

Total DOC 14C from samples collected from the North Pacific Subtropical Gyre and Central North Atlantic

Website: <https://www.bco-dmo.org/dataset/811503>

Data Type: Cruise Results

Version: 1

Version Date: 2020-05-14

Project

» [The Microbial Nitrogen Pump: Coupling 14C and Compound-specific Amino Acids to Understand the Role of Microbial Transformations in the Refractory Ocean DON Pool](#) (DON Microbial Nitrogen Pump)

Contributors	Affiliation	Role
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Abstract

Total DOC 14C from samples collected from the North Pacific Subtropical Gyre and Central North Atlantic. These data were published in Broek et al. (2019) and Broek et al. (2017).

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Coverage

Spatial Extent: N:31.6667 E:-64.1667 S:22.75 W:-158

Temporal Extent: 2014 - 2019

Dataset Description

Total DOC 14C from samples collected from the North Pacific Subtropical Gyre and Central North Atlantic. These data were published in Broek et al. (2019) and Broek et al. (2017).

Methods & Sampling

Sample Collection

Samples were collected on two separate research cruises aboard the R/V Kilo Moana in August 2014 and May 2015. Sampling was conducted at the Hawaii Ocean Time Series Station ALOHA (A Long-Term Oligotrophic Habitat Assessment; 22° 45'N, 158° 00'W) and the Bermuda Atlantic Time Series Site (BATS; 31° 40'N, 64° 10'W) in the Central North Atlantic.

Surface water was sampled via the vessel's underway sampling system. The intake pipe is situated on the

forward starboard hull section of the vessel approximately 7.5 m below the waterline. The laboratory seawater tap was allowed to flush for 2 hours prior to each sampling. Seawater was pre-filtered through 53 μm Nitex mesh, and pumped through a 0.2 μm polyethersulfone (PES) cartridge filter (Shelco Filters, Micro Vantage, water grade, 9.75" DOE, polycarbonate housing) prior to introduction to the ultrafiltration system. Large volume subsurface water samples were collected using successive casts of a rosette equipped with 24 x 12 L Niskin bottles.

Tangential-Flow Ultrafiltration

The main UF system was constructed using a modified design of the system described in Roland et al. (2009), and expanded on by Walker et al. (2011). Briefly, the system was comprised of four-spiral wound PES UF membranes, having a nominal molecular weight cut off of 2.5 kD (GE Osmonics GH2540F30, 40-inch long, 2.5-inch diameter). The membranes were mounted in stainless steel housings, plumbed in parallel to a 100 L fluorinated HDPE reservoir, with flow driven by a 1.5 HP stainless steel centrifugal pump (Goulds Pumps, Stainless steel centrifugal pump, NPE series 1 x 1-1/4 -6, close coupled to a 1-1/2 horsepower, 3500 RPM, 60 Hz, 3 phase, Open Drip Proof Motor; 5.75 Inch Impeller Diameter, Standard Viton Mechanical Seals). All other system plumbing components contacting seawater were composed of polytetrafluoroethylene (PTFE) or stainless steel.

The system was run continuously at a membrane pressure of 40-50 psi, resulting in permeation flow rates of 1-2 L/min, depending primarily on the temperature of the feed seawater. Sample water was fed into the system using peristaltic pumps and platinum cured silicone tubing at a flow rate matched to the system permeation rates to ensure a constant system volume of approximately 100 L.

