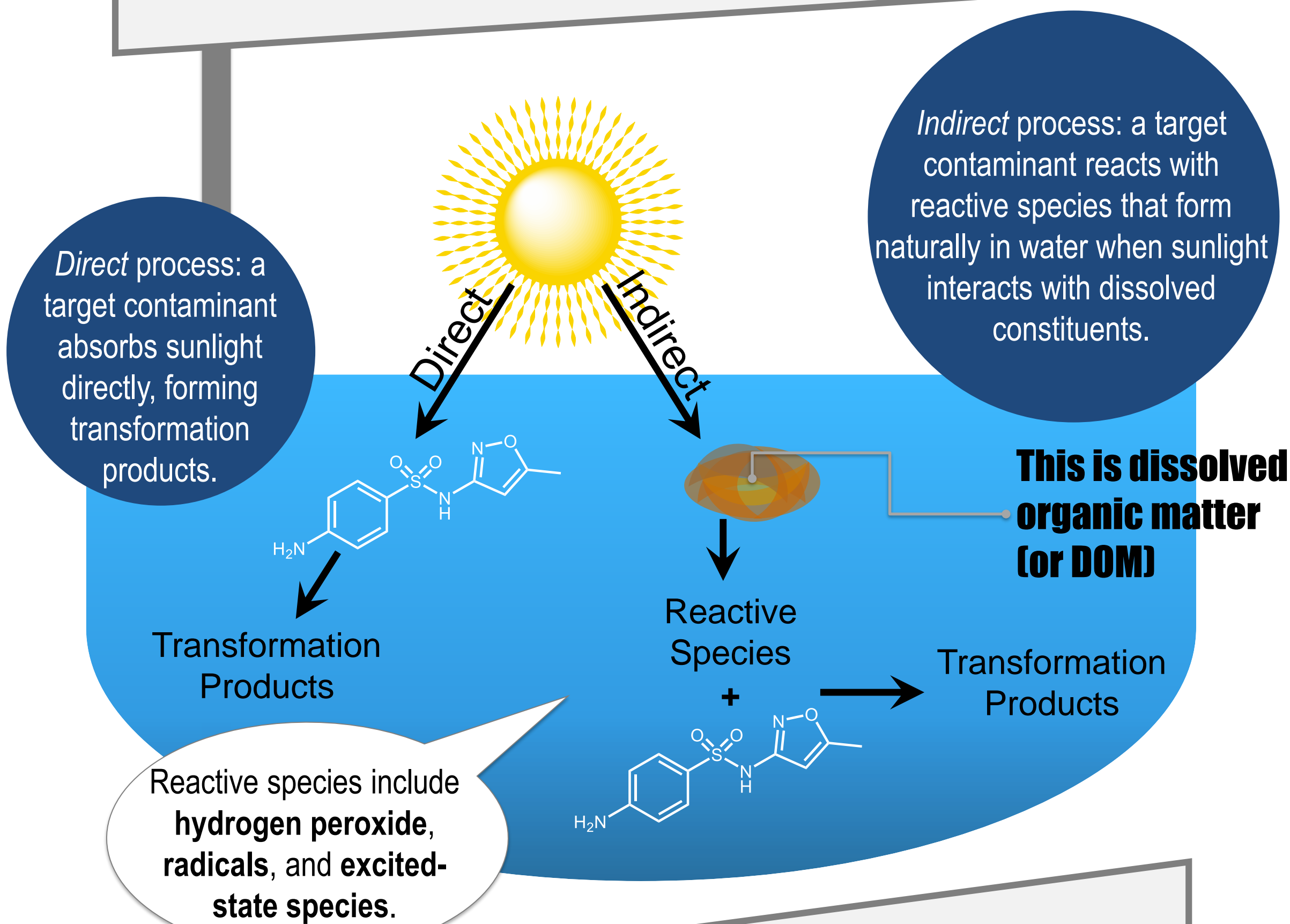
- (1) Stormwater **transports** contaminants of emerging concern (CECs) to surface water bodies.
- (2) Many contaminants that do not sorb to particles can be transported **long distances**.
- (3) Sunlight-driven transformation processes are important in **controlling CEC fate**.

CECs are defined here as trace organic contaminants, such as pesticides, pharmaceuticals, and endocrine disruptors.

