[DEPRECATED] 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

Website: https://www.bco-dmo.org/dataset/711831
Data Type: Cruise Results
Version: 1
Version Date: 2017-08-01

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
This version of this dataset has been deprecated and replaced by multiple datasets. Please use the new datasets, which have the following DOIs and metadata landing pages: 10.26008/1912/bco-dmo.811368.1 (https://www.bco-dmo.org/dataset/811368); 10.26008/1912/bco-dmo.811204.1 (https://www.bco-dmo.org/dataset/811204); 10.26008/1912/bco-dmo.811580.1 (https://www.bco-dmo.org/dataset/811580); 10.26008/1912/bco-dmo.811547.1 (https://www.bco-dmo.org/dataset/811547); 10.26008/1912/bco-dmo.811503.1 (https://www.bco-dmo.org/dataset/811503); 10.26008/1912/bco-dmo.811458.1 (https://www.bco-dmo.org/dataset/811458). This dataset contains: Recovery parameters, isotopic composition (d15N, d13C, D14C), and elemental composition (C:N) of HMW and LMW DOM collected from the North Pacific Subtropical Gyre.

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Coverage

Temporal Extent: 2014-08-29 - 2015-05-10

Dataset Description

This version of this dataset has been deprecated and replaced by multiple datasets. Please use the new datasets, which have the following DOIs and metadata landing pages:
10.26008/1912/bco-dmo.811368.1 (https://www.bco-dmo.org/dataset/811368); 10.26008/1912/bco-dmo.811204.1 (https://www.bco-dmo.org/dataset/811204); 10.26008/1912/bco-dmo.811580.1

(https://www.bco-dmo.org/dataset/811580); 10.26008/1912/bco-dmo.811547.1 (https://www.bco-dmo.org/dataset/811547); 10.26008/1912/bco-dmo.811503.1 (https://www.bco-dmo.org/dataset/811503); 10.26008/1912/bco-dmo.811458.1 (https://www.bco-dmo.org/dataset/811458).

This dataset contains: Recovery parameters, isotopic composition (d15N, d13C, D14C), and elemental composition (C:N) of HMW and LMW DOM collected from the North Pacific Subtropical Gyre.

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 deg 45'N, 158 deg 00'W).

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 um Nitex mesh, and pumped through a 0.2 um 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 12 x 24 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 2C) until the next phase of processing. Samples requiring storage for longer than 12 hours were frozen and stored at -20 deg 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 MΩ 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 deg C for transport. In the laboratory, samples were further concentrated by rotary evaporation using pre-combusted glassware (450 deg 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 um 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 +/- 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 um 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 um 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 deg 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.

Total DOM: Subsamples for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentration measurements were collected into pre-combusted 40 mL borosilicate glass vials following 0.2 um-filtration. Samples were stored at -20 deg C until analysis. Subsamples for [DOC] and [TDN] were also taken from the UF system permeate to evaluate mass balance. An "integrated" permeate sample (e.g., Benner et al., 1997) was prepared by sampling and combining equal volumes (100 mL) collected at constant time intervals throughout the ultrafiltration. DOC and TDN concentration measurements were made using the high temperature oxidation method with a Shimadzu TOC-V in the Carlson lab at UCSB (https://labs.eemb.ucsb.edu/carlson/craig/services). DOC concentration measurement errors represent the standard deviation of n=3 replicate measurements. Total DON concentrations were determined by subtracting the sum of dissolved inorganic nitrogen (DIN) species (nitrate, nitrite, ammonia) from TDN. DIN concentrations were determined using a Lachat QuickChem 8000 Flow Injection Analyzer. Ammonia concentrations were below the limit of quantification (0.36 uM) for all samples using QuickChem Method 31-107-06-1-B. Nitrate and nitrite concentrations were measured as the sum of the two analytes using QuickChem Method 31-107-04-1-C. The limit of detection for [NO3+NO2] using this method was 0.5 uM and the average precision of replicate standard measurements was +/- 1.4 uM. In the case of [DON], measurement errors represent the propagated analytical uncertainty from the subtraction of [DIN] from [TDN]. DOC concentrations measurements were also determined via UV oxidation, cryogenic purification and manometric determination at UC Irvine.

Elemental and Isotopic Analyses: znatural abundance radiocarbon (D14C) 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 D14C signature of total seawater DOC (< 0.2 um) 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., 2016b). Results are reported as age-corrected D14C (o/oo) 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 14C results are reported as background and 13C corrected fraction modern (Fm; Supplemental Table 1), D14C, and conventional radiocarbon age (ybp) (Table 1).

Stable carbon (d13C) and nitrogen (d15N) 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 0.1o/oo for both d13C and d15N. 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

14C Results are reported as age-corrected D14C (0/00) 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).

Microsoft Excel 2013.

BCO-DMO Data Processing Notes:
-reformatted column names to comply with BCO-DMO standards.
-removed second header line that contained units
-renamed all standard deviation columns to include info describing what they were the standard deviation of. For example: "DOC_stdev"
-May 2020: deprecated this version of dataset.