Seawater samples of 3000-4000 L were concentrated to a final retentate volume of 15-20 L, drained from the system into acid washed PC carboys and refrigerated (less than 12 hours at 2°C) until the next phase of processing. Samples requiring storage for longer than 12 hours were frozen and stored at -20°C. The UF system was then reconfigured to a smaller volume system, consisting of a single membrane having a smaller nominal molecular weight cutoff (GE Osmonics GE2540F30, 40-inch long, 2.5-inch diameter, 1 kD MWCO), and a 2.5 L PES reservoir for further volume reduction and subsequent salt removal (diafiltration). Using this smaller system, samples were reduced to 2-3 L under lower pressure (25 psi, permeation rate = 250 mL/min). Samples were then diafiltered using 40 L of 18.2 M Ω Milli-Q (ultrapure) water, adding water to the sample retentate reservoir at the same rate of membrane permeation. Reduced and diafiltered samples were stored in acid washed PC bottles at -20°C for transport. In the laboratory, samples were further concentrated by rotary evaporation using pre-combusted glassware (450 °C, 5 h). A molecular sieve and a liquid nitrogen trap were placed between the vacuum pump and rotovap chamber to ensure no contamination of isolated material by back streaming of hydrocarbons or other contaminants. After reduction to 50-100 mL, samples were dried to powder via centrifugal evaporation in PTFE centrifuge tubes. Dry material was homogenized with an ethanol cleaned agate mortar and pestle, transferred to pre-combusted glass vials, and stored in a desiccation cabinet until subsequent analyses.

Solid Phase Extraction

Solid phase extraction was conducted using PPL sorbent (Agilent Bondesil PPL, 125 μm particle size, part # 5982-0026) following the general recommendations of Dittmar et al. (2008) and Green et al. (2014), including loading rates, seawater to sorbent ratios, and elution volumes and rates. Between 300 and 500 g of sorbent was used for each extraction, depending on sample volume and DOC concentration, with average loading of 4.2 ± 1.5 L UF permeate per g sorbent representing 1.9 ± 0.6 mg DOC per g sorbent or a DOC to sorbent mass ratio of $1:600 \pm 200$. This is in line with both the recommendations of Dittmar et al. (2008) (maximum loading = 10 L seawater per g sorbent) and Li et al. (2016) (DOC to sorbent ratio = 1:800). Permeate from the UF system was fed through PTFE tubing to a pair of 200 L HDPE barrels. The permeate water was then acidified in 200 L batches to pH 2 by adding 400 mL of 6 M HCl (Fisher Chemical, ACS Plus grade). Batch samples were mixed continuously during collection, acidification, and loading using a peristaltic pump and platinum cured Si and PTFE tubing positioned at the surface and bottom of each barrel. Acidified batches of seawater permeate were then pumped through the SPE sorbent. SPE flow rates were matched to UF permeation rates (1-2 L/min), such that a pair of 200 L barrels allowed one barrel to be filled while the contents of the other was passed through the sorbent.

Three custom SPE column configurations were used to contain the sorbent material. The column configuration was modified several times for ease of use on subsequent cruises. First, an open, gravity fed, large (49 mm ID x 1000 mm length, 1875 mL volume) glass chromatography column with 40 μm fritted disk and PTFE stopcock (Kimble-Chase, Kontes) was used. Next, we tested a custom built high-pressure SS housing (10 cm ID x 3.5 cm bed height), and finally a parallel combination of 2 medium-pressure glass chromatography columns (Kimble-Chase, Kontes, Chromaflex LC, 4.8 mm ID x 30 cm, 543 mL volume). While all designs proved to be functionally equivalent, the latter parallel combination of 2 medium-pressure glass columns ultimately provided

the best configuration in order to maximize flow rates while simultaneously optimizing the ratio of sorbent bed height to loading speed. Further, the commercial availability and ease of use associated with this configuration made it our preferred design.

Following sample loading, the SPE sorbent was desalted with 6 L of pH 2 ultrapure water at a low flow rate (250-300 mL/min). After desalting, the SPE sorbent was transferred to a glass chromatography column (75 mm ID x 300 mm length, 40 μ m fritted disk, PTFE stopcock) with ultrapure water rinses to ensure quantitative transfer. Isolated organic material was then eluted from the sorbent with five to six 500 mL additions of methanol. The eluted methanol solution was stored in pre-combusted amber glass bottles at -20°C for transport. Similar to UF samples, the methanol-eluted solutions were first reduced by rotary evaporation to 50-100 mL. Samples were then dried to powder via centrifugal evaporation in PTFE centrifuge tubes. Dry material was homogenized with an ethanol cleaned agate mortar and pestle, transferred to pre-combusted glass vials, and stored in a desiccation cabinet until elemental and isotopic analyses.

