

# Ramped pyrolysis oxidation (RPO) thermogram data of DOC from water samples collected during R/V Western Flyer Benthic-Pelagic Coupling expedition to Station M in the eastern Pacific Ocean in April 2018

**Website:** <https://www.bco-dmo.org/dataset/892564>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2023-03-24

## Project

» [Investigating the contribution of carotenoid degradation products to refractory dissolved organic matter \(DOM\)](#) (CDP in rDOM)

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## Abstract

The >5000-year radiocarbon age ( $^{14}\text{C}$ -age) of much of the  $630 \pm 30$  Pg C oceanic dissolved organic carbon (DOC) reservoir remains an enigma in the marine carbon cycle. The fact that DOC is significantly older than dissolved inorganic carbon (DIC) at every depth in the ocean forms the basis of our current framing of the marine DOC cycle where some component persists over multiple cycles of ocean mixing. As a result,  $^{14}\text{C}$ -depleted, aged DOC is hypothesized to be present as a uniform reservoir with a constant  $^{14}\text{C}$  signature and concentration throughout the water column. However, a key requirement of this model would be direct observations of DOC with similar  $^{14}\text{C}$  signatures in the surface and deep ocean. To address this data gap, we applied a thermal fractionation method to investigate DOC in water samples collected from a range of water column depths during the R/V Western Flyer cruise to Station M off the coast of central California in April 2018. This dataset presents thermogram data and evolved  $\text{CO}_2$  from ramped pyrolysis oxidation (RPO) procedures.

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## Coverage

**Spatial Extent:** Lat:34.833333 Lon:-123

**Temporal Extent:** 2018-04-19 - 2018-04-23

## Methods & Sampling

### Sample collection

Samples were collected during a cruise aboard the R/V Western Flyer to Station M off the coast of central California in April 2018 (34° 50'N, 123° 00'W; 4100 meters depth). 30 to 40 Liters of seawater were collected at five depths ranging from 45 to 3700 meters. Water was acidified to pH 2 using trace metal grade hydrochloric acid (HCl) and extracted using 1 g PPL cartridges (Bond Elut, Agilent). A fraction of the extracted PPL-DOM sample was dried extensively to remove methanol and then subjected to a 2 M acid hydrolysis.

### Field collection of samples

Samples were collected during a cruise aboard the R/V Western Flyer to Station M off the coast of central California in April 2018 (34° 50'N, 123° 00'W; 4100 meters depth). 30 to 40 Liters of seawater were collected at five depths ranging from 45 to 3700 meters. Water was then acidified to pH 2 using trace metal grade hydrochloric acid (HCl). Solid phase extraction columns (1g Bond Elut PPL cartridges by Agilent) were first activated overnight with liquid chromatography/mass spectrometry (LC/MS) grade methanol and then rinsed with LC/MS grade water, LC/MS grade methanol, and LC/MS grade water adjusted to pH 2 using trace metal grade HCl. The acidified seawater was passed through the PPL cartridges under gravitational pressure over 1-2 days. This PPL solid phase extraction method has been used extensively to isolate marine DOM (Dittmar et al., 2008; Petras et al., 2017 and more) and provides yields of 35-60%. Following acidification, the method preferentially extracts hydrophobic compounds but is also able to isolate some semi-polar compounds (Johnson et al., 2017; Petras et al., 2021) whose overall concentrations may change with depth. In addition to the relatively high yield, previous work has shown that  $\Delta^{14}\text{C}$  of PPL-DOM is similar to that of the bulk (Lechtenfeld et al., 2014; Lewis et al., 2021). Typically, 5L of seawater was extracted with one 1g PPL cartridge.

Before eluting the PPL resin, and immediately following the extraction, the cartridge was rinsed with three column volumes of pH 2 LC/MS grade water and dried under ultra-high purity nitrogen gas. Organic matter retained on the cartridge was then eluted with 10 mL of methanol/1 g PPL cartridge (PPL-DOM) and stored at -20 °C. Seawater for total organic carbon concentration [TOC] and dissolved organic carbon concentration [DOC] analysis (i.e., seawater pre-filtered through combusted Whatman corporation GF/F filters) was collected into combusted 40-mL borosilicate vials, immediately acidified to pH 2 using trace metal grade 12 N HCl (Fisher Scientific), capped with acid-washed vial caps with septa, and stored at room temperature until measurement. \*[Which of these steps captures the PPL DOM that is referenced in the data table?]\*

