Primary results from the design and validation of an LED-based photochemical reactor

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Project
» EAGER: Development of a Prototype Sensor Package to Quantify In-Situ Rates of Aquatic Carbon Cycling Processes (Carbon Cycling Rate Sensor)

Contributors	Affiliation	Role
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Abstract
This dataset provides the primary results from the design and validation of an LED-based photochemical reactor presented in Ward et al., 2021 (doi: 10.1021/acs.estlett.1c00172).

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Coverage

Temporal Extent: 2018 - 2021

Methods & Sampling

All methods are described in Ward et al., 2021. A summary is provided below. This study was conducted in the Ward Lab at Woods Hole Oceanographic Institution in Woods Hole, MA, USA between 2018 and 2021.

Description of the LED Reactor Assembly:
Each LED reactor is comprised of an inner housing, containing the samples, and an outer housing, on which is affixed an LED chip. On top of the outer housing is a washer that provides the base for the LED chips, which are mounted to a printed circuit board and a heat sink. Passive cooling by the heat sink is sufficient to maintain the samples at room temperature, 22 ± 1 °Celsius, without any additional cooling. The LED chips face down toward the inner housing which contains four quartz tubes. The inner housing is machined specifically for the dimensions of the tubes but can accommodate a variety of reaction vessel shapes and sizes depending on the reaction of interest. Both housings are painted black matte to minimize light scattering and to decrease stray light in the laboratory. A separate power supply is used for each reactor.

Spectroradiometry and Chemical Actinometry:
Spectral irradiance measurements in all reactors were made with a NIST-calibrated Black Comet spectroradiometer equipped with a cosine corrector (StellarNet Inc.). Chemical actinometry was assessed in the 309, 348, 369, and 406 nanometer (nm) reactors by measuring the hydroxylation of benzoic acid to salicylic acid in the presence of nitrite. Actinometry was not assessed in the 275 nm reactor because the apparent quantum yield (AQY) of salicylic acid production has not been reported at that wavelength. Salicylic

acid production was quantified fluorometrically using an Aqualog (Horiba Scientific).

Photochemical Oxidation Experiments:
Photochemical oxidation (dissolved O_2 consumption) experiments were conducted as an example test of the LED reactors' long-term precision in measuring AQY spectra and oxidation rates. These experiments used Suwannee River natural organic matter (SROM; 2R101N) acquired from the International Humic Substances Society (http://humic-substances.org/). In total, six experiments were conducted over a six-month period using four replicate solutions of SROM. Triplicate experiments were conducted for one SROM solution on three consecutive days (referred to as experiments 2a, 2b, and 2c). The coefficient of variation (CV) of photochemical oxidation rates was 11%.

Before each experiment, solutions of SROM were prepared in Milli-Q water (Millipore) at a concentration of 20 milligrams (mg) SROM per liter (L) (~10 mg C L^{-1}). The solutions were adjusted to pH 7.0 ± 0.1 and allowed to equilibrate on a stir-plate for 24 hours prior to filtration with a 0.2 micrometer (µm) Sterivex filter (Millipore). SROM was then transferred to Milli-Q rinsed quartz tubes (15 millimeter (mm) outer diameter, 100 mm length; Technical Glass Products, Inc.) and sealed with a Viton-lined GL-18 cap with no headspace. The tubes were placed vertically in the inner housing with the flat bottom facing the LED. To minimize the impact of photon dose-dependence (i.e., the change in AQY as the samples absorb more light over time), we adjusted the emission intensity of the LEDs via the power supplies such that the moles of photons absorbed by SROM under all LEDs were equal within 5% (Figure 2b and Table S2 of Ward et al. (2021)). The total number of moles of photons absorbed by SROM was calculated by multiplying rates of light absorption (Q_a; mol photons m^{-2} s^{-1}, determined via equation 1 of Ward et al. (2021)) by the exposed surface area of the quartz tubes (1.1 cm^2) and the time of the light exposure (43,200 seconds).