Can we design a treatment pond that takes advantage of sunlight-driven transformation processes to lower downstream loads of CECs?

What are sunlight-driven transformation processes?

Physical and chemical processes that occur when sunlight interacts with dissolved constituents in natural and engineered water bodies. They are broadly classified as *direct* and *indirect* processes.



Dissolved organic matter (or DOM) is a major water constituent that controls the rate and efficiencies of *direct* and *indirect* processes:

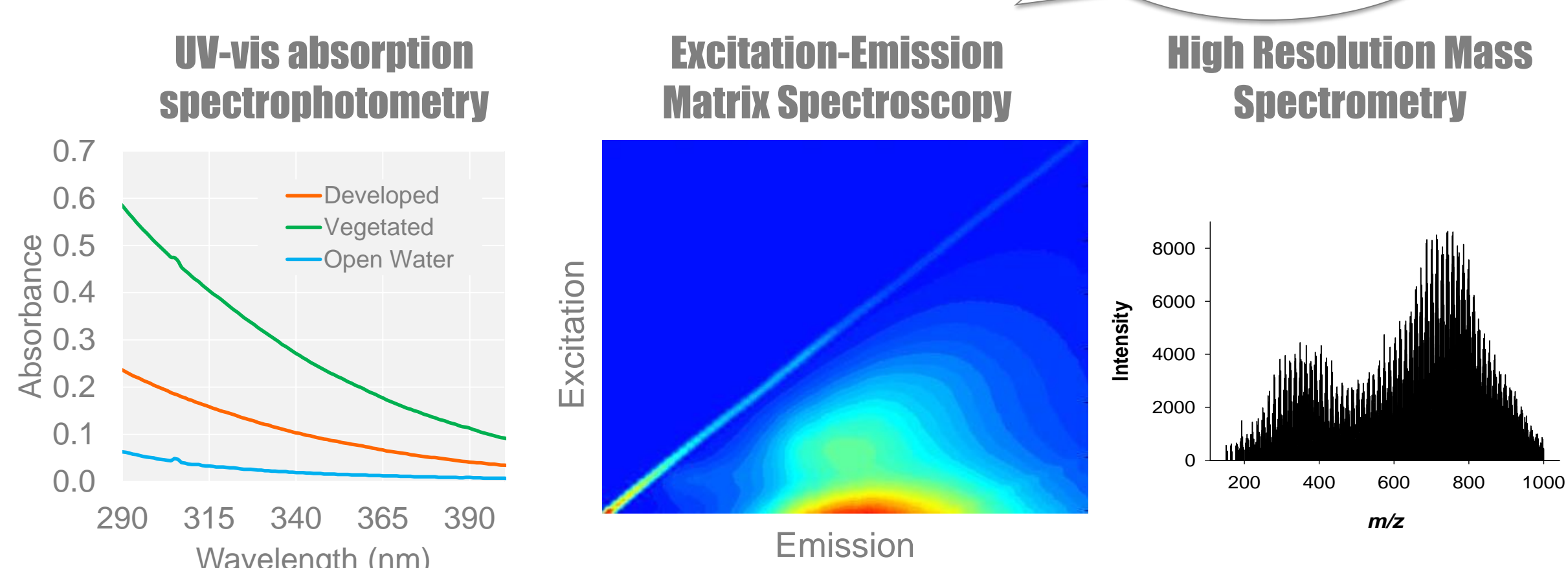
- (1) In direct processes, DOM acts as a screen, blocking light from reaching CECs;
- (2) In indirect processes, DOM acts as a sensitizer, forming reactive species that can transform CECs.

The excited state of DOM (T^*) is an especially important reactive species because it reacts with CECs and forms other reactive species.

What is Dissolved Organic Matter?

It is a heterogeneous mixture of organic material that originates from living cells (e.g., exudates) or the degradation of plant and microbial cells. Its composition can change depending on *land cover* and other environmental parameters.

