Fluorescence spectra from exudation experiments in outdoor tanks with Sargassum samples collected off the coast of Bermuda and in the Sargasso Sea in 2016

Website: https://www.bco-dmo.org/dataset/938831
Version: 1
Version Date: 2024-09-25

Project
» Collaborative Research: Phlorotannins - An Important Source of Marine Chromophoric Dissolved Organic Matter? (Sargassum DOM)

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Abstract
Fluorescence spectra from exudation experiments in outdoor tanks with Sargassum samples collected aboard the R/V Henry Stommel off the coast of Bermuda and R/V Hugh.R. Sharp in the Sargasso Sea in 2016. This dataset includes formula assignments for outdoor exudation experiments under natural (sunlight) conditions (n = 4). These data were published in Powers et al. (2019).

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Coverage

Location: Bermuda and Sargasso Sea
Temporal Extent: 2016-06 - 2016-09

Dataset Description

See "Related Datasets" section for other datasets from these exudation experiments.

Methods & Sampling

Sargassum (urn:lsid:marinespecies.org:taxname:144132) was collected during two sampling events in July and in late September/early October 2016, described in detail in a previous study (Powers et al., 2019, Global Biogeochemical Sciences (GBC), *33*(11), 1423-1439). *Sargassum* samples were collected using a hand-held net aboard the R/V *Sharp* in the Sargasso Sea during July 2016 for controlled laboratory exudation experiments. *Sargassum* was housed onboard in a tank (<3 days) with continuously flowing seawater and transported back to the Chesapeake Biological Laboratory (CBL) immediately upon return to another tank with filtered ambient bay water (adjusted to salinity = 35) that was circulated through a UV treatment system **(**Neotech Aqua Solutions, Inc.) to keep background DOC levels low. **These are exudation experiments are referred to as CBL exudation experiments.** *Sargassum* samples were also collected aboard the R/V *Henry Stommel* 9 km off the coast of Bermuda in late September 2016 and were transferred to outdoor tanks housed at the Bermuda Institute of Ocean Sciences, with continuously flowing seawater within 2 h of collection. **These exudation experiments are referred to as BDA exudation experiments.** All exudation experiments are described in detail below.

Exudation experiments

Three types of exudation experiments were conducted during this study. One set of experiments was conducted indoors at CBL (listed as “CBL” EXP1 and 2 in the excel sheet). For these experiments, *Sargassum* subsamples (approximately 100 g wet weight) were rinsed with 24 h UV-treated artificial seawater (Instant Ocean) and transferred to small tanks equipped with a Radion LED lamp (Eco Tech Marine) containing 7 L 24 h UV-treated artificial seawater. Lamps were set for a 14 h day/10 h night cycle and tanks were maintained at 29 °C with Eheim Jager TruTemp Quantum heaters. One tank containing no *Sargassum* served as a blank and was sampled for dissolved organic carbon (DOC) concentrations, total dissolved nitrogen (TDN) and optical properties. To minimize any stress from transfer, the water was drained and replaced before monitoring DOC/TDN and optical property exudation from the *Sargassum* samples. CBL EXP3 were the same as EXP1 and 2 with the exception that *Sargassum* was in mid-senescent conditions (based on visual inspection).

Another set of exudation experiments was conducted in outdoor tanks at the Bermuda Institute of Ocean Sciences (listed as “BDA” EXP1, 3 and 6 in the excel sheet). For these incubations, *Sargassum* was placed in small tanks containing open ocean seawater within a large tank of continuously flowing seawater. Temperature (°C) and solar intensity (Lux) in the tanks monitored with HOBO® pendant temperature/light data loggers. Temperatures ranged between 26 and 27.5 °C. Tanks were either left uncovered and exposed to full solar irradiation (listed as “UV” or “U” experiments in the excel sheet) or tanks were covered with a Plexiglas cover that had irradiation cut off at 345 nm and UVA (320 to 400 nm) transmission reduced to 65% (listed as “Plexi” or “P” experiments in the excel sheet).

