Optical properties (absorbance and fluorescence) from samples collected during a Sargassum inundation event in Puerto Rico in 2018

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

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Abstract
Optical properties (absorbance and fluorescence) from samples collected during a Sargassum inundation event in Puerto Rico in 2018. Water samples were collected between 30 May and 6 June, 2018 at various sites around Puerto Rico during a Sargassum inundation event.

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Coverage

Temporal Extent: 2018-05-30 - 2018-06-06

Dataset Description

See "Related Datasets" for other data from the same samples.

Methods & Sampling

Location description:

Water samples were collected between 30 May and 6 June, 2018 at various sites around Puerto Rico (blue squares in figure above). Sampling was concentrated in Fajardo at Laguna Grande, a 50 hectare saltwater

lagoon located in the Las Cabezas de San Juan Nature Reserve in the northeast corner of Puerto Rico (Detailed map in figure above). Laguna Grande has an average depth of 3 m, a maximum depth of 5 m, and is connected to the Atlantic Ocean at the beach in Las Croabas, Fajardo by a shallow 1.5 km channel (USGS). The lagoon is surrounded by mangrove swamps, tidal flats and brackish lagoons. It has been estimated that Laguna Grande flushes 13% of its water volume during every tidal cycle on average (USGS), corresponding to an average flushing rate of once every 7.7 days. Sargassum wracks were inundating both Laguna Grande and Las Croabas when sampling began, so no samples were collected before the event. However, because Sargassum was beaching in Las Croabas and entering the lagoon through the channel, it was expected that the entire lagoon would be impacted by Sargassum regardless of sampling time during the tidal cycle.

Sampling and analytical procedures:

At various sites throughout the lagoon and Las Croabas and offshore near Salinas (Figure above), samples for DOM characterization were collected in 10 L low density polyethylene cubitainers that had been previously cleaned with 0.1 N NaOH and rinsed several times with ultrapure MilliQ water. All containers were rinsed at least three times with sample before collection. Samples for DOM characterization were filtered through 0.7 µm GF/F filters (Whatman ®) that had been previously combusted for 4 h at 500 °C into 1 or 2 L glass bottles. Subsamples were reserved in 40 mL glass vials and acidified to pH 2 using concentrated HCl for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) measurements or left untreated for optical property (absorbance and fluorescence) analyses and stored at 4°C. The remaining ~1 L samples were then acidified to pH 2 using concentrated HCl and DOM was isolated using a solid phase extraction (SPE) technique. Briefly, samples were then drawn through clean Teflon tubing (rinsed with pH 2 ultrapure water) and connected to 1 g Bond Elut Priority PolLutant (PPL) cartridges (Agilent). PPL cartridges were previously activated with methanol (LC-MS Chromasolv, Sigma Aldrich) and rinsed with 0.1% formic acid water (LC-MS Chromasolv Sigma Aldrich). After extraction, all cartridges were rinsed with at 0.1% formic acid water and dried in a vacuum manifold. Dried cartridges were wrapped in foil and stored at 4 °C until returning to the Chesapeake Biological Laboratory. Before elution, cartridges were re-rinsed with 0.1% formic acid water and dried again under a hood using a vacuum manifold. DOM samples were then eluted with 10 mL ultrapure methanol into clean amber glass vials and stored at -20 °C until mass spectrometric analysis (described below).

DOC and TDN analyses

DOC and TDN were determined using a Shimadzu Total Organic Carbon Analyzer (TOC-VCPH), and ultrapure water served as both DOC and TDN blanks. DOC standards were prepared in ultrapure water using potassium hydrogen phthalate and ranged from 0 to 20 mg C L-1. TDN standards were prepared in the same manner using potassium nitrate and ranged from 0 to 10 mg N L-1. Like samples, all standards and blanks were acidified to pH 2 using concentrated HCl prior to analysis. If any samples fell outside of the calibration curve, they were diluted with ultrapure water and reanalyzed.

Determination of optical properties

Samples were pipetted into a 1 cm fluorescence cuvette. Absorbance and fluorescence were simultaneously recorded at 3 nm intervals between excitation wavelengths of 230 and 550 nm using a Horiba Aqualog system. Ultrapure water served as the absorbance and fluorescence blank, and was subtracted from all scans. To generate excitation-emission matrix spectra (EEMS), a fluorescence emission spectrum was recorded at a fixed wavelength range between 230 and 597 nm (~3.3 nm intervals) for every excitation wavelength using 1 - 15 sec integration time depending on sample absorbance. Rayleigh scattering signals were removed from all EEM spectra in Matlab® using methods described in Zepp et al. 2004, and any inner filter effects were corrected using the Aqualog software. EEM spectra were normalized to the water Raman scattering peak, thus all EEMS are reported in water Raman units (RU). 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)

Fluorescence Index, FI Ratio of fluorescence emission at 470 nm / 520 nm at 370 nm excitation Indicative of DOM source (McKnight et al. 2001)

normalized HIX (nHIX) Integrated emission from 435-480 / (300-345 + 435-480) nm at 254 nm excitation Indicative of DOM source and processing (Ohno 2002a)

Biological Index (BIX) Ratio of the fluorescence intensity at 380 nm to 430 nm at 310 nm excitation Indication

of recent microbial activity (Huguet et al. 2009)

In addition to the absorbance scans that accompany fluorescence scans, separate absorbance (A(λ)) scans were recorded for all samples between 230 and 700 nm. Raw A(λ)) spectra were corrected for any offsets by subtracting the absorbance at 700 nm from each spectrum. Corrected absorbances (Acorr(λ)) were converted to the Naperian absorption coefficient (a(λ)) with the following equation

$a(\lambda) = 2.303 \times Acorr(\lambda)/L$

where λ is the wavelength and L is the pathlength of the spectrofluorometer cuvette (i.e. 0.01 m). Spectral slopes were determined from 275-295 nm (S(275-295)) and from 350 – 400 nm (S(350-400)) as the slope of the log-normalized absorbance spectrum from 275-295 nm and 350-400 nm, respectively. Slope ratio (SR) is the ratio of S(275-295) to S(350-400) as defined previously (Helms et al. 2008). E2:E3 ratio is the ratio of absorbance at 250 nm to that 365 nm (De Haan and De Boer 1987). Fluorescence and absorbance data files are located in the “PuertoRicoAbsFluor.zip” (see Supplemental files).

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Parameters

Parameters for this dataset have not yet been identified

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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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NSF Division of Ocean Sciences (NSF OCE)	OCE-1536888
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