Stable carbon isotopic signatures of solid-phase extracted DOC from seawater collected on three GO-SHIP Repeat Hydrography Cruises in 2015-2018 along transects P16N, P18, and I07N.

Website: https://www.bco-dmo.org/dataset/924605
Data Type: Cruise Results
Version: 1
Version Date: 2024-04-09

Project
» Cycling of Dissolved Organic Matter in the Pacific and Indian Oceans Using Radiocarbon (DOC 14C and 13C)

Contributors	Affiliation	Role
Druffel, Ellen R.M.	University of California-Irvine (UC Irvine)	Principal Investigator
Lewis, Christian Blair	University of California-Irvine (UC Irvine)	Scientist
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Abstract
These data include stable carbon isotopic measurements (d13C) of solid-phase extracted dissolved organic matter (SPE-DOC) from three GO-SHIP Repeat Hydrography Cruises transects P16N (151°W; 2015), P18 (103-110°W; 2016/2017), and I07N (50-70°E; 2018) aboard the NOAA Ship Ronald H. Brown. The "weighted average depth" refers to that of seawater integrated between 0-200m and 2-4km depth. These data are used to compare carbon isotopic compositions of recalcitrant DOC to bulk DOC, yielding new insights toward the importance of the microbial carbon pump toward the sequestration of DOC in the global deep-ocean. This data accompanies an article currently in review at Geophysical Research Letters.

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Coverage

Location: Eastern Pacific Ocean, North Pacific Ocean, Western Indian Ocean
Spatial Extent: **N**:57 **E**:68 **S**:-69 **W**:-152
Temporal Extent: 2015-05-23 - 2018-04-23

Methods & Sampling

Seawater samples were obtained from three GO-SHIP Repeat Hydrography transects to measure stable carbon isotopic composition of solid-phase extracted dissolved organic matter (SPE-DOC $\delta^{13}C$). Transect P16N (151°W) sampled in the year 2015, P18 (103-110°W) in 2016 and 2017, and

transect I07N (50-70°E) in 2018 aboard the NOAA Ship Ronald H. Brown (see Figure 1), at or within 1 station of an associated total DOC sample (Druffel et al., 2019, 2021, 2023). “Surface” and “deep” samples were collected at 0-200 meters and 2000-4000 meters, respectively. Due to the integration of seawater among different stations and depth, we report the weighted average depth which is the weighted mean that incorporates the relative amount of each water depth into the final value. (See Supplemental Files section for the equation).

Due to excess water availability, two samples (called "seawater duplicates or SD) were collected from P18 stations 77-79 (in deep water), and 168 (in surface water). For seawater samples from P18 and IO7N, solid phase extraction (SPE) was performed at sea using PPL cartridges (Bond Elut-PPL, 1 gm 6 ml, Part No. 12255002) according to Dittmar et al. (2008) and stored in the dark at 4°C until elution at UC Irvine. Seawater samples from the P16N cruise were processed after four years of freezing. Samples were then acidified to pH 2 with sulfuric acid (ACS grade, Lot #160,128) and extracted onto PPL cartridges. Before elution, PPL cartridges were dried under a steady stream of ultra-high purity N_2 gas for 30 min to remove residual MilliQ water (3 ppb DOC). SPE-DOC was eluted with LC/MS grade methanol following established methods (Dittmar et al., 2008). However, the elution volume of methanol was increased to 32 mL to increase yield of SPE-DOC (Lewis et al., 2020). SPE-DOC was eluted into pre-weighed and pre-combusted (540°C/2h) 50 mL centrifuge vials (VWR product #89091-460), and weighed after elution to determine the exact volume.

Splits were dried in a centrifugal evaporator with a −60°C chiller trap (Savant SpeedVac SC200) for a minimum of 12 hours. Pre-baked cupric oxide and silver wire were added, and the outside of these quartz tubes were cleaned with acetone, dried, and placed inside larger 9 mm diameter, 20 cm long quartz vials. These “double tube” samples were sealed under vacuum and combusted at 850°C for two hours. Sample CO_2 was extracted cryogenically on a vacuum line and quantified manometrically.

