Consensus Reference Material Collection Data of marine dissolved organic matter collected in the Florida Strait between 2019 and 2023

Website: https://www.bco-dmo.org/dataset/914491
Data Type: Cruise Results
Version: 1
Version Date: 2023-12-22

Project
» Preparation and Distribution of DOC Consensus Reference Materials (DOC-CRM)

Contributors	Affiliation	Role
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Abstract
The laboratory of Prof. Dennis A. Hansell at the University of Miami is supported by the U.S. National Science Foundation to provide the international community of marine dissolved organic matter analysts the reference waters needed for testing their analytical results against those of a select group of expert analysts. Three depths of the water column are sampled in the Florida Strait, typically twice each year, to collect and distribute those waters as reference materials. The deepest water (i.e., deep seawater reference (DSR)) is collected in the Florida Straits at 700 m depth. A mid depth seawater reference (MSR), is collected at 150 m depth and surface seawater reference (SSR) is collected at 5 m. In the data table that follows, the relevant information for each collection during NSF Grant OCE-1844886, awarded to the Hansell laboratory, is provided. These details include the ship employed and its cruise designations, the dates of collection, the batch and lot numbers designated for the reference waters, the locations and depths sampled, the concentrations of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) in each lot. Finally, hyperlinks to the associated CTD and underway data, archived by RVDATA.US, are provided.

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Coverage

Spatial Extent: **Lat**:25.5 **Lon**:-79.9
Temporal Extent: 2019-03-19 - 2023-02-16

Methods & Sampling

The seawater is collected by Niskin bottles mounted on a CTD rosette. Upon recovery to the ship's deck, the water is transferred to pre-cleaned 20 L carboys through silicone tubing, directly from the Niskin bottle sample valve to a bulkhead fitted carboy cap. Transfer takes only a few minutes through one of the larger sampling valves. These steps have proven contamination-free.

The sealed carboys are returned to the shore laboratory immediately after collection, acidified with blank-checked, ultra-pure hydrochloric acid (2 ml HCl per liter of water). The water is tested at each transfer step to ensure absence of contamination. Pre-combusted vials are filled from a silicone tube attached to the carboy valve. The other end of the silicone tube is attached to a clean, long-nosed pipette. The pipette tip is placed cleanly and without flow at the bottom of the vial, and then the flow is started.

Low carbon water is generated in a Milli-Q A10 system. The system reduces DOC in deionized water to very low levels by utilizing high intensity, multi-wavelength (185 and 284 nm) UV light. Specifications call for the unit to generate water with a DOC content of <0.4 µM C (<5 ppb). The water is homogenized, acidified and distributed from a clean carboy as described above.

During vial filling, we randomly but regularly remove vials for immediate analysis to evaluate for contamination. Evaluation of these subsets ensures that there is little variability between batches of material prepared on different days. The volumes (20 and 40 ml) are suitable for DOC analyses by direct injection (normally 100 µl) into high temperature combustions systems and by chemical or photo-oxidation techniques.

Reference Material Consensus – Consensus on the concentration of organic carbon in the deep sea reference water is performed by a group of independent expert laboratories. We maintain a pool of 4-6 labs for each assessment. The CRM program is intended to run for several years, but the longevity of any one laboratory may not be that long. A group of 4-6 certification labs allows for loss of one or two labs, and replacement by other labs, while maintaining continuity over the years. Currently, the laboratories of Craig Carlson, Dennis Hansell, Hiroshi Ogawa, Elizabeth Minor, Chiara Santinelli and Rainer Amon provide the service.

Shortly after batch preparation, and upon successful reanalysis of the CRM's by our laboratory, each expert/consensus laboratory receives 10-20 samples of the low carbon water (LCW) and of reference seawaters. Analyses of the concentration of DOC in the seawater is relative to the LCW, with each laboratory using its own standards and calibration procedures. The value presently assigned to the LCW is 1 µM.

CRM Storage and Distribution - The newly prepared samples are stored in the dark at room temperature. Samples are not frozen because it is unnecessary, because we wish to avoid alternating freezing/thawing/freezing cycles likely for the more remote recipients of the material, and because freezing weakens (through expansion of the water) the integrity of the glass vial walls.

Shipment to the users is by 'overnight' delivery in shock-protected boxes. Shipping costs are borne by the participating laboratory unless special circumstances make such payments (and, therefore, participation in the program) difficult. For example, some laboratories in less developed countries may not be able to afford the shipping costs. We find ways to keep such laboratories in the program.