A fraction of the extracted PPL-DOM sample was dried extensively to remove methanol and then subjected to a 2 M acid hydrolysis. Briefly, the organic matter was transferred to an ampoule with 2 mL of 2 M hydrochloric acid and sealed under a nitrogen atmosphere before being placed in a drying oven at 80°C for 18 hours. Following hydrolysis, the sample was diluted with LC/MS grade water to pH 2 and then re-extracted onto a PPL cartridge as described above. The organic matter retained by the cartridge was then eluted in methanol and dried down for frozen storage.

### Laboratory sampling

Ramped pyrolysis/oxidation (RPO) procedure was performed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility in Woods Hole, MA, USA. Samples were transferred while dissolved in a small amount of methanol into quartz cups (pre-combusted at 850°C, 1 hour) and then dried down under ultra-high purity nitrogen gas. Samples were further dried in an oven at 50°C for multiple days in an attempt to remove all methanol. Each quartz cup containing a single sample was then placed inside the RPO reactor via a quartz insert tube. The RPO instrument continuously heats the sample at a set rate, monitors evolved  $\text{CO}_2$  during the pyrolysis/oxidation reactions as “thermograms” (Rosenheim et al., 2008), and can be used to trap  $\text{CO}_2$  for isotope analysis.

The RPO methodology has been described previously and further information describing the detailed protocol can be found in other publications (Hemingway et al., 2017; Rosenheim et al., 2008). In summary, all samples were operated in oxidation mode (carrier gas 92% He, 8%  $\text{O}_2$ ) with a flow rate of 35 mL min<sup>-1</sup> and a ramp rate of either 20 or 5 °C min<sup>-1</sup>. Samples analyzed at 20°C min<sup>-1</sup> ranged in size from 6.4 to 36.8  $\mu\text{mol C}$  and all resulting  $\text{CO}_2$  was collected for isotope analysis. Samples analyzed at 5°C min<sup>-1</sup> ranged in size from 48.2 to

185.2  $\mu\text{mol C}$ , where these amounts represent the sums of six fractions collected during each  $5^\circ\text{C min}^{-1}$  ramp, with each fraction ranging in size from 4.4 to 43.6  $\mu\text{mol C}$ . In total we ran ten  $20^\circ\text{C min}^{-1}$  ramps and six  $5^\circ\text{C min}^{-1}$  ramps of samples from Station M.

## Data Processing Description

The amount of  $\text{CO}_2$  for each RPO fraction, the fractions's  $\delta^{13}\text{C}$  values, and Fm values were corrected for blank carbon contributions from the RPO system after Hemingway et al. 2017a (resulting in corrections of no more than 3‰ for any sample).  $\delta^{13}\text{C}$  was additionally corrected to ensure  $^{13}\text{C}$  mass balance, using the 'ramped pyrox' python package developed by Hemingway et al., 2017b and available online at <http://pypi.python.org/pypi/rampedpyrox>.

## Problems/Issues

Residual methanol may be contributing to the first fraction collected for some of the samples when this fraction was small ( $\sim 50 \mu\text{g}$ ). This would result in a lower  $\Delta^{14}\text{C}$  signature for the first fraction, potentially masking the presence of younger carbon. This contamination would not have affected the bulk isotope measurements which were made on larger samples, and which did not have anomalous  $\delta^{13}\text{C}$  values. The potential for residual methanol to linger even after several drying steps, should be kept in mind when interpreting unexpectedly depleted  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values for PPL DOC samples.

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## Data Files

File
<b>RPO thermogram data from Station M samples</b> filename: rpo_thermograms.csv (Comma Separated Values (.csv), 4.42 MB) MD5:5bdb752184bc019f32b695b99eb615fd Ramped Pyrolysis Oxidation (RPO) thermogram data of samples from Station M.