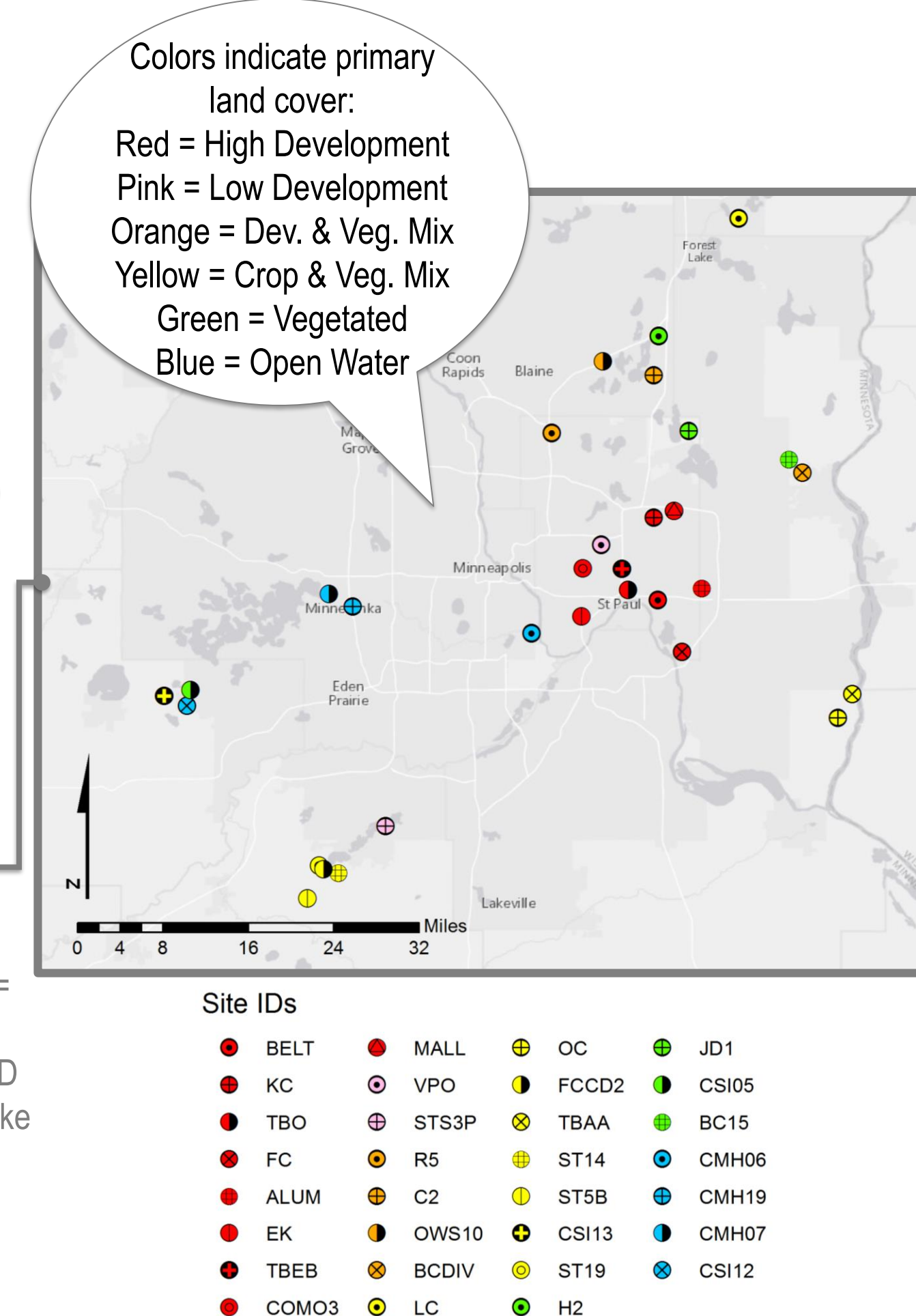
There are several ways to characterize DOM. Each method gives different information.



