Dissolved organic matter sulfur and carbon analysis of samples collected between 2010 and 2021 from various locations globally

Website: https://www.bco-dmo.org/dataset/927046
Data Type: Cruise Results, Other Field Results
Version: 1
Version Date: 2024-05-09

Project
» Resolving sources of marine DOM via novel sulfur isotope analyses (S isotopes in marine DOM)

Contributors	Affiliation	Role
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Abstract

The following dataset of SPE (solid phase extracted) DOM (dissolved organic matter) accompanies Phillips et al. 2022 (doi: 10.1073/pnas.2209152119). Our project sought to address the question of where long-lived organic molecules that are dissolved in the oceans come from, in particular molecules containing sulfur (S). Our approach was to measure the relative abundance of two stable sulfur isotopes (S-32 and S-34) in these molecules, which is technically very difficult due to the presence of million-fold higher sulfate ions in seawater. We developed a new preparatory chemistry to adequately isolate these organic molecules, and a new elemental analyzer/mass spectrometry method to measure their isotope abundances with high precision at trace levels. We conducted these S isotope measurements on 100 samples of dissolved organic matter (DOM) that had been previously collected by our collaborators from around the world (Northeast Pacific oxygen minimum zone, Northeast Pacific Shelf, North Pacific Gyre, San Pedro Basin, Caeté Estuary, South Pacific Gyre, and the North Sea). We also collected 2 dozen new samples from oceanographic stations in the North Pacific Gyre (Hawaii Ocean Timeseries) and North Atlantic Gyre (Bermuda Atlantic Time Series). The dataset includes 1) sample information such as sample ID, sample location, station name, collection depth (ranging from 0 to 4800 meters), latitude and longitude, month and year sampled (ranging from 2010 to 2021); 2) elemental analysis such as sulfur isotope values (δ34S), carbon (C) isotope values (δ13C), and C:S molar ratios; 3) physical parameters from collaborators' CTD analysis, such as oxygen, salinity, fluorescence, and temperature; and 4) chemical data from collaborators such as dissolved nitrate, phosphate, silicate, and calculated DOC (dissolved organic carbon) and DOS (dissolved organic sulfur) concentrations. Our data show that DOM molecules have (34S/32S) isotope ratios that are entirely consistent with being formed from ocean sulfate, and inconsistent with being formed by reactions of hydrogen sulfide in anoxic porewaters. This result negates one of the leading hypotheses for how long-lived DOM forms, i.e. by reactions in anoxic sediments. Instead, this sharpens our focus on understanding how relatively short-lived biomolecules in the surface ocean are transformed into long-lived DOM molecules.

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Coverage

Spatial Extent: **N**:53.74 **E**:7.7 **S**:-13 **W**:-158
Temporal Extent: 2010 - 2021

Dataset Description

Samples spanned basins and water depths, including the North Atlantic Gyre, Northeast Pacific oxygen minimum zone, Northeast Pacific Shelf, North Pacific Gyre, San Pedro Basin, Caeté Estuary, South Pacific Gyre, and the North Sea. Samples spanned depths of 0 to 4800 meters. Exact location data, including latitude, longitude, and collection depth are provided in the dataset. Most data in this dataset represent measurements of aliquots of archived samples from collaborators; these were collected on many different cruises, on many different dates, around the world. New samples represented in this dataset include: 12 samples collected at station HOT on the R/V Kilo Moana in November 2020 (KM2013) and 12 samples collected at station BATS in September 2020 (AE2014).

