# FT-ICR MS data from samples collected during a Sargassum inundation event in Puerto Rico in 2018

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**Version**: 1
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**Project**
» Collaborative Research: Phlorotannins - An Important Source of Marine Chromophoric Dissolved Organic Matter? (Sargassum DOM)

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**Abstract**
Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) data 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).

**Ultrahigh Resolution Mass Spectrometry (MS) Analysis**

We used ultrahigh resolution mass spectrometry to characterize DOM in all samples and the possible production of DBPs formed during the desalination process. PPL extracts were diluted between 1:5 to 1:10 (depending on initial DOC concentrations) with ultrapure methanol prior to analysis with a Bruker Solarix 12 Tesla Fourier transform (FT) ion cyclotron resonance (ICR) mass spectrometer housed at the Helmholtz Zentrum Munich. We used negative ion mode electrospray ionization (ESI) with a spray voltage of –3.6 kV. The flow rate was held constant at 2 µL min-1 and 1,000 scans were averaged. The autosampler was programmed to wash with 600 µL of 80:20 MeOH:water to prevent carryover, and blank methanol samples were injected approximately every 10 samples. Exact molecular formulas (mass error <0.5 ppm) were assigned using proprietary software, which is based on the combinations of the elements 12C1-∞, 1H1-∞, 16O1-∞, 14N0-5, 32S0-2, 79Br0-3, as well as the 13C, 34S, and 81Br isotopologues. Molecular formula assignments with Br were confirmed manually using isotope simulation in the Bruker data analysis software. Isotope simulation allows for confirmation of 81Br isotopologue at 49.31% natural abundance.

**Data Processing Description**

Formula assignments are for each sample analyzed by FT-ICR MS are listed in this dataset. All m/z ions in methanol blanks that were detected in samples were excluded from the dataset. Formula assignments with double bond equivalents (DBE) < 0, non-integer DBE values, O/C > 1 and H/C < 0.3 were excluded from the dataset. All Br-containing assignments were confirmed manually using the Bruker DataAnalysis Software (version 4.4).

**BCO-DMO Processing Description**

Supplemental file:

* The originally provided excel sheet "PuertoRico_FTMS.xlsx" was attached as a supplemental file to this dataset and contains the data table in wide form (a mass peak intensity column per sample named with the sample ID). See Supplemental files section. This excel file contains two "salinas inside mat 180605" columns and two "mangrove lagunetta 180602" columns.

Primary Data File for this dataset:

* Sheet 1 of submitted file "PuertoRico_FTMS.xlsx" was imported into the BCO-DMO data system for this dataset and unpivoted to become a "narrow" form of the data table where there is one column that contains the sample id, and one column that contains the mass peak intensity for that sample. Narrow form of the dataset output as 938823_v1_sargassum-pr-2018-ftms.csv (see Data Files section).

* Unique column names are required for BCO-DMO import so two sets of identically named columns got (a) and (b) suffixes in the primary data table for this dataset output as 938823_v1_sargassum-pr-2018-ftms.csv. e.g. "salinas inside mat 180605 (a)"

**Problem Description**

See "BCO-DMO Processing notes" for explanation of how two sets of identically named samples were suffixed with (a) and (b) in sample_id column of data file 938823_v1_sargassum-pr-2018-ftms.csv

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## Parameters

*Parameters for this dataset have not yet been identified*

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## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | Bruker Solarix 12 Tesla Fourier transform (FT) ion cyclotron resonance (ICR) mass spectrometer located at the Helmholtz Zentrum, Munich, Germany. |
| **Generic Instrument Name** | Mass Spectrometer |
| **Generic Instrument Description** | General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components. |

| | |
|---|---|
| **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. |

| | |
|---|---|
| **Dataset-specific Instrument Name** | |
| **Generic Instrument Name** | Total Organic Carbon Analyzer |
| **Dataset-specific Description** | Shimadzu Total Carbon Analyzer (TOC-VCPH) |
| **Generic Instrument Description** | A unit that accurately determines the carbon concentrations of organic compounds typically by detecting and measuring its combustion product (CO2). See description document at: http://bcodata.whoi.edu/LaurentianGreatLakes_Chemistry/bs116.pdf |

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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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