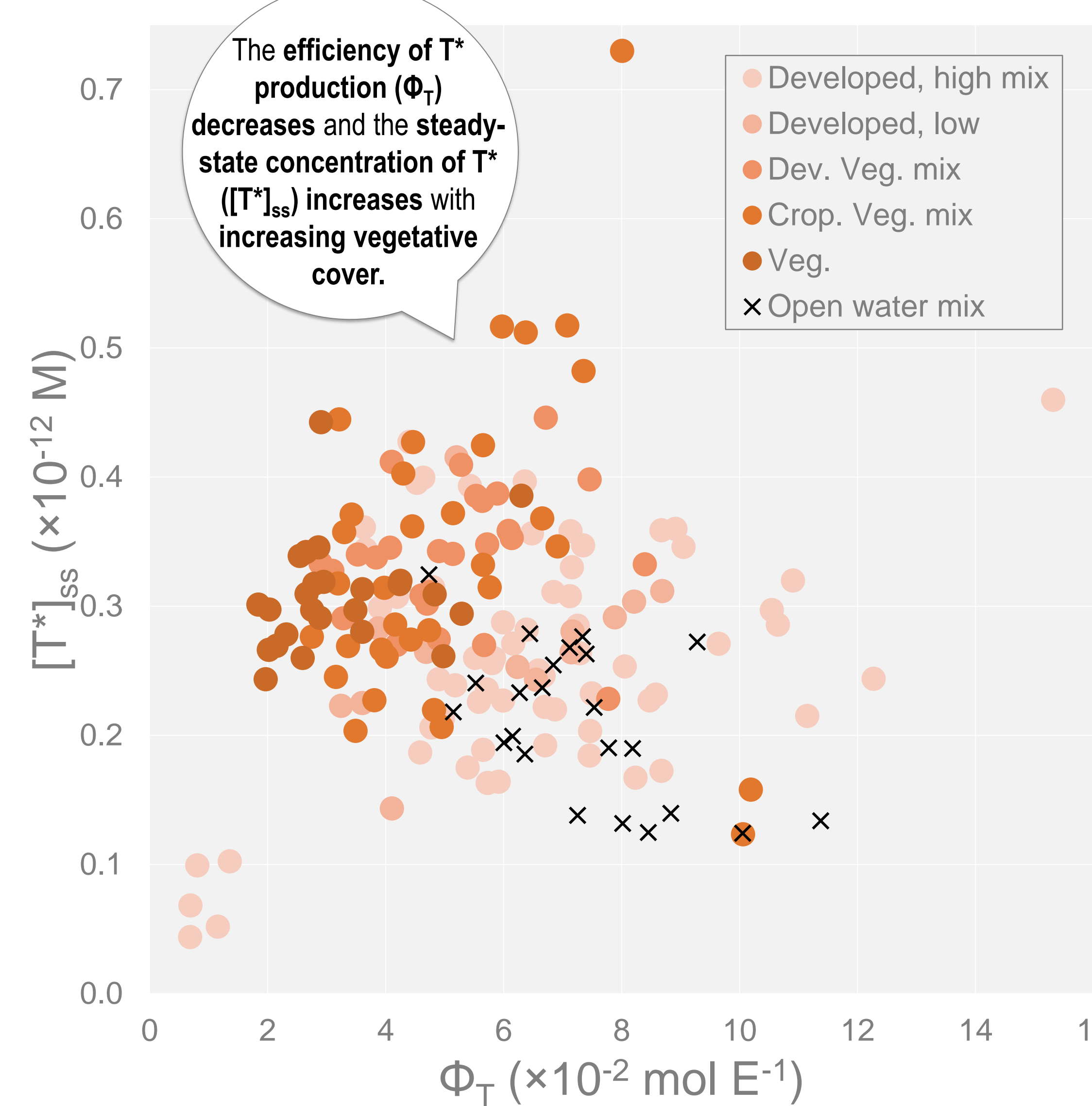
Study design:

We partnered with CRWD, MCWD, RWMWD, RCWD, PLSLWD, and WCD to collect **185 stormwater samples**.

Abbreviations:
CRWD = Capital Region Watershed District; MCWD = Minnehaha Creek Watershed District; RWMWD = Ramsey Washington Metro Watershed District; RCWD = Rice Creek Watershed District; PLSLWD = Prior Lake Spring Lake Watershed District; WCD = Washington Conservation District



What we have found:



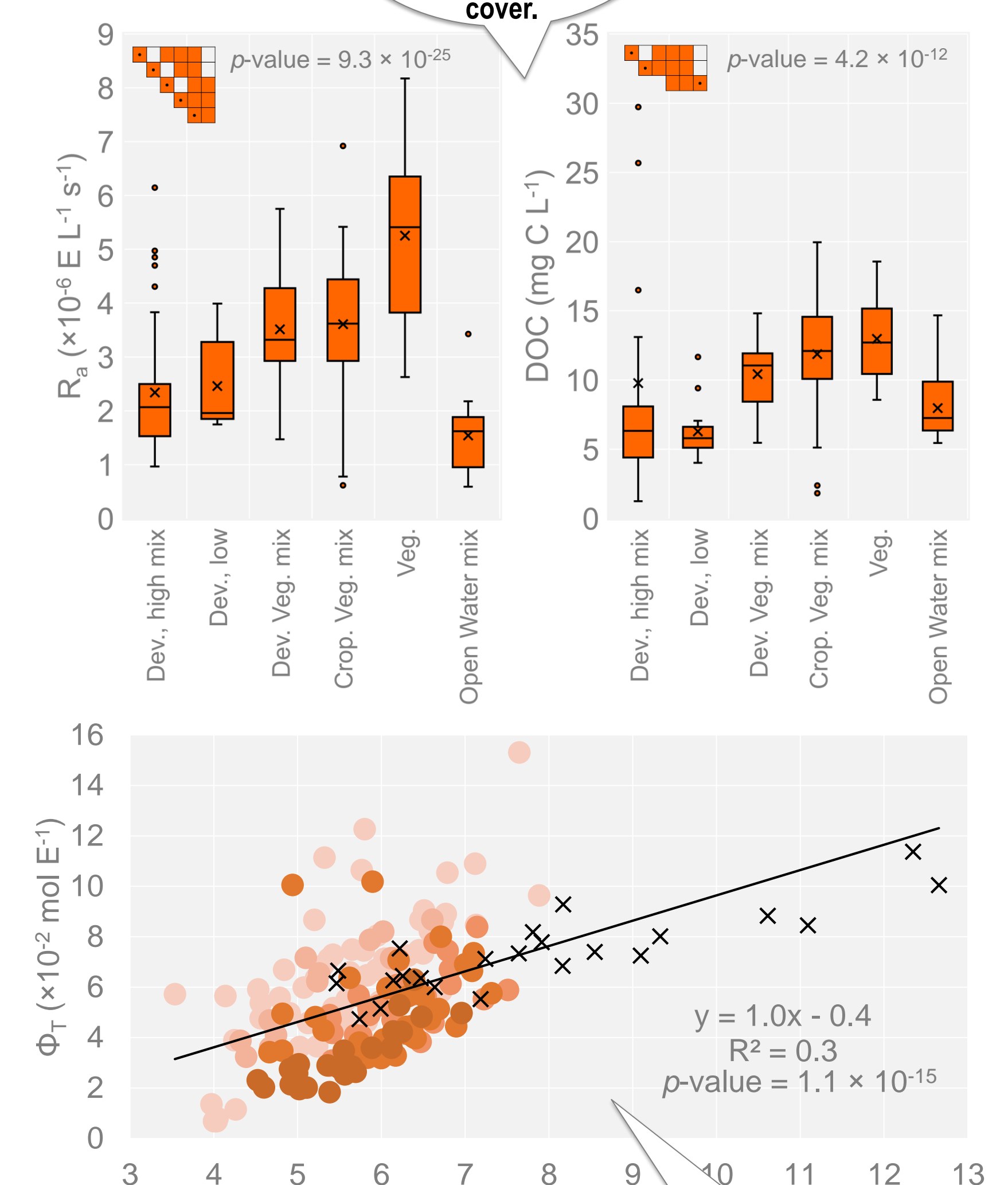
What we measured:

- (1) R_a = the rate at which DOM absorbs sunlight.
- (2) $[T^*]_{ss}$ = the steady-state concentration of the reactive species, T^* (just like water flowing into and out of a tank).
- (3) Φ_T = the efficiency with which the reactive species, T^* , is formed.

$$r_{CEC} \sim \frac{\alpha}{R_a} \times k_{dir} + k_{T^*} \times [T^*]_{ss}$$

Because DOM controls sunlight-driven transformation processes of CECs, we characterized 3 important variables of the stormwater DOM.

Both the rate of light absorption (R_a) and dissolved organic carbon (DOC) increase with increasing vegetative cover.