Elemental and Isotopic Analyses

Natural abundance radiocarbon ($\Delta^{14}\text{C}$) determinations of all isolated fractions were performed at the Lawrence Livermore National Laboratory, Center for Accelerator Mass Spectrometry (LLNL-CAMS) by AMS following standard graphitization procedures (Santos et al., 2007; Vogel et al., 1984). The $\Delta^{14}\text{C}$ signature of total seawater DOC ($< 0.2 \mu\text{m}$) was determined by UV-oxidation and AMS at the UC Irvine Keck Carbon Cycle AMS Lab (Beaupré et al., 2007; Druffel et al., 2013; Walker et al., 2016). Results are reported as age-corrected $\Delta^{14}\text{C}$ (‰) for geochemical samples and have been corrected to the date of collection and are reported in accordance with conventions set forth by Stuiver and Polach (1977). Isotopic ^{14}C results are reported as background and ^{13}C corrected fraction modern (Fm), $\Delta^{14}\text{C}$, and conventional radiocarbon age (ybp).

Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope ratios were determined via elemental analyzer isotope ratio mass spectrometry (EA-IRMS) at the University of California, Santa Cruz, Stable Isotope Laboratory (UCSC-SIL; <http://emerald.ucsc.edu/~silab/>). Approximately 1 mg of each dry isolated DOM sample was weighed into tin capsules (Costec, 5 x 9 mm) for analysis. EA-IRMS analysis was conducted using a Carlo Erba CHNS-O EA1108-elemental analyzer interfaced via a ConFlo III device with a ThermoFinnigan Delta Plus XP isotope ratio mass spectrometer (Thermo Fisher Scientific). Standards, EA-IRMS protocols, and correction routines followed standard UCSC-SIL protocols. Analytical uncertainties of $n=3$ replicate measurements of isotopic standards ranged from ± 0.05 to 0.1‰ for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Carbon to nitrogen elemental ratios were similarly determined by elemental analysis. The presented ratios are atomic ratios (C/N) normalized to the mass of C and N, but have been abbreviated as C/N throughout.

Data Processing Description

^{14}C Results are reported as age-corrected $\Delta^{14}\text{C}$ (‰) for geochemical samples and have been corrected to the date of collection and are reported in accordance with conventions set forth by Stuiver and Polach (1977).

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Data Files

File
14C_total.csv (Comma Separated Values (.csv), 947 bytes) MD5:f4b635eb62ecd3f880dd5c25da9d6897
Primary data file for dataset ID 811503

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Related Publications

Beaupré, S. R., Druffel, E. R. M., & Griffin, S. (2007). A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon. *Limnology and Oceanography: Methods*, 5(6), 174-184. doi:[10.4319/lom.2007.5.174](https://doi.org/10.4319/lom.2007.5.174)