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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](https://doi.org/10.4319/lom.2008.6.230)  
*Methods*

Hemingway, J. D., Galy, V. V., Gagnon, A. R., Grant, K. E., Rosengard, S. Z., Soulet, G., ... McNichol, A. P. (2017). Assessing the Blank Carbon Contribution, Isotope Mass Balance, and Kinetic Isotope Fractionation of the Ramped Pyrolysis/Oxidation Instrument at NOSAMS. *Radiocarbon*, 59(1), 179–193. doi:10.1017/rdc.2017.3  
<https://doi.org/10.1017/RDC.2017.3>  
*Methods*

Hemingway, J. D., Rothman, D. H., Rosengard, S. Z., & Galy, V. V. (2017). Technical note: An inverse method to relate organic carbon reactivity to isotope composition from serial oxidation. *Biogeosciences*, 14(22), 5099–5114. doi:[10.5194/bg-14-5099-2017](https://doi.org/10.5194/bg-14-5099-2017)  
*Methods*

Hemingway, J.D. rampedpyrox: open-source tools for thermoanalytical data analysis, 2016-, <http://pypi.python.org/pypi/rampedpyrox> [online; accessed May 20, 2019] doi. 10.5281/zenodo.3960330.  
*Software*

Johnson, W. M., Kido Soule, M. C., & Kujawinski, E. B. (2017). Extraction efficiency and quantification of dissolved metabolites in targeted marine metabolomics. *Limnology and Oceanography: Methods*, 15(4), 417–

428. doi:[10.1002/lom3.10181](https://doi.org/10.1002/lom3.10181)

*Methods*

Lechtenfeld, O. J., Kattner, G., Flerus, R., McCallister, S. L., Schmitt-Kopplin, P., & Koch, B. P. (2014). Molecular transformation and degradation of refractory dissolved organic matter in the Atlantic and Southern Ocean. *Geochimica et Cosmochimica Acta*, 126, 321–337. <https://doi.org/10.1016/j.gca.2013.11.009>

*Methods*

Lewis, C. B., Walker, B. D., & Druffel, E. R. M. (2021). New Radiocarbon Constraints on the Global Cycling of Solid-Phase Extractable Dissolved Organic Carbon. *Geophysical Research Letters*, 48(14).

doi:10.1029/2020gl090995 <https://doi.org/10.1029/2020GL090995>

*Methods*

McNichol, A. P., Osborne, E. A., Gagnon, A. R., Fry, B., & Jones, G. A. (1994). TIC, TOC, DIC, DOC, PIC, POC — unique aspects in the preparation of oceanographic samples for <sup>14</sup>C-AMS. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 92(1–4), 162–165.

[https://doi.org/10.1016/0168-583x\(94\)95998-6](https://doi.org/10.1016/0168-583x(94)95998-6) [https://doi.org/10.1016/0168-583X\(94\)95998-6](https://doi.org/10.1016/0168-583X(94)95998-6)

*Methods*

Meador, T. B., Aluwihare, L. I., & Mahaffey, C. (2007). Isotopic heterogeneity and cycling of organic nitrogen in the oligotrophic ocean. *Limnology and Oceanography*, 52(3), 934–947. Portico.

<https://doi.org/10.4319/lo.2007.52.3.0934>

*Methods*

Petras, D., Koester, I., Da Silva, R., Stephens, B. M., Haas, A. F., Nelson, C. E., Kelly, L. W., Aluwihare, L. I., & Dorrestein, P. C. (2017). High-Resolution Liquid Chromatography Tandem Mass Spectrometry Enables Large Scale Molecular Characterization of Dissolved Organic Matter. *Frontiers in Marine Science*, 4.

<https://doi.org/10.3389/fmars.2017.00405>

*Methods*

Petras, D., Minich, J. J., Cancelada, L. B., Torres, R. R., Kunselman, E., Wang, M., White, M. E., Allen, E. E., Prather, K. A., Aluwihare, L. I., & Dorrestein, P. C. (2021). Non-targeted tandem mass spectrometry enables the visualization of organic matter chemotype shifts in coastal seawater. *Chemosphere*, 271, 129450.