Stable carbon isotopic measurements ($\delta^{13}C$) were made using a Gas Bench II and Thermo Electron Delta Plus mass spectrometer, and corrected using calibrated isotopic standards (NIST NBS-19). Measurements are reported as standard permille (‰) relative to V-PDB (Vienna Pee-Dee Belemnite) scale. Duplicate and triplicates taken from certain SPE-DOC extracts from all three cruises show our SPE-DOC $\delta^{13}C$ measurement precision averages better than 0.2‰ providing confidence that the variability seen throughout different ocean regions is real.

This work was supported by the National Science Foundation Chemical Oceanography Program (OCE-1458941 and OCE-1951073 to E.R.M.D.), the U.S. American Chemical Society Petroleum Research Fund New Directions Grant (55430-ND2 to E.R.M.D. and B.D.W.), the Fred Kavli Foundation, and the Keck Carbon Cycle AMS Laboratory. A portion of this work was funded by the Natural Sciences and Engineering Research Council (NSERC) of Canada through a Discovery Grant, Accelerator and Launch Supplements (RGPIN-2020-06501, RGPAS-2020-00071, DGECR-202000256; to B.D.W.), the New Frontiers in Research Fund (NFRFE-2019-00794 to B.D.W.) and the Canada Research Chairs program (to B.D.W.). A portion of this work was also funded by the New Zealand Ministry of Business, Innovation and Employment (MBIE) through the Global Change through Time programme (Strategic Science Investment Fund, contract C05X1702)

Data Processing Description

$\delta^{13}C$ values are blank-corrected for a known amount of extraneous carbon previously reported (Lewis et al., 2020). This is done using a mass-balance calculation. The included data includes the raw and corrected values.

δ13C measurements are reported as standard permille (‰) relative to V-PDB (Vienna Pee-Dee Belemnite) scale. Additional corrections are required for extraneous carbon added during sample workup. The blank correction procedure is reported in Lewis et al. (2020).

The code used to analyze the data and produce figures can be found in Lewis (2024) GitHub repo, and in the Supplemental Files section below.

BCO-DMO Processing Description

- Imported data from source file "OPEN_ACCESS_DATA_FILE_BCODMO.xlsx"
- Created new columns for Sample_note and Cruise_ID
- Created a date column based on the EXPOCODE
- Modified parameter (column) names to conform with BCO-DMO naming conventions. The only allowed characters are A-Z,a-z,0-9, and underscores. No spaces, hyphens, commas, parentheses, or Greek letters.

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Data Files

File	
924605_v1_spe_doc_c13.csv	(Comma Separated Values (.csv), 3.65 KB) MD5:d9aba6b9634f7c5dd002073d238d8a66
Primary data file for dataset ID 924605, version 1. Stable carbon isotopic signatures of solid-phase extracted DOC.	

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Supplemental Files

File	
Equation to calculate Weighted Average Depth filename: weighted_average_depth.pdf	(Portable Document Format (.pdf), 56.70 KB) MD5:b093b96ad724ce2cf4e3220e6e3bb1a9
Figure1.png	(Portable Network Graphics (.png), 279.38 KB) MD5:e97acb19b4ebc1d36c2138007fa30b2f
Map of transect lines for P16N, P18, and I07N as sampled aboard the NOAA Ship Ronald H. Brown. P16N (151°W) was sampled in the year 2015, P18 (103-110°W) in 2016 and 2017, and transect I07N (50-70°E) in 2018.	
Lewis_13C_SPE_reboot2.py	(Python Script, 59.44 KB) MD5:ab90995287180b3c9c2aa4b19edc22a6
Python script to merge data for the three cruises (I07N, P16N, P18) and combine information for SPE-DOC with the depths as weighted averages. This is a copy of Python script https://github.com/christianlewis091/science_projects/blob/main/UCI_13C/13C_SPE_reboot2.py (commit de56136d30f9cb5362ccc70994b78ac1653ca5ac) contributed to BCO-DMO by the author.	