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Data Files

File
DOM.csv (Comma Separated Values (.csv), 4.12 KB) MD5:fb5002acfc1067a6a3c46fc6651afd9e Primary data file for dataset ID 711831

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Related Datasets

Replaced By New Versions

McCarthy, M., & Guilderson, T. (2020). C and N stable isotopes and elemental ratios of high and low molecular weight (HMW, LMW) DOM collected from the North Pacific Subtropical Gyre and Central North Atlantic determined by elemental analyzer isotope ratio mass spectrometry (EA-IRMS) (Version 1) [Data set]. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/BCO-DMO.811368.1 https://doi.org/10.26008/1912/bco-dmo.811368.1

McCarthy, M., & Guilderson, T. (2020). DOC and DON concentrations of waters collected from the North Pacific Subtropical Gyre and Central North Atlantic (Version 1) [Data set]. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/BCO-DMO.811204.1 https://doi.org/10.26008/1912/bco-dmo.811204.1

McCarthy, M., & Guilderson, T. (2020). HMW and LMW DOC recovery parameters from waters collected from the North Pacific Subtropical Gyre and Central North Atlantic (Version 1) [Data set]. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/BCO-DMO.811580.1 https://doi.org/10.26008/1912/bco-dmo.811580.1

McCarthy, M., & Guilderson, T. (2020). High and low molecular weight (HMW, LMW) DOC 14C collected from the North Pacific Subtropical Gyre and Central North Atlantic (Version 1) [Data set]. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/BCO-DMO.811547.1 https://doi.org/10.26008/1912/bco-dmo.811547.1

McCarthy, M., & Guilderson, T. (2020). Total DOC 14C from samples collected from the North Pacific Subtropical Gyre and Central North Atlantic (Version 1) [Data set]. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/BCO-DMO.811503.1 https://doi.org/10.26008/1912/bco-dmo.811503.1

McCarthy, M., &; Guilderson, T. (2020). Amino acid enantiomeric ratios (D/L) of high and low molecular weight

(HMW, LMW) DOM collected from the North Pacific Subtropical Gyre and Central North Atlantic (Version 1) [Data set]. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/BCO-DMO.811458.1 https://doi.org/10.26008/1912/bco-dmo.811458.1

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Parameters

Parameter	Description	Units
Sample_Type	Description of sample	unitless
Date_Collected	Date that sample was collected; YYYY/MM/DD	unitless
Depth	Water depth	meters
DOC	DOC concentration or recovery	micromoles per liter
DOC_stdev	DOC concentration or recovery standard deviation	micromoles per liter
DON	DON concentration or recovery	micromoles per liter
DON_stdev	DON concentration or recovery standard deviation	micromoles per liter
Volume	Water volume processed	liters
CF	UF Concentration factor	unitless
SPE_Loading	SPE sorbent:DOC ratio	gram per gram
Percent_Recovery_C	Percent recovery of DOC	percent
Percent_Recovery_N	Percent recovery of DON	percent
C_N_a	Atomic C:N ratio	unitless
C_N_a_stdev	Atomic C:N ratio standard deviation	unitless
CAMS_UCI_num	AMS analysis number	unitless
Fm	14C derived fraction modern	unitless

Fm_stdev	14C derived fraction modern standard deviation	unitless
D14C	14C/12C isotopic ratio	permil (0/00)
D14c_stdev	14C/12C isotopic ratio standard deviation	permil (0/00)
C14_age	14C derived age	years before present
C14_stdev	14C derived age standard deviation	years before present
d13C	13C/12C isotopic ratio	permil (0/00)
d13C_stdev	13C/12C isotopic ration standard deviation	permil (0/00)
d15N	15N/14N isotopic ratio	permil (0/00)
d15N_stdev	15N/14N isotopic ratio standard deviation	permil (0/00)

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Instruments

Dataset-specific Instrument Name	HVEC 10 MV Model FN Tandem Van de Graaff Accelerator
Generic Instrument Name	Accelerator Mass Spectrometer
Dataset-specific Description	Used to analyze 14C
Generic Instrument Description	An AMS measures "long-lived radionuclides that occur naturally in our environment. AMS uses a particle accelerator in conjunction with ion sources, large magnets, and detectors to separate out interferences and count single atoms in the presence of 1x1015 (a thousand million million) stable atoms, measuring the mass-to-charge ratio of the products of sample molecule disassociation, atom ionization and ion acceleration." AMS permits ultra low-level measurement of compound concentrations and isotope ratios that traditional alpha-spectrometry cannot provide. More from Purdue University: http://www.physics.purdue.edu/primelab/introduction/ams.html

Dataset-specific Instrument Name	Carlo Erba CHNS-O EA1108-elemental analyzer interfaced via a ConFlo III device
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	Used to analyze 13C, 15N, and C/N
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	Lachat Quick-Chem 8000 Flow injection analyzer
Generic Instrument Name	Flow Injection Analyzer
Dataset-specific Description	Used to analyze DIN
Generic Instrument Description	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

Dataset-specific Instrument Name	ThermoFinnigan Delta Plus XP isotope ratio mass spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Used to analyze 13C, 15N, and C/N
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	Shimadzu TOC-V
Generic Instrument Name	Shimadzu TOC-V Analyzer
Dataset-specific Description	Used to analyze DOC and TDN
Generic Instrument Description	A Shimadzu TOC-V Analyzer measures DOC by high temperature combustion method.

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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

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Project Information

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)

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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