- Broek, T. A. B., Bour, A. L., Ianiri, H. L., Guilderson, T. P., & McCarthy, M. D. (2019). Amino acid enantiomers in old and young dissolved organic matter: Implications for a microbial nitrogen pump. *Geochimica et Cosmochimica Acta*, 247, 207–219. doi:[10.1016/j.gca.2018.12.037](https://doi.org/10.1016/j.gca.2018.12.037)
Results
- Broek, T. A. B., Walker, B. D., Guilderson, T. P., & McCarthy, M. D. (2017). Coupled ultrafiltration and solid phase extraction approach for the targeted study of semi-labile high molecular weight and refractory low molecular weight dissolved organic matter. *Marine Chemistry*, 194, 146–157.
doi:[10.1016/j.marchem.2017.06.007](https://doi.org/10.1016/j.marchem.2017.06.007)
Results
- 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](https://doi.org/10.4319/lom.2008.6.230)
Methods
- Druffel, E. R. M., Griffin, S., Walker, B. D., Coppola, A. I., & Glynn, D. S. (2013). Total Uncertainty of Radiocarbon Measurements of Marine Dissolved Organic Carbon and Methodological Recommendations. *Radiocarbon*, 55(3), 1135–1141. doi:[10.1017/S0033822200048049](https://doi.org/10.1017/S0033822200048049)
<https://doi.org/10.1017/S0033822200048049>
Methods
- Green, N. W., Perdue, E. M., Aiken, G. R., Butler, K. D., Chen, H., Dittmar, T., ... Stubbins, A. (2014). An intercomparison of three methods for the large-scale isolation of oceanic dissolved organic matter. *Marine Chemistry*, 161, 14–19. doi:[10.1016/j.marchem.2014.01.012](https://doi.org/10.1016/j.marchem.2014.01.012)
Methods
- Li, Y., Harir, M., Lucio, M., Kanawati, B., Smirnov, K., Flerus, R., ... Hertkorn, N. (2016). Proposed Guidelines for Solid Phase Extraction of Suwannee River Dissolved Organic Matter. *Analytical Chemistry*, 88(13), 6680–6688. doi:[10.1021/acs.analchem.5b04501](https://doi.org/10.1021/acs.analchem.5b04501)
Methods
- Roland, L. A., McCarthy, M. D., Peterson, T. D., & Walker, B. D. (2009). A large-volume microfiltration system for isolating suspended particulate organic matter: fabrication and assessment versus GFF filters in central North Pacific. *Limnology and Oceanography: Methods*, 7(1), 64–80. doi:[10.4319/lom.2009.7.64](https://doi.org/10.4319/lom.2009.7.64)
Methods
- Santos, G. M., Southon, J. R., Griffin, S., Beaupre, S. R., & Druffel, E. R. M. (2007). Ultra small-mass AMS 14C sample preparation and analyses at KCCAMS/UCI Facility. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 259(1), 293–302. doi:[10.1016/j.nimb.2007.01.172](https://doi.org/10.1016/j.nimb.2007.01.172)
Methods
- Stuiver, M., & Polach, H. A. (1977). Discussion Reporting of 14C Data. *Radiocarbon*, 19(3), 355–363. doi:[10.1017/S0033822200003672](https://doi.org/10.1017/S0033822200003672) <https://doi.org/10.1017/S0033822200003672>
Methods
- Vogel, J. S., Southon, J. R., Nelson, D. E., & Brown, T. A. (1984). Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 5(2), 289–293. doi:[10.1016/0168-583X\(84\)90529-9](https://doi.org/10.1016/0168-583X(84)90529-9) [https://doi.org/10.1016/0168-583X\(84\)90529-9](https://doi.org/10.1016/0168-583X(84)90529-9)
Methods
- Walker, B. D., Beaupré, S. R., Guilderson, T. P., Druffel, E. R. M., & McCarthy, M. D. (2011). Large-volume ultrafiltration for the study of radiocarbon signatures and size vs. age relationships in marine dissolved organic matter. *Geochimica et Cosmochimica Acta*, 75(18), 5187–5202. doi:[10.1016/j.gca.2011.06.015](https://doi.org/10.1016/j.gca.2011.06.015)
Methods
- Walker, B. D., Griffin, S., & Druffel, E. R. M. (2016). Effect of Acidified Versus Frozen Storage on Marine Dissolved Organic Carbon Concentration and Isotopic Composition. *Radiocarbon*, 59(3), 843–857. doi:[10.1017/rdc.2016.48](https://doi.org/10.1017/rdc.2016.48) <https://doi.org/10.1017/RDC.2016.48>
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Related Datasets

Replaces Old Versions

McCarthy, M., & Guilderson, T. (2017). Recovery parameters, isotopic composition, and elemental composition of HMW and LMW DOM collected in the North Pacific Subtropical Gyre on R/V Kilo Moana (KM1506, KM1515) during 2015. Biological and Chemical Oceanography Data Management Office. doi:[10.1575/1912/bco-dmo.711831.1](https://doi.org/10.1575/1912/bco-dmo.711831.1)

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Parameters

Parameter	Description	Units
location	Sample collection location. HOT = Hawaii Ocean Time Series station ALOHA (22° 45'N, 158° 00'W) in North Pacific Subtropical Gyre (NPSG); BATS = Hawaii Ocean Time Series station ALOHA (22° 45'N, 158° 00'W) in North Pacific Subtropical Gyre (NPSG)	unitless
year	Year of sample collection; format: YYYY	unitless
season	Season of sample collection	unitless
sample_type	DOM Fraction	unitless
depth	Sample depth	meters (m)
UCIAMS_num	UCI Keck AMS analysis#	unitless
Fm	14C derived fraction modern	unitless
Fm_stdev	Standard deviation of Fm	unitless
d14C	14C/12C isotopic ratio	permil (‰)
d14C_stdev	Standard deviation of d14C	permil (‰)
C14_age	14C derived age	years before present
C14_age_stdev	Standard deviation of C14_age	years before present