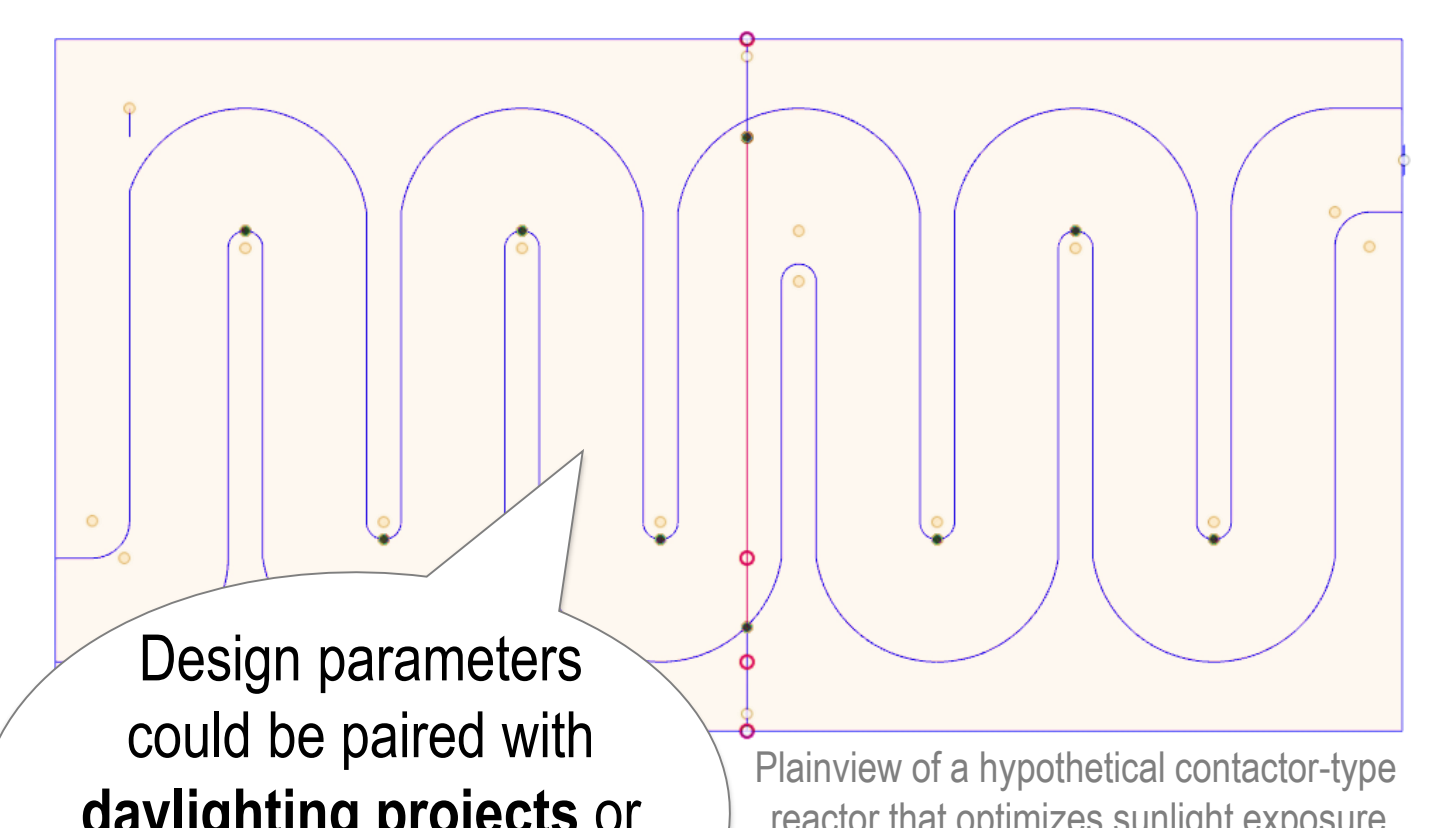
The efficiency of T^* production (Φ_T) increases with $E2/E3$, a proxy for the degree of DOM photobleaching.

Key findings:

- (1) Watersheds with highly vegetated land cover have high concentrations of DOC, resulting in high $[T^*]_{ss}$. This will increase rates of *indirect* transformation processes.
- (2) Watersheds with highly vegetated land cover will also have relatively high R_a . This will slow down rates of *direct* transformation processes.

How this information can be used:

Given site-specific characteristics and CEC-specific transformation rates, a treatment pond that optimizes sunlight exposure can be designed.



$$\tau = V/Q \quad c = c_0 e^{-k(V/Q)}$$

Further Reading

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Zepp, R.G.; et al. *Environ. Sci. Technol.* **1985**, 19, 74.

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