<https://doi.org/10.1016/j.chemosphere.2020.129450> <https://doi.org/10.1016/J.CHEMOSPHERE.2020.129450>

*Methods*

Rosenheim, B. E., Day, M. B., Domack, E., Schrum, H., Benthien, A., & Hayes, J. M. (2008). Antarctic sediment chronology by programmed-temperature pyrolysis: Methodology and data treatment. *Geochemistry, Geophysics, Geosystems*, 9(4), n/a–n/a. doi:10.1029/2007gc001816

<https://doi.org/10.1029/2007GC001816>

*Methods*

Walker, B. D., Beaupré, S. R., Guilderson, T. P., McCarthy, M. D., & Druffel, E. R. M. (2016). Pacific carbon cycling constrained by organic matter size, age and composition relationships. *Nature Geoscience*, 9(12), 888–891. <https://doi.org/10.1038/ngeo2830>

*Methods*

White, M. E., Nguyen, T. B., Koester, I., Lardie Gaylord, M. C., Beman, J. M., Smith, K. L., McNichol, A. P., Beaupré, S. R., & Aluwihare, L. I. (2023). Refractory Dissolved Organic Matter has Similar Chemical Characteristics but Different Radiocarbon Signatures With Depth in the Marine Water Column. *Global Biogeochemical Cycles*, 37(4). Portico. <https://doi.org/10.1029/2022gb007603>

<https://doi.org/10.1029/2022GB007603>

*Results*

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## Related Datasets

### IsRelatedTo

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White, M. E., Nguyen, T., Koester, I., Lardie Gaylord, M., Beman, J. M., Smith, K., McNichol, A., Beaupré, S. R., Aluwihare, L. (2023) **Ramped pyrolysis oxidation (RPO) carbon isotope data from DOC in water samples collected during R/V Western Flyer Benthic-Pelagic Coupling expedition to Station M in the eastern Pacific Ocean in April 2018**. Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-03-27 doi:10.26008/1912/bco-dmo.892660.1 [[view at BCO-DMO](#)]

## Results

Hemingway, J. D. (2018). Ramped Pyrolysis/Oxidation (RPO) Database [Data set]. Zenodo.  
<https://doi.org/10.5281/ZENODO.1158742> <https://doi.org/10.5281/zenodo.1158742>

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## Parameters

Parameter	Description	Units
Latitude	Latitude of sample collection	decimal degrees
Longitude	Longitude of samples collection	decimal degrees
Depth	Depth of sample collection	meters (m)
Sample_Type	Type of sample undergoing RPO. PPL DOM = Priority PoLutant DOM obtained from solid phase extraction, Hydrolyzed PPL DOM = PPL DOM hydrolyzed with 2M hydrochloric acid and re-extracted onto PPL resin	unitless
Ramp_Rate	Rate of increase of temperature during thermal oxidation	degrees Celsius per min (°C/min)
Time	Time of measurement (HH:MM:SS)	unitless
Temp	Temperature of ramped oxidation oven	degrees Celsius
CO2_scaled	Concentration of evolved carbon dioxide	per mil

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## Instruments

<b>Dataset-specific Instrument Name</b>	National Ocean Sciences Accelerator Mass Spectrometer
<b>Generic Instrument Name</b>	Accelerator Mass Spectrometer
<b>Dataset-specific Description</b>	All bulk and RPO-fraction isotope measurements were performed at NOSAMS. Radiocarbon measurements were completed via accelerator mass spectrometry (AMS) following standard graphitization methods.
<b>Generic Instrument Description</b>	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 $1 \times 10^{15}$ (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: <a href="http://www.physics.purdue.edu/primelab/introduction/ams.html">http://www.physics.purdue.edu/primelab/introduction/ams.html</a>

<b>Dataset-specific Instrument Name</b>	drying oven
<b>Generic Instrument Name</b>	Drying Oven
<b>Dataset-specific Description</b>	The samples were placed in a drying oven at 80°C for 18 hours.
<b>Generic Instrument Description</b>	a heated chamber for drying

<b>Dataset-specific Instrument Name</b>	tube furnace
<b>Generic Instrument Name</b>	furnace
<b>Dataset-specific Description</b>	As part of the ramped oxidation pyrolysis (RPO) setup, tube furnaces with independent temperature controllers were used for both combustion and pyrolysis.
<b>Generic Instrument Description</b>	An enclosed chamber designed to produce heat.

<b>Dataset-specific Instrument Name</b>	nondispersive infrared CO2 detector
<b>Generic Instrument Name</b>	Gas Analyzer
<b>Dataset-specific Description</b>	Evolved carbon dioxide (CO2) was measured by a flow-through infrared gas analyzer and thermograms were constructed by plotting gas concentrations over time.
<b>Generic Instrument Description</b>	Gas Analyzers - Instruments for determining the qualitative and quantitative composition of gas mixtures.