Methods & Sampling

Seawater samples (of ~5 to 20 liters (L) were collected from Niskin bottles into acid-washed polyethylene containers and filtered through a 0.80/0.45 micrometer (µm) capsule filter (AcroPak 500) prior to acidification to pH 2 with reagent grade 12 N hydrochloric acid. Samples were then stored at 4 degrees Celsius (°C) in the dark until back on shore. In the lab, dissolved organic carbon (DOC) concentrations were measured prior to solid phase extraction (SPE) via high-temperature combustion on a Shimadzu Total Organic Carbon Analyzer (Shimadzu Corp). Dissolved organic matter (DOM) was concentrated using SPE with Bond Elute PPL cartridges (Agilent; 1 gram, 6 milliliter (mL) size) following Dittmar et al. (2008). DOM samples were eluted in GC-grade methanol. Extracts were dried under a stream of N2 gas and transferred to 2 mL GC vials and then to 150 microliter (µL) glass inserts. Aliquots corresponding to ~4.5 micrograms (µg) sulfur (~350 µg DOC) were transferred in methanol from 2 mL GC vials into smooth-walled tin EA capsules (~ 2.9 millimeters (mm), OEA Laboratories). Methanol was evaporated at room temperature (~2 hours) prior to folding. Tin capsules containing dried DOM were folded closed with clean tweezers, loaded into an autosampler, and then combusted and analyzed by combustion elemental analyzer / isotope ratio mass spectrometer following Phillips et al. (2021).

Data Processing Description

Isotope data were recorded using Isodat v3.0 (Thermo Scientific). Isodat calibrates the integrated ion-current ratios against internal reference gas standards, and reports them as δ13C and δ34S values relative to the VPDB and VCDT isotopic scales, respectively. All δ values are reported as ‰ (permil, ppt) deviations from the relevant zero points. Subsequent data processing in spreadsheets included subtraction of capsule blanks, discarding outliers, linearity (peak size) correction, and further calibration to external standards. Sulfur isotope and concentration standards included a methionine working standard, seawater sulfate, and silver sulfide reference materials (IAEA S1, S2, S3). Additionally, a working standard of DOMSPE extracted in a large batch (~200 L) from the Scripps Institution of Oceanography (SIO) pier was run in at least triplicate with each sample set. C:S ratios were obtained by dividing corrected carbon and sulfur amounts (molar ratio), as calculated from EA peak areas. DOS concentrations were calculated as the product of measured total DOC concentration and DOMSPE C:S ratio.

Extracts supplied by collaborators were often limited by sample size to single or duplicate analyses, so we could not always estimate precision directly for each sample. Instead, uncertainties in isotopic compositions and C:S ratios for samples are reported using the SD of our DOM SIO pier standard measurements, divided by the square root of number of sample replicates analyzed. These SEs (1σ) were ≤0.2‰ for δ34S values and δ13C values and ≤6 for C:S ratios, and we therefore refer to DOSSPE concentrations as apparent or calculated throughout.

BCO-DMO Processing Description

- Imported original file "pnas.2209152119.sd01.xlsx" into the BCO-DMO system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Converted the Month column from string to numeric.
- Saved final file as "927046_v1_dom_sulfur_and_carbon_analysis.csv".

Problem Description

Note that not all samples have both carbon and sulfur isotopes.

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Data Files

File
927046_v1_dom_sulfur_and_carbon_analysis.csv(Comma Separated Values (.csv), 11.17 KB) MD5:b70bfd15971b07539e02658cc039d90c Primary data file for dataset ID 927046, version 1

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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

Phillips, A. A., White, M. E., Seidel, M., Wu, F., Pavia, F. F., Kemeny, P. C., Ma, A. C., Aluwihare, L. I., Dittmar, T., & Sessions, A. L. (2022). Novel sulfur isotope analyses constrain sulfurized porewater fluxes as a minor component of marine dissolved organic matter. Proceedings of the National Academy of Sciences, 119(41). https://doi.org/10.1073/pnas.2209152119
Results

Phillips, A. A., Wu, F., & Sessions, A. L. (2021). Sulfur isotope analysis of cysteine and methionine via preparatory liquid chromatography and elemental analyzer isotope ratio mass spectrometry. Rapid Communications in Mass Spectrometry, 35(4). Portico. https://doi.org/10.1002/rcm.9007
Methods