CRM Stability - Our experience is that changes in DOC have not been seen for either the seawater or the LCW on the time frame of at least 2 years. It could be, however, that the samples undergo change on longer time scales, perhaps due to absorption of DOM onto the glass walls. At the time of distribution, we assign shelf lives of 1 year to the reference material.

CRM Use - We distribute a document describing the appropriate handling of reference materials received by the participating laboratories. In it, the purpose of the reference materials, a description of the material distributed, the recommended protocols for handling the materials, cautions, and appropriate statistical tools for evaluating results are listed.

Data Processing Description

DOC analysis is performed by a high temperature combustion method using a Shimadzu Model TOC-L. The system configuration and operating parameters are as follows: Ultra high purity O2 is used as a carrier gas, flowing through the system at 150 ml min-1. 100 µl of sample is injected with automation through a Teflon/sliding injection port into a quartz combustion tube packed with Pt gauze and 5% Pt on alumina catalyst heated to 680°C. Samples are acidified with 37% HCl (15 µl per 10 ml of sample; 0.15%) and, immediately prior to injection, sparged with ultra-high purity, CO2 free oxygen for 1.5 minutes to remove inorganic carbon. Samples are combusted in the furnace and the resulting gas passed through water traps and a final copper halide trap before entering the detector.

To minimize the system blank, conditioning of the combustion tube is required prior to analysis of samples. Conditioning is performed through repeated injections of Milli-Q water and/or seawater. After conditioning, the system blank is assessed with LCW. Typical relative standard deviations of replicate TOC analyses are 2%. The

instrument response factor is determined with potassium hydrogen phthalate in Milli-Q® water (0, 40, 80, 160 uM C). The instrument blank is measured every 4-6 samples using LCW.

The TDN content of seawater is similarly defined as the concentration of combined nitrogen remaining in a seawater sample after particulate nitrogen has been removed. TDN is determined via the high temperature combustion method with Shimadzu TOC analyzer attached to a Shimadzu TNM analyzer. Combined dissolved nitrogen in the sample is converted to nitric oxide (NO). The resulting gas stream is then passed through the Shimadzu internal electronic dehumidifier, a copper mesh halide trap, a 0.45 µm filter, and into the chemiluminescence analyzer, where the dried NO gas reacts with O3 to produce an excited nitrous oxide. The resulting fluorescence signal is detected by the Shimadzu TNM chemiluminescence detector. The resulting peak area is integrated with Shimadzu chromatographic software.

The full analytical protocol is described in Halewood et al. 2022.

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Data Files

File
914491_v1_reference.csv (Comma Separated Values (.csv), 2.58 KB) MD5:da5d5ce524b5407a9e03c092a23e4416 Primary data file for dataset ID 914491, version 1

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Related Publications

Halewood, E., Opalk, K., Custals, L., Carey, M., Hansell, D. A., & Carlson, C. A. (2022). Determination of dissolved organic carbon and total dissolved nitrogen in seawater using High Temperature Combustion Analysis. Frontiers in Marine Science, 9. https://doi.org/10.3389/fmars.2022.1061646
Methods

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Parameters

Parameter	Description	Units
Cruise_ID	Cruise ID	unitless
Collection_Date	Collection Date	unitless
Latitude	Latitude of sample, south is negatice	decimal degrees
Longitude	Longitude of sample, west is negative	decimal degrees
Batch_ID	Batch ID	unitless
Designations	Sample description	unitless

Sampling_Depths	Sampling depth: DSR (deep seawater reference, 700m), MSR (mid depth seawater reference, 150m) or SSR (surface seawater reference, 5m)	unitless
DOC_Conc_uM_Min	The minimum value of dissolved organic carbon (DOC) concentrations. Analytical precision is roughly 1 micromoles carbon per liter, but the data are provided as a range here. The concentrations of the reference waters are determined by a group of expert laboratories, so it is their range of results that we report. There is not an analytical method and result that is certifiable to a NIST standard, hence the need for the consensus values provided to the user community.	micromoles carbon per liter (uM/L)
DOC_Conc_uM_Max	The maximum value of dissolved organic carbon (DOC) concentrations. Analytical precision is roughly 1 micromoles carbon per liter, but the data are provided as a range here. The concentrations of the reference waters are determined by a group of expert laboratories, so it is their range of results that we report. There is not an analytical method and result that is certifiable to a NIST standard, hence the need for the consensus values provided to the user community.	micromoles carbon per liter (uM/L)
TDN_Conc_uM_Min	The minimum value of total dissolved nitrogen (TDN) concentrations. Reported similarly to the DOC values as described above but with units of micromoles nitrogen per liter. The precision is roughly 0.5 micromoles nitrogen per liter.	micromoles nitrogen per liter (uM/L)
TDN_Conc_uM_Max	The maximum value of total dissolved nitrogen (TDN) concentrations. Reported similarly to the DOC values as described above but with units of micromoles nitrogen per liter. The precision is roughly 0.5 micromoles nitrogen per liter.	micromoles nitrogen per liter (uM/L)
Ship	Ship name	unitless
Ship_Data	DOI number for shipboard data archived at R2R	unitless