The incident photon spectral irradiance reaching the quartz tube (mol photon m^{-2} s^{-1} nm^{-1}) is determined with 1-nm resolution and the summation is performed with 1-nm increments across the relevant wavelengths for each LED (e.g., 332 to 376 nm for the 348 nm LED). Naperian absorption coefficients of SROM (m^{-1}) were measured using a Perkin Elmer 650 spectrophotometer and calculated as the geometric mean of the light-exposed and dark control treatments to account for photo-bleaching, which was minimal in all experiments (< 5%). The pathlength (z) was 10 cm, equivalent to the height of each vial. Photochemical O_2 consumption was calculated as the concentration of dissolved O_2 in the dark-control tubes minus that in the light-exposed tubes using membrane inlet mass spectrometry (Bay Instruments, Inc.).

Apparent Quantum Yields:
Apparent quantum yields (AQYs) for the photochemical oxidation of SROM (mol O2 mol $photons^{-1}$) were calculated for each tube in each LED reactor by dividing the moles of O_2 consumed by SROM by the moles of photons absorbed by SROM. The AQY data were fit to an exponential curve with 1-nm increments.

Data Processing Description

Data Processing:
All data processing is described in the methods summary above and was conducted using Microsoft Excel.

BCO-DMO Processing:
- replaced "-" with "nd" ("no data");
- re-organized data into one table;
- added column for Experiment ID number;
- added new columns for Replicate and AQY.

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Related Publications

Ward, C. P., Bowen, J. C., Freeman, D. H., & Sharpless, C. M. (2021). Rapid and Reproducible Characterization of the Wavelength Dependence of Aquatic Photochemical Reactions Using Light-Emitting Diodes. Environmental Science & Technology Letters, 8(5), 437–442. https://doi.org/10.1021/acs.estlett.1c00172
Results

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Parameters

Parameter	Description	Units
Experiment	Experiment ID number	unitless
Wavelength	Wavelength	nanonmoles (nm)
Replicate	Replicate number	unitless
AQY	Apparent quantum yield	mmol O2 mol photon-1

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Instruments

Dataset-specific Instrument Name	Membrane inlet mass spectrometer (Bay Instruments, Inc.)
Generic Instrument Name	Membrane Inlet Mass Spectrometer
Generic Instrument Description	Membrane-introduction mass spectrometry (MIMS) is a method of introducing analytes into the mass spectrometer's vacuum chamber via a semipermeable membrane.

Dataset-specific Instrument Name	Aqualog (Horiba Scientific)
Generic Instrument Name	Spectrometer
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	Perkin Elmer 650 spectrophotometer
Generic Instrument Name	Spectrophotometer
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Dataset-specific Instrument Name	Black Comet spectroradiometer
Generic Instrument Name	Spectroradiometer
Dataset-specific Description	Black Comet spectroradiometer equipped with a cosine corrector (StellarNet Inc.)
Generic Instrument Description	A Spectroradiometer or Spectraradiometer is an instrument that measures the intensity and nature of electromagnetic radiation. An ocean color radiometer makes the measurements in a manner optimized for the determination of ocean chlorophyll concentration.

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Project Information

EAGER: Development of a Prototype Sensor Package to Quantify In-Situ Rates of Aquatic Carbon Cycling Processes (Carbon Cycling Rate Sensor)

Coverage: Woods Hole, MA

NSF Award Abstract:
In this project the researchers plan to develop a novel, new sensor package capable of measuring rates of aquatic carbon cycling. In the coastal and open ocean, rates of carbon cycling processes are not completely understood. This project will pave the way for future full-scale development of the sensor package that could substantially improve our confidence in the marine carbon cycle measurements and predictions for how the ocean may respond to human stressors in the future. The proposed work will advance the careers of two early career scientists. In addition, they plan to recruit undergraduate students through the Woods Hole Oceanographic Institution Summer Student Fellow Program, the semester at WHOI program, and the Woods Hole Partnership Program

The PIs will develop a prototype sensor package to resolve technical challenges and conduct preliminary tests of the quantification of photosynthesis rates, bacterial respiration rates and quotients, and photochemical oxidation rates and quotients. The focus of this EAGER proposal will be on overcoming critical technical challenges in order to develop this prototype. The development work proposed will pave the road for future development and testing of a full-scale, deployable in-situ device. If successful they will develop a prototype of a first of its kind to sensing system to simultaneously measure the in-situ rates of photosynthesis, microbial respiration, and photochemical oxidation in any surface water. The risk areas are in the pumping and plumbing systems and mitigation of biofouling. They have been working on a number of ways to resolve these issues but will have to do a lot of testing to see what works best.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1841092

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