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Parameters

Parameter	Description	Units
Sample_ID	Sample ID number	unitless
Sample_Location	Location where sample was collected	unitless
Station	Station number where sample was collected	unitless
Depth	Depth of sample collection	meters (m)

Latitude	Latitude of sample collection; positive values = North	decimal degrees
Longitude	Longitude of sample collection; positive values = East	decimal degrees
Year	4-digit year of sample collection	unitless
Month	2-digit month of sample collection	unitless
d34S	delta 34S; ratio of sulfur 34 relative to sulfur 32	per mil (‰)
n_d34S	Number of replicates used to determine d34S	unitless
std_error_d34S	Standard error of d34S	per mil (‰)
d13C	delta 13C; ratio of stable isotopes 13C:12C	per mil (‰)
n_d13C	Number of replicates used to determine d13C	unitless
std_error_d13C	Standard error of d13C	per mil (‰)
C_to_S_ratio	C:S ratio (molar); determined from SPE extracts	unitless
n_C_to_S_ratio	Number of replicates used to determine C:S	unitless
std_error_C_to_S_ratio	Standard error of C_to_S_ratio	unitless
Oxygen	Oxygen	micromolar (uM)
Salinity	Salinity	psu
Flourescence	Fluorescence	relative fluorescence units
Temperature	Water temperature	degrees Celsius
Nitrate	Nitrate	micromolar (uM)
Phosphate	Phosphate	micromolar (uM)

Silicate	Silicate	micromolar (uM)
DOC	Dissolved organic carbon	micromolar (uM)
DOS	Dissolver organic sulfur; DOS is calculated from DOC concentrations (measured)	nanomolar (nM)

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Instruments

Dataset-specific Instrument Name	ConFlo IV Universal Interface
Generic Instrument Name	Continuous Flow Interface for Mass Spectrometers
Dataset-specific Description	SPE extracts were analyzed for their C and S concentrations and stable isotope compositions (δ13C and δ34S) via combustion elemental analyzer (EA) / isotope ratio mass spectrometry (IRMS). The system comprised a Thermo Scientific Flash EA IsoLink CN, coupled to a Delta V Plus IRMS via a ConFlo IV Universal Interface. The EA was configured with dual columns (combustion: WO3 over Cu; reduction: Cu metal) and a temperature-programmable GC column oven that allows both CO2 and SO2 to be eluted in the same run, as described by Phillips et al. (2021). Due to the high C:S molar ratios of DOM, CO2 was diluted by 88.4% following combustion via the ConFlo. Urea standards were run at the same settings to account for any possible fractionation of 13C by this dilution.
Generic Instrument Description	A Continuous Flow Interface connects solid and liquid sample preparation devices to instruments that measure isotopic composition. It allows the introduction of the sample and also reference and carrier gases. Examples: Finnigan MATConFlo II, ThermoScientific ConFlo IV, and Picarro Caddy. Note: This is NOT an analyzer

Dataset-specific Instrument Name	Thermo Scientific Flash EA IsoLink CN
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	SPE extracts were analyzed for their C and S concentrations and stable isotope compositions (δ13C and δ34S) via combustion elemental analyzer (EA) / isotope ratio mass spectrometry (IRMS). The system comprised a Thermo Scientific Flash EA IsoLink CN, coupled to a Delta V Plus IRMS via a ConFlo IV Universal Interface. The EA was configured with dual columns (combustion: WO3 over Cu; reduction: Cu metal) and a temperature-programmable GC column oven that allows both CO2 and SO2 to be eluted in the same run, as described by Phillips et al. (2021). Due to the high C:S molar ratios of DOM, CO2 was diluted by 88.4% following combustion via the ConFlo. Urea standards were run at the same settings to account for any possible fractionation of 13C by this dilution.
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	Delta V Plus IRMS
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	SPE extracts were analyzed for their C and S concentrations and stable isotope compositions (δ13C and δ34S) via combustion elemental analyzer (EA) / isotope ratio mass spectrometry (IRMS). The system comprised a Thermo Scientific Flash EA IsoLink CN, coupled to a Delta V Plus IRMS via a ConFlo IV Universal Interface. The EA was configured with dual columns (combustion: WO3 over Cu; reduction: Cu metal) and a temperature-programmable GC column oven that allows both CO2 and SO2 to be eluted in the same run, as described by Phillips et al. (2021). Due to the high C:S molar ratios of DOM, CO2 was diluted by 88.4% following combustion via the ConFlo. Urea standards were run at the same settings to account for any possible fractionation of 13C by this dilution.
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).