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Related Publications

Dittmar, T., Koch, B., Hertkorn, N., & Kattner, G. (2008). A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnology and Oceanography: Methods, 6(6), 230–235. doi:10.4319/lom.2008.6.230
Methods

Druffel, E. R. M., Griffin, S., Lewis, C. B., Rudresh, M., Garcia, N. G., Key, R. M., … Walker, B. D. (2021). Dissolved Organic Radiocarbon in the Eastern Pacific and Southern Oceans. Geophysical Research Letters, 48(10). doi:10.1029/2021gl092904 https://doi.org/10.1029/2021GL092904
Methods

Druffel, E. R. M., Griffin, S., Wang, N., Garcia, N. G., McNichol, A. P., Key, R. M., & Walker, B. D. (2019). Dissolved Organic Radiocarbon in the Central Pacific Ocean. Geophysical Research Letters, 46(10), 5396–5403. Portico. https://doi.org/10.1029/2019gl083149
Methods

Druffel, E. R. M., Lewis, C. B., Griffin, S., Flaherty, A., Rudresh, M., Hauksson, N. E., Key, R. M., McNichol, A. P., Hwang, J., & Walker, B. D. (2023). Dissolved Organic Radiocarbon in the West Indian Ocean. Geophysical Research Letters, 50(19). Portico. https://doi.org/10.1029/2023gl104732
Methods

Lewis, C. (2024) Github repository: science_projects. Github. Available from https://github.com/christianlewis091/science_projects
Software

Lewis, C. B., Walker, B. D., & Druffel, E. R. M. (2020). Isotopic and optical heterogeneity of solid phase extracted marine dissolved organic carbon. Marine Chemistry, 219, 103752. doi:10.1016/j.marchem.2020.103752
Methods

Lewis, C. B., Walker, B. D., & Druffel, E. R. M. (2024; in press). Stable isotopic (δ13C) evidence for global microbial sequestration of refractory dissolved organic matter. Geophysical Research Letters (in press)
Results

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Related Datasets

IsRelatedTo

Druffel, E. R., Lewis, C. (2022) **Concentrations and radiocarbon signatures of SPE-DOC extracted from seawater samples on GO-SHIP cruises P16N, P18, and IO7N in the North Pacific, Eastern Pacific, and Western Indian Oceans.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2021-06-28 doi:10.26008/1912/bco-dmo.853101.1 [view at BCO-DMO]

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Parameters

Parameter	Description	Units
SPE_DOC_UCID	Sample ID (UC Irvine Identification number)	unitless
Sample_note	Sample note; SD = seawater duplicate taken whenever excess water was available; PD = PPL duplicate where two or more splits were taken from the same SPEDOC extract for measurement repeatability assessment	unitless
EXPOCODE	GO-SHIP Expedition Code	unitless
GO_SHIP_Section	Name of GO-SHIP repeat hydrography section	unitless
Cruise_ID	Cruise ID	unitless
Sampling_Date	Sampling date	unitless
Latitude	Latitude of sample collection	decimal degrees
Longitude	Longitude of sample collection	decimal degrees
Station_Number	Station number of the closest DOC 14C sample	unitless
Surface_or_Deep	Depth range where surface samples are integrated between 0-200 m; deep samples are collected between 2-4 km	unitless
Weighted_Average_Depth	Weighted mean depth of integrated seawater sample. This is calculated by taking a weighted mean of the various subsets of water that were available on the ship. For instance, if we collected 1L from 5m, 0.5L from 10m, the weighted average depth reflects the relative abundance of water from either depth.	meters (m)
SPE_DOC_d13C_corrected	Delta 13C value of solid phase extracted DOC, blank corrected for extraneous C added during sample work-up, reported relative to V-PDB (Vienna Pee-Dee Belemnite) scale.	per mil
SPE_DOC_d13C_corr_1_sigma	One sigma error of SPE-DOC d13C	per mil
Percent_change_from_blank_correction	Relative change in sample value before and after correction	percent (%)

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Instruments

Dataset-specific Instrument Name	Savant SpeedVac SC200 centrifugal evaporator with a −60°C chiller trap
Generic Instrument Name	centrifugal evaporator
Dataset-specific Description	Splits were dried in a Savant SpeedVac SC200 centrifugal evaporator with a −60°C chiller trap.
Generic Instrument Description	A centrifugal evaporator is a device used in chemical and biochemical laboratories for the efficient and gentle evaporation of solvents from many samples at the same time, and samples contained in microtitre plates.

