# Fluorescence spectra from niskin bottle samples collected with depth profiles during R/V Hugh R. Sharp cruise HRS1608 Mid-Atlantic Bight in 2016

Website: https://www.bco-dmo.org/dataset/938774

Data Type: Cruise Results

Version: 1

Version Date: 2024-10-03

#### **Project**

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

Contributors	Affiliation	Role
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#### Abstract

Fluorescence spectra from niskin bottle samples collected with depth profiles during R/V Hugh R. Sharp cruise HRS1608 Mid-Atlantic Bight in 2016.

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#### Coverage

Location: Mid-Atlantic Bight

**Spatial Extent**: N:37.98133 **E**:-74.10417 **S**:34.34967 **W**:-75.8035

Temporal Extent: 2016-07-18 - 2016-07-22

#### Methods & Sampling

Samples were transferred from Niskin bottles to clean 10L low-density polyethylene cubitainers using silicon tubing. Containers were rinsed three times with sample before final collection.

Subsamples for fluorescence and absorbance were 0.2  $\mu$ m filtered using Whatman GD/X cellulose acetate syringe filters. Filters were rinsed with ~20mL sample before collecting samples in combusted 40mL amber glass vials. Samples stored at 4°C until analysis (within 1 week of collection). See "Related Datasets" section for the absorbance data. For fluorescence and absorbance measurements, samples were transferred to 1 cm quartz fluorescence cuvette and analyzed using a Horiba Aqualog spectrofluorometer. Absorbance was recorded from excitation wavelengths 240 to 600 at 3 nm intervals. Fluorescence 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.

## **Data Processing Description**

**Fluorescence .dat files:** columns are excitation wavelength (nm) and rows are emission wavelength (nm). The value in each cell is the blank corrected and normalized (by fluorescence of a quinine sulfate standard, described in detail below) fluorescence for each exciation/emission pair.

Blank corrected EEM spectra were corrected for any inner filter effects using the Aqualog software. All spectra were normalized to the fluorescence of a 1 ppb quinine sulfate (QS) standard in 0.1 N  $\rm HClO_4$  (STARNA) at excitation 347.5 nm, corrected for sample integration time. A 0.1 N  $\rm HClO_4$  solution (STARNA) was used as the QS blank. Therefore all EEM spectra are reported in QS units (QSU). Rayleigh scattering signals were removed from EEM spectra using the Matlab  $\rm \$$  (version 2015a) routine outlined previously (Zepp et al. 2004 doi:  $\rm 10.1016/j.marchem.2004.02.006$ ).

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)

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)

#### **BCO-DMO Processing Description**

Preprocessing for version 1:

- \* Sheet "fluorescence" of submitted file "Cruise\_fluor\_abs.xlsx" was imported into the BCO-DMO data system for this dataset. Values "NA" and "NaN" were imported as missing data values. The other sheet in the file "absorbance" was added to BCO-DMO as a related dataset.
- \*\* 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 Cruise optical properties.rtf"
- \* Column names adjusted to conform to BCO-DMO naming conventions designed to support broad re-use by a variety of research tools and scripting languages. [Only numbers, letters, and underscores. Can not start with a number]
- \* DateTime with timezone column added (ISO 8601 format).

- \* Three out of bounds latitudes (originally provided as decimal decimal minutes "345 56.14") were removed (all were at time 2016-07-21T15:56Z).
- \* Lat lon columns converted to decimal degrees.

#### Dataset Version 1:

- \* Submitter used the revised data described above and resubmitted the data table as "938783\_v1\_cruise-opt-prop-fluor REVISED.csv" which corrected three out of bounds latitudes (originally provided as decimal decimal minutes "345 56.14") with the correct value in decimal degree format 35.93567 (should have been 35 56.14 in "Cruise fluor abs.xlsx").
- \* raw .dat files were bundled into a .zip file and attached as a supplemental file to this dataset.

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#### **Data Files**

#### File

938774\_v1\_cruise-opt-prop-fluor.csv(Comma Separated Values (.csv), 5.12 KB)

MD5:e210305b3fd0f02c3c4573f56c39234b

Primary data file for dataset ID 938774, version 1

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# **Supplemental Files**

#### File

#### Raw fluorescence Aqualog (.dat files)

filename: SharpCruise optics fluor.zip

(ZIP Archive (ZIP), 2.22 MB) MD5:d344f1f276f4f902e60db0460411e401

Raw fluorescence data exported from Aqualog (.dat files). Columns are excitation wavelength (nm) and rows are emission wavelength (nm). The value in each cell is the blank corrected and normalized (by fluorescence of a quinine sulfate standard, described in detail below) fluorescence for each exciation/emission pair.

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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

De Haan, H., & De Boer, T. (1987). Applicability of light absorbance and fluorescence as measures of concentration and molecular size of dissolved organic carbon in humic Lake Tjeukemeer. Water Research, 21(6), 731–734. https://doi.org/10.1016/0043-1354(87)90086-8

Methods

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnology and Oceanography, 53(3), 955–969. doi:10.4319/lo.2008.53.3.0955 Methods

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., & Parlanti, E. (2009). Properties of fluorescent dissolved organic matter in the Gironde Estuary. Organic Geochemistry, 40(6), 706–719. doi:10.1016/j.orggeochem.2009.03.002

Methods

Ohno, T. (2002). Fluorescence Inner-Filtering Correction for Determining the Humification Index of Dissolved Organic Matter. Environmental Science & Technology, 36(4), 742–746. doi:10.1021/es0155276

#### Methods

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

Methods

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#### **Related Datasets**

#### IsRelatedTo

Gonsior, M., Blough, N. V., Del Vecchio, R., Powers, L. (2024) **Absorbance spectra from niskin bottle samples collected with depth profiles during R/V Hugh R. Sharp cruise HRS1608 Mid-Atlantic Bight 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/938783 [view at BCO-DMO] *Relationship Description: Data generated from measurements of the same samples.* 

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#### **Parameters**

Parameter	Description	Units
date	Sampling date	unitless
Time	Time of cast (in UTC time zone)	unitless
ISO_DateTime_UTC	DateTime of cast with time zone (in ISO 8601 format)	unitless
Lat	Latitude	decimal degrees
Long	Longitude	decimal degrees
Salinity	Salinity. Practical Salinity Scale 1978 (PSS-78)	unitless
depth_sample	sampling depth	meters (m)
depth_sample_comment	sampling depth description (e.g. "Chl max")	unitless
file_name	associated fluorescence file (.dat). These files are included in SharpCruise_optics_fluor.zip (See supplemental files).	
Apeak	Apeak fluorescence intensity. 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)	QSU

Apeak_ex_wave	Apeak excitation wavelength	nm
Apeak_em_wave	Apeak emission wavelength	nm
Cpeak	Cpeak fluorescence intensity. 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)	QSU
Cpeak_ex_wave	Cpeak excitation wavelength	nm
Cpeak_em_wave	Cpeak emission wavelength	nm
FI	fluorescence index. FI Ratio of fluorescence emission at 470 nm / 520 nm at 370 nm excitation Indicative of DOM source (McKnight et al. 2001)	unitless
BIX	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)	unitless
nHIX	normalized humification index. 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)	unitless

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# Instruments

Dataset-specific Instrument Name	Horiba Aqualog spectrofluorometer
Generic Instrument Name	Spectrometer
	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	
<b>End Date</b>	2016-07-22	

# **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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