The third set of experiments was performed to investigate the impacts of stress and senescent conditions on the release of DOC/TDN/optical properties by *Sargassum* (listed as “BDA” EXP 5 and 7 in the excel sheet). The optimal temperature range for pelagic *Sargassum* sp. is 24 to 30 °C (Hanisak & Samuel, 1987), so one tank was kept indoors and left at 20 °C. All other treatments were conducted outdoors. One tank contained mid-senescent *Sargassum* and was kept under low light (no direct sunlight) where the temperature did not change from 25 °C over the course of 12 h. The other tanks contained healthy *Sargassum* but were left outdoors for 12 h in direct sunlight with no temperature control. In these tanks the temperature ranged from 25 °C at the start of the experiment up to 49 °C after 12 h (Table 1). Although 49 °C is unrealistic for the open ocean, similar conditions may be present during annual *Sargassum* inundation events that occur in coastal environments.

For all experiments, subsamples of tank water were 0.2 µm-filtered (Whatman 25 mm GD/X syringe filters) into clean combusted (500 °C) 40 mL amber glass vials at discrete time points. Optical properties (absorbance and fluorescence spectra) of samples were either analyzed immediately or stored at 4 °C until analysis (within 1 to 10 d of collection). At the same time points, additional samples were acidified to pH 2 using concentrated HCl (Sigma Aldrich 32 %, pura) and analyzed for DOC and TDN concentrations using a Shimadzu TOC-V (see Powers et al., 2019, GBC).

Data Processing Description

DOC and TDN measurements. Samples were acidified to pH 2 using concentrated HCl (Sigma Aldrich 32 %, pura) and analyzed for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations using a Shimadzu TOC-V. Ultrapure water was used as a DOC/TDN blank and potassium hydrogen phthalate

and potassium nitrate were used for DOC and TDN standards, respectively.

Optical properties. For fluorescence and absorbance measurements, samples were transferred to 1 cm quartz fluorescence cuvette and analyzed using a Horiba Aqualog spectrofluorometer. For all time points collected during exudation experiments, raw absorbance spectra (A(λ)) were collected using a Horiba Aqualog at 3 nm intervals between 240 and 600 nm. A(λ) were then converted to Naperian absorption coefficient spectra (a(λ)) using the equation below.

$$a(\lambda) = 2.303 \times A(\lambda)/L \quad (1)$$

where L (m) is the pathlength of the spectrophotometer cell (0.01 m).

Spectral slope coefficients from 300 to 500 nm (S300-500, nm-1) were determined by fitting a(λ) spectra to the equation

$$a(\lambda) = a300*EXP(-S300\text{-}500(\lambda - 300)) \quad (2)$$

using a nonlinear curve fitting routine in Matlab 2015a®. A(λ) at various wavelengths was normalized to DOC concentration and the pathlength of the cell to determine changes in the carbon-normalized A(λ) during incubation experiments.

$$Anorm(\lambda) = A(\lambda)/([DOC] \times L) \quad (3)$$

For instance, specific UV absorbance at 254 nm (SUVA254; m-1 L mg-1), or A(254) normalized to pathlength (m) and DOC concentration (mg L-1).

Fluorescence was recorded from excitation wavelengths 240 to 600 at 3 nm intervals. Emission was recorded from ~243 to 297 nm at fixed ~3.3 nm intervals to created excitation-emission matrix (EEM) spectra. Integration time = 2s. Ultrapure water used as the fluorescence blank and was subtracted from all EEM spectra. Blank corrected EEM spectra were corrected for any inner filter effects using the Aqualog software. All spectra were normalized to the water Raman scattering signal so that all fluorescence data is reported in Raman units (RU). Rayleigh scattering signals were removed from EEM spectra using the Matlab ® (version 2015a) routine outlined previously (Zepp et al. 2004 doi: 10.1016/j.marchem.2004.02.006).

The following additional parameters were also calculated:

Apeak: intensity and location of maximum in the "A" region (ex/em <260 nm/400 – 460 nm) in (intensity x ex. location x em. location) (Coble et al. 1996)

Cpeak: intensity and location of maximum in the "C" region (ex/em 320 – 360 nm/420 – 460 nm) in (intensity x ex. location x em. location) (Coble et al. 1996)

Tpeak: intensity and location of maximum in the "T" region (ex/em <260 nm /320 – 350 nm) in (intensity x ex. location x em. location) (Coble et al. 1996)

These parameters (A, C, T peaks) were normalized to tank volume and *Sargassum* biomass for every time point. Therefore they are reported in RUxL/g.