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Deployments

AE2014

Website	https://www.bco-dmo.org/deployment/927101
Platform	R/V Atlantic Explorer
Start Date	2020-09-16
End Date	2020-09-21
Description	More information from R2R: https://www.rvdata.us/search/cruise/AE2014

KM2013

Website	https://www.bco-dmo.org/deployment/927104
Platform	R/V Kilo Moana
Start Date	2020-11-17
End Date	2020-11-22
Description	See more information from R2R: https://www.rvdata.us/search/cruise/KM2013

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Project Information

Resolving sources of marine DOM via novel sulfur isotope analyses (S isotopes in marine DOM)

Coverage: Global oceans (survey)

NSF Award Abstract:
Organic molecules that contain sulfur in the ocean are poorly understood. Organic sulfur is abundant, and

likely helps stabilize dissolved organic matter, binds important trace metals, and provides trace nutrients to phytoplankton. However, it is not known whether organic sulfur molecules derive from biological processes, or from non-biological “sulfurization” reactions involving hydrogen sulfide (H2S). Existing knowledge predicts that the two pathways should generate very different -- and easily measurable -- distributions of sulfur isotopes (i.e., elemental sulfur with varied atomic mass). This study will use a new, highly sensitive method to measure the sulfur isotope values of dissolved organic molecules to distinguish between the two formation pathways. If successful, this method will be used to calculate how much dissolved organic sulfur results from each pathway. This project will provide an opportunity for a local high school student to engage in laboratory research during a one year internship, in partnership with a local all-girls high school. Additionally, the graduate student supported by this project will host a “Day in the Life” information session on the Women Doing Science Instagram social media platform. She will answer questions about oceanography and marine science careers from followers of this Instagram account while on a research cruise collecting samples for the project.

Several lines of evidence have recently converged to focus interest on marine dissolved organic sulfur (DOS), including the recognition that many heterotrophic bacteria require exogenous sources of ‘fixed’ organic sulfur; that organosulfur molecules -- particularly thiols -- play a major role in binding and sequestering trace metals; and that at 6700 Tg S, DOS is the second largest (after dissolved sulfate) sulfur pool in the oceans. Perhaps most importantly, DOS is thousands of years old, implying that it is not rapidly recycled and challenging the expectation that DOS derives mainly from labile biomolecules such as cysteine, methionine and dimethylsulfoniopropionate (DMSP). A plausible alternative is that abiotic sulfurization reactions with H2S from anoxic porewaters and the water column is a source of recalcitrant marine DOS. Distinguishing between these formation pathways is critical for understanding DOS dynamics, but thus far has been difficult. Based on existing data, it is thought that DOS formed from marine phytoplankton should have a sulfur isotope value (δ34S) near +20‰ (VCDT). Alternatively, DOS formed from abiotic sulfurization should be more variable, with average values of -20‰. Because these isotope values are distinct, they should be able to distinguish between the two pathways. The primary obstacle to analysis has been the low (µM) concentration of DOS, and difficulties associated with concentrating it in seawater. This study will use new analytical techniques developed at Caltech to measure the δ34S values of DOS at several locations, and compound-specific δ34S values for cysteine and methionine from the Bermuda (BATS) and Hawaii (HOT) time series locations. This work will contribute new information about the marine sulfur cycle, and improve understanding of the role that DOS plays in stabilizing carbon in the deep oceans.

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-2023687

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