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Instruments

Dataset-specific Instrument Name	Carlo Erba CHNS-O EA1108-elemental analyzer
Generic Instrument Name	Elemental Analyzer
Generic Instrument Description	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

Dataset-specific Instrument Name	ThermoFinnigan Delta Plus XP isotope ratio mass spectrometer (Thermo Fisher Scientific)
Generic Instrument Name	Isotope-ratio 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	rosette equipped with 24 x 12 L Niskin bottles
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	underway sampling system
Generic Instrument Name	Pump - Surface Underway Ship Intake
Generic Instrument Description	The 'Pump-underway ship intake' system indicates that samples are from the ship's clean water intake pump. This is essentially a surface water sample from a source of uncontaminated near-surface (commonly 3 to 7 m) seawater that can be pumped continuously to shipboard laboratories on research vessels. There is typically a temperature sensor near the intake (known as the hull temperature) to provide measurements that are as close as possible to the ambient water temperature. The flow from the supply is typically directed through continuously logged sensors such as a thermosalinograph and a fluorometer. Water samples are often collected from the underway supply that may also be referred to as the non-toxic supply. Ideally the data contributor has specified the depth in the ship's hull at which the pump is mounted.

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Deployments

KM1506

Website	https://www.bco-dmo.org/deployment/636095
Platform	R/V Kilo Moana
Start Date	2015-05-03
End Date	2015-05-12
Description	Original cruise data are available from the NSF R2R data catalog

KM1515

Website	https://www.bco-dmo.org/deployment/657964
Platform	R/V Kilo Moana
Start Date	2015-08-15
End Date	2015-09-12

AE1520

Website	https://www.bco-dmo.org/deployment/811215
Platform	R/V Atlantic Explorer
Start Date	2015-08-21
End Date	2015-08-25

AE1608

Website	https://www.bco-dmo.org/deployment/811286
Platform	R/V Atlantic Explorer
Start Date	2016-05-03
End Date	2016-05-11

KM1418

Website	https://www.bco-dmo.org/deployment/636002
Platform	R/V Kilo Moana
Start Date	2014-08-29
End Date	2014-09-11
Description	Original cruise data are available from the NSF R2R data catalog

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Project Information

The Microbial Nitrogen Pump: Coupling ^{14}C and Compound-specific Amino Acids to Understand the Role of Microbial Transformations in the Refractory Ocean DON Pool (DON Microbial Nitrogen Pump)

Coverage: North Pacific Subtropical Gyre (HOT station), North Atlantic Subtropical Gyre (BATS time series station), California Margin

Dissolved organic nitrogen is one of the most important - but perhaps least understood - components of the modern ocean nitrogen cycle. While dissolved organic nitrogen represents a main active reservoir of fixed and seemingly biologically-available nitrogen, at the same time most of ocean's dissolved organic nitrogen pool is also apparently unavailable for use by organisms. Recently, the idea of the "Microbial Carbon Pump" has emerged, providing a renewed focus on microbes as primary agents for the formation of biologically-available dissolved material. However, the role that microbes play in transformation of biologically-available dissolved organic nitrogen is still lacking. In order to fill gaps in this knowledge, researchers from the University of California Santa Cruz will apply a series of new analytical approaches to test the role of microbial source and transformation in formation of the ocean's biologically-available dissolved organic nitrogen pool. Results from this study will address one of the major unknowns of both chemical oceanography and the ocean nitrogen

cycle.

Broader Impacts:

This proposal will provide oceanographers new tools to test ideas of microbial organic matter sequestration in a world where the oceans are rapidly changing. High school, undergraduate, graduate and post-doctoral education will be furthered through active participation in lab, field, and data synthesis activities.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1358041

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