Dataset-specific Instrument Name	Thermo Electron Delta Plus mass spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Stable carbon isotopic measurements (δ13C) were made using a Gas Bench II and Thermo Electron Delta Plus mass spectrometer
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset-specific Instrument Name	Gas Bench II
Generic Instrument Name	Thermo-Fisher Scientific Gas Bench II
Dataset-specific Description	Stable carbon isotopic measurements (δ13C) were made using a Gas Bench II and Thermo Electron Delta Plus mass spectrometer
Generic Instrument Description	An on-line gas preparation and introduction system for isotope ratio mass spectrometry that is designed for high precision isotope and molecular ratio determination of headspace samples, including water equilibration, carbonates and atmospheric gases. The instrument allows for the use of a dual viscous flow inlet system of repetitive measurements of sample and standard gas on a continuous flow isotope ratio mass spectrometer (CF-IRMS) system. The sample volume is the sample vial (instead of a metal bellows), and the reference gas volume is a pressurized gas tank. The instrument consists of a user programmable autosampler, a gas sampling system, a maintenance-free water removal system, a loop injection system, an isothermal gas chromatograph (GC), an active open split interface, a reference gas injection system with three reference ports, and one or two optional LN2 traps for cryofocusing. The gas sampling system includes a two port needle which adds a gentle flow of He into the sample vial, diluting and displacing sample gas. Water is removed from the sample gas through diffusion traps. The loop injector aliquots the sample gas onto the GC column, which separates the molecular species. The reference gas injection system allows accurate referencing of each sample aliquot to isotopic standards. The system can be used with several options including a carbonate reaction kit that allows injection of anhydrous phospohric acid into sample vials.

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Deployments

RB1503_leg1

Website	https://www.bco-dmo.org/deployment/787503
Platform	NOAA Ship Ronald H. Brown
Report	http://dx.doi.org/10.7942/C2WC7C
Start Date	2015-04-10
End Date	2015-05-12
Description	2015 P16N, Climate Variability and Predictability (CLIVAR), R/V Ronald H Brown, RB1503, leg 1. Cruise aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown (the Brown) acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). Expocode: 33RO20150525. The Cruise Report and additional data from the cruise are available from CCHDO: Cross, J. and Siedlecki, S. (2015). Hydrographic Cruise 33RO20150410, exchange version. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/33RO20150410. Access date 2021-05-21. CCHDO cruise DOI: 10.7942/C2WC7C Cruise information is also available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RB1503

33RO20150524

Website	https://www.bco-dmo.org/deployment/924870
Platform	NOAA Ship Ronald H. Brown
Start Date	2015-05-24
End Date	2015-05-25

33RO20150523

Website	https://www.bco-dmo.org/deployment/924869
Platform	NOAA Ship Ronald H. Brown
Start Date	2015-05-23
End Date	2015-05-24

33RO20150526

Website	https://www.bco-dmo.org/deployment/924871
Platform	NOAA Ship Ronald H. Brown
Start Date	2015-05-26
End Date	2015-05-27

33RO20150527

Website	https://www.bco-dmo.org/deployment/924872
Platform	NOAA Ship Ronald H. Brown
Start Date	2015-05-27
End Date	2015-05-28

RB1606_leg1

Website	https://www.bco-dmo.org/deployment/821809
Platform	NOAA Ship Ronald H. Brown
Report	http://dx.doi.org/10.7942/C21T0F
Start Date	2016-11-19
End Date	2016-12-24
Description	P18 US GO-SHIP Reoccupation Leg 1 (2016/2017). Leg 1 of the 2016/2017 occupation of the P18 hydrographic section aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). The Cruise Report and additional data from the cruise are available from CCHDO: Sonnerup, R., Carter, B., Purkey, S., and Bourbonnais, A. (2017) . Hydrographic Cruise: 33RO20161119, exchange version. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/33RO20161119. Access date 2021-05-21. CCHDO cruise DOI: 10.7942/C21T0F