BCO-DMO Processing Description

Data from submitted file "Sargassum_Exudation_SPEDOM_DOC_phenols." was imported into the BCO-DMO data system for this dataset. Values "ND" were imported as missing data values.
** Missing data values are displayed differently based on the file format you download. They are blank in csv files, "NaN" in MatLab files, etc.

* Metadata for this dataset was extracted from file DATASET_Sargassum_exudation_bulk_properties.rtf

* Value "#VALUE!" in column S300_to_500 was removed. The line was not removed, just the #VALUE! removed for the row with experiment:"EX3 BDA" time:0 V:4.09.

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Related Publications

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry, 51(4), 325–346. doi:10.1016/0304-4203(95)00062-3
Methods

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Methods

Hanisak, M. D., & Samuel, M. A. (1987). Growth rates in culture of several species of Sargassum from Florida, USA. Hydrobiologia, 151–152(1), 399–404. https://doi.org/10.1007/bf00046159
https://doi.org/10.1007/BF00046159
Methods

Powers, L. C., Hertkorn, N., McDonald, N., Schmitt-Kopplin, P., Del Vecchio, R., Blough, N. V., & Gonsior, M. (2019). Sargassum sp. Act as a Large Regional Source of Marine Dissolved Organic Carbon and Polyphenols. Global Biogeochemical Cycles, 33(11), 1423–1439. Portico. https://doi.org/10.1029/2019gb006225
https://doi.org/10.1029/2019GB006225
Results

Zepp, R. G., Sheldon, W. M., & Moran, M. A. (2004). Dissolved organic fluorophores in southeastern US coastal waters: correction method for eliminating Rayleigh and Raman scattering peaks in excitation–emission matrices. Marine Chemistry, 89(1–4), 15–36. https://doi.org/10.1016/j.marchem.2004.02.006
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Related Datasets

IsRelatedTo

Gonsior, M., Blough, N. V., Del Vecchio, R., Powers, L. (2024) **DOC and TDN concentrations & phenolic content from exudation experiments in outdoor tanks with Sargassum samples collected off the coast of Bermuda and in the Sargasso Sea in 2016.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-09-25 http://lod.bco-dmo.org/id/dataset/938791 [view at BCO-DMO]
Relationship Description: These datasets all utilized samples from the same outdoor exudation experiments.

Gonsior, M., Blough, N. V., Del Vecchio, R., Powers, L. (2024) **FT-ICR MS data from exudation experiments in outdoor tanks with Sargassum samples collected off the coast of Bermuda and in the Sargasso Sea in 2016.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-09-25 http://lod.bco-dmo.org/id/dataset/938799 [view at BCO-DMO]
Relationship Description: These datasets all utilized samples from the same outdoor exudation experiments.

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Parameters

Parameter	Description	Units
EXP	exudation experiment number and location	unitless
filename	Aqualog file name (see Supplemental File "SargassumExudationAbsFluor.zip") for .dat files.	unitless
time	time point sample collected during exp	hours

V	Tank volume	liters (L)
biomass	Sargassum biomass (wet weight)	grams (g)
DOC_mg_L	DOC concentration	milligrams per liter (mg/L)
DOC_mg_g	DOC concentration normalized to V and biomass	milligrams per gram (mg/g)
TDN_mg_L	TDN concentration	milligrams per liter (mg/L)
TDN_mg_g	TDN concentration normalized to V and biomass	milligrams per gram (mg/g)
A254	Absorbance at 254 nm	unitless
A305	Absorbance at 305 nm	unitless
A412	Absorbance at 412 nm	unitless
a305_V_g	Absorbance coefficient at 305 nm normalized to volume V and biomass. a305*V/g	L 1/m 1/g
a412_V_g	Absorbance coefficient at 412 nm normalized to volume V and biomass. a412*V/g	L 1/m 1/g
A254_DOC	A254/DOC. DOC normalized absorbance at 254 nm (SUVA).	L 1/m 1/g
A305_DOC	A305/DOC. DOC normalized absorbance at 305 nm.	L 1/m 1/g
A412_DOC	A412/DOC. DOC normalized absorbance at 412 nm.	L 1/m 1/g
S300_to_500	S(300-500). Spectral slope determined from 300-500 nm.	1/nm
Tpeak	Tpeak normalized to volume V and biomass	RU L/g
Apeak	Apeak normalized to volume V and biomass	RU L/g
Cpeak	Cpeak normalized to volume V and biomass.	RU L/g