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	Shimadzu TOC-L Analyzer
Dataset-specific Description	DOC analysis is performed by a high temperature combustion method using a Shimadzu Model TOC-L. See methods section for complete description of the system configuration as well as Halewood et al., 2022 for the full analytical protocol.
Generic Instrument Description	A Shimadzu TOC-L Analyzer measures DOC by high temperature combustion method. Developed by Shimadzu, the 680 degree C combustion catalytic oxidation method is now used worldwide. One of its most important features is the capacity to efficiently oxidize hard-to-decompose organic compounds, including insoluble and macromolecular organic compounds. The 680 degree C combustion catalytic oxidation method has been adopted for the TOC-L series. http://www.shimadzu.com/an/toc/lab/toc-l2.html

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Deployments

WS19080

Website	https://www.bco-dmo.org/deployment/914532
Platform	R/V F.G. Walton Smith
Start Date	2019-03-21
End Date	2019-03-21

WS19302

Website	https://www.bco-dmo.org/deployment/914538
Platform	R/V F.G. Walton Smith
Start Date	2019-10-29
End Date	2019-10-29

WS20226

Website	https://www.bco-dmo.org/deployment/914671
Platform	R/V F.G. Walton Smith
Start Date	2020-08-13
End Date	2020-08-13

WS21315

Website	https://www.bco-dmo.org/deployment/914699
Platform	R/V F.G. Walton Smith
Start Date	2021-11-11
End Date	2021-11-11

WS21103

Website	https://www.bco-dmo.org/deployment/914697
Platform	R/V F.G. Walton Smith
Start Date	2021-04-13
End Date	2021-04-13

WS22283

Website	https://www.bco-dmo.org/deployment/914701
Platform	R/V F.G. Walton Smith
Start Date	2022-10-20
End Date	2022-10-20

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Project Information

Preparation and Distribution of DOC Consensus Reference Materials (DOC-CRM)

Website: https://hansell-lab.rsmas.miami.edu/consensus-reference-material/index.html

Coverage: University of Miami, Florida, USA

NSF Award Abstract:

Dissolved organic carbon (DOC) in the ocean is part of the global carbon cycle. DOC interacts with the Earth's climate system through its connection to carbon dioxide in the atmosphere. Keeping track of DOC requires the cooperation of many marine laboratories worldwide. Making sure that all of these laboratories are making accurate DOC measurements requires that each can access a standardized sample of seawater for which the DOC concentration is set by international agreement. This award funds the University of Miami to continue a consensus reference material (CRM) program that was first developed in 1998 in support of consistent, high quality measurements of dissolved organic carbon by the international ocean chemistry community. With continuation of this work, the US and international communities can make consistent measurements of a major marine carbon reservoir and advance society's ability to assess changes in the marine carbon cycle and the role of the ocean in climate change.

With continued strong international efforts to investigate the marine carbon cycle, the existing CRM program provides the necessary benchmark for globally comparable marine DOC measurements. Water from the deep Florida Strait (approximately 42 umol/kg DOC) will be collected, placed in ampoules, and distributed to the US and international community. Over the time period of this program, approximately 228,000 vials of reference waters have been distributed to approximately 240 US and international laboratories in 43 nations, currently at a rate of about 23,000 vials/year. With continuation of the reference material program for a seventh 3-year period of support, distribution of deep ocean water containing biologically refractory dissolved organic carbon and low carbon reference water will continue to aid the analytical work of the community studying dissolved organic matter in the ocean. A website is maintained that provides direct and convenient links to a growing number of DOC data collected from the global ocean.

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-1844886

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