RB1606_leg2

Website	https://www.bco-dmo.org/deployment/821815
Platform	NOAA Ship Ronald H. Brown
Report	http://dx.doi.org/10.7942/C21T0F
Start Date	2016-12-30
End Date	2017-02-03
Description	P18 US GO-SHIP Reoccupation Leg 2 (2016/2017). Leg 2 or the 2016/2017 occupation of the P18 hydrographic section aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). The Cruise Report and additional data from the cruise are available from CCHDO: Sonnerup, R., Carter, B., Purkey, S., and Bourbonnais, A. (2017). Hydrographic Cruise: 33RO20161119, exchange version. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/33RO20161119. Access date 2021-05-21. CCHDO cruise DOI: 10.7942/C21T0F

RB1803

Website	https://www.bco-dmo.org/deployment/852241
Platform	NOAA Ship Ronald H. Brown
Report	http://dx.doi.org/10.7942/C25H2B
Start Date	2018-04-23
End Date	2018-06-06
Description	IO7N GO-SHIP/CO2 Repeat Hydrography Cruise aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). Expocode 33RO20180423. Ports: Durban (South Africa) to Victoria (Seychelles) The Cruise Report and additional data from the cruise are available from CCHDO: Volkov, D. and Menezes, V. (2018). Hydrographic Cruise 33RO20180423, exchange version. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/33RO20180423. Access date 2021-05-21. CCHDO cruise DOI: 10.7942/C25H2B

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Project Information

Cycling of Dissolved Organic Matter in the Pacific and Indian Oceans Using Radiocarbon (DOC 14C and 13C)

Coverage: East Pacific, Southern, and Indian oceans

NSF Award Abstract:
Controls on the Aging of Marine Dissolved Organic Carbon

Most of the organic carbon in ocean water is in the dissolved form. Surprisingly, the age of this dissolved organic carbon is thousands of years old, even though it is thought to form during photosynthesis in the surface ocean. One explanation for the age of this carbon is the amount of time that it takes for carbon to circulate through the ocean. Investigators at the University of California Irvine (UCI) will investigate the aging of dissolved organic carbon in the Pacific, Southern and Indian oceans using C-14 isotopes. This work is important for knowing how carbon produced from human activities will be distributed on Earth in the future. This project will support the work of two graduate and two undergraduate students, providing hands-on experience that will prepare them for careers as scientists and educators. Both graduate students will be involved in a variety of educational activities. They will also help teach a short course on applications of C-14 in Ecology and Earth System Science for graduate students, technicians, postdocs and researchers during summer. UCI is a Hispanic-serving institution (27% of undergraduates identify as Hispanic), and 60% of students who attend UCI are first generation family representatives.

This study will examine the concentration, isotopic (14C, 13C) and molecular composition of dissolved organic carbon (DOC) in depth profiles from the Pacific, Southern and Indian Oceans. This information will help to determine the main controls on DOC cycling in the world’s oceans. The project will test the hypothesis that circulation is the primary control on DOC cycling in the deepest water (>3500 meters). The research will also investigate two alternative processes that could influence the age of DOC in deep water (2000-3000 meters): (1) dissolution of surface-derived particles and (2) input of ancient carbon from hydrothermal vents and flanks. Spectroscopic and spectrometric measurements designed to characterize a portion of the DOC will be performed on surface and deep water. Results will be incorporated into an inverse model of DOC cycling to determine the main processes controlling the DOC cycle in the ocean. DOC may serve as a sink for excess carbon dioxide produced from human activities and the size of the refractory DOC pool in the ocean could increase as circulation slows. Measuring the 14C age of DOC in the surface and deep ocean is important for understanding how the global carbon cycle will change as the Earth's climate shifts.

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-1951073

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