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	Shimadzu Total Organic Carbon Analyzer TOC-VCPH
Generic Instrument Description	The Shimadzu Total Organic Carbon Analyzer TOC-VCPH is a PC-controlled, total organic carbon analyzer (high-sensitivity model), designed to measure total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), and non-purgeable organic carbon (NPOC); an optional accessory enables the measurement of particulate organic carbon (POC) and total nitrogen (TN) as well. The instrument uses the 680 degrees Celsius combustion catalytic oxidation method to analyze aqueous samples, and optionally solid and gas samples.

Dataset-specific Instrument Name	Horiba Aqualog spectrofluorometer
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.

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Deployments

HRS1608

Website	https://www.bco-dmo.org/deployment/938772
Platform	R/V Hugh R. Sharp
Start Date	2016-07-18
End Date	2016-07-22

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Project Information

Collaborative Research: Phlorotannins - An Important Source of Marine Chromophoric Dissolved Organic Matter? (Sargassum DOM)

Coverage: Mid-Atlantic Bight (July 2016), Sargasso Sea (July and September 2016), Coastal Bermuda (September/October 2016) and Coastal Puerto Rico (Laguna Grande, Fajardo; Las Croabas, Fajardo; Salinas; May/June 2018)

NSF Award Abstract:

Chromophoric dissolved organic matter (CDOM), the sunlight absorbing components in filtered water, is important in the study of marine and freshwater ecosystems as it can be used to trace the mixing of surface waters, as a proxy for carbon cycles, and other biogeochemical processes. Although its importance in ocean studies has been firmly established over the last several decades, sources and structural composition of CDOM within the oceans remains unclear and continues to be a subject of debate. Sargassum, a brown alga, is

widely distributed in temperate and subtropical marine waters and may be important source of CDOM to the Sargasso Sea and Gulf of Mexico where Sargassum is abundant. This project will investigate the contribution of macro brown algae-derived compounds to the marine CDOM pool. Results from this study will have implications for the marine carbon cycle and satellite remote sensing of ocean color to assess mixing of surface water masses and biogeochemical processes. The project will provide educational opportunities for a postdoctoral scholar, summertime undergraduate internships (through a local NSF-sponsored Research Experiences for Undergraduates (REU) program), and workshop and research opportunities for local high schools students.

Sources of marine CDOM remain debatable and a comprehensive understanding of its origins, distribution and fate have been difficult. Marine CDOM, and in particular the "humic-like" component, have been suggested to originate from terrestrial sources, primarily lignins. However, recent evidence indicates that the exudation of phlorotannins produced by macro brown algae may contribute significantly to the marine CDOM pool. Phlorotannins, a class of polyphenols that are only found in, and continuously exuded by macro brown algae such as Sargassum, strongly absorb ultraviolet light and may have been underestimated in their contribution to the marine CDOM pool within certain geographic locales. Upon partial oxidation, light absorption by these specific compounds extends into longer wavelengths in the visible creating an absorption spectrum similar to that of lignin. These phlorotannins and their transformation products absorb light that might explain in part the "humic-like" signatures observed in open ocean environments. This study aims to characterize the optical properties and molecular composition of Sargassum-derived CDOM including its aerobic oxidation and photochemical behavior, as well as quantify Sargassum-derived CDOM to better estimate its possible contribution to the CDOM pool in the Sargasso Sea and Gulf of Mexico.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1536888
NSF Division of Ocean Sciences (NSF OCE)	OCE-1536927

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