<b>Dataset-specific Instrument Name</b>	mass flow controller
<b>Generic Instrument Name</b>	Mass Flow Controller
<b>Dataset-specific Description</b>	The RPO system consists of a flow system (with mass flow controllers and infrared gas analyzer), a furnace system, and a vacuum separations system.
<b>Generic Instrument Description</b>	Mass Flow Controller (MFC) - A device used to measure and control the flow of fluids and gases

## Deployments

### Benthic-Pelagic Coupling 2018 expedition

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/892573">https://www.bco-dmo.org/deployment/892573</a>
<b>Platform</b>	R/V Western Flyer
<b>Start Date</b>	2018-04-18
<b>End Date</b>	2018-04-24
<b>Description</b>	This cruise is part of a long term time-series study at a site called Station M, 200 kilometers off the coast of Santa Barbara, California. The study is run by the Pelagic-Benthic Coupling Group at MBARI with the goal of understanding the supply of carbon—in the form of sinking organic matter (e.g., pieces of dead organisms, fecal material, and mucous)—and how its variation over time affects the deep-sea communities far below the surface. Website: <a href="https://www.mbari.org/news/pelagic-benthic-coupling-2018-expedition/">https://www.mbari.org/news/pelagic-benthic-coupling-2018-expedition/</a>

## Project Information

### Investigating the contribution of carotenoid degradation products to refractory dissolved organic matter (DOM) (CDP in rDOM)

**Coverage:** Eastern North Pacific Ocean

#### NSF Award Abstract:

This research project will identify biological sources and chemical structures that are responsible for the long-term storage of carbon in the ocean. Each year, microscopic marine plants remove about as much carbon dioxide from the atmosphere as do land plants. Respiration returns much of this carbon to the ocean as carbon dioxide, but some is locked in the remnants of living organisms. These remaining compounds are modified by pathways that involve bacteria, sunlight, chemical reactions, and other processes that lead to storage of carbon for thousands to millions of years. Some compounds eventually contribute to the petroleum reservoir. Building on previous results, this project will study the reactions and oceanic lifetime of a particular set of biochemicals, called carotenoids, as a possible organic carbon storage pathway. Carotenoids are abundant in very many marine organisms, increasing the likelihood that they are part of this long-term carbon storage and petroleum formation. These compounds also have unique chemical properties that make them subject to specific chemical reactions. For this reason, they have been marketed as powerful antioxidants. Therefore, scientific outcomes from this research on carotenoid chemistry will not only inform ocean carbon cycles but could also benefit studies of their properties as antioxidants. The project will determine the lifetime of carotenoids and their degradation products in seawater to provide new insights into pathways that transfer carbon from the atmosphere through biota and into long-term storage reservoirs. Graduate students and underrepresented undergraduate students will be engaged in the research.

Previous work has identified specific chemical backbones of compounds that are broadly distributed within the marine dissolved organic matter (DOM) reservoir. A high-resolution analytical approach that combines nuclear magnetic resonance (NMR) spectroscopy with comprehensive gas chromatography-mass spectrometry (GC-MS) has detected DOM compounds with unique structures closely related to carotenoids. Photochemical reactions of a representative carotenoid in laboratory experiments has further linked compounds detected in seawater to carotenoid degradation products (CDP). These preliminary studies show promise that the work funded here will be able to identify specific CDP structures and establish the quantitative significance, lifetimes, and timescales of CDP accumulation in seawater. The project will combine laboratory experiments, high resolution analyses, and chemical synthesis methods to determine the chemical composition of CDP and their abundance in seawater. The novel analytical methods developed through this research will be relevant for other

carotenoid-focused studies in petroleum formation, soil chemistry, as well as food chemistry. Ramped pyrolysis oxidation (PyrOx) coupled to radiocarbon measurements will be used to determine the radiocarbon content of CDP-enriched DOM and seek to estimate the accumulation timescale of these dissolved molecules in the environment, and it is hypothesized that deeper, older ocean water will contain a relatively higher proportion of radiocarbon-depleted CDP. Collecting samples from different depths in the North Pacific Ocean where CDP-enriched DOM will be isolated following established sample processing methods will provide insights and new information on the mechanisms that control the amount and timescale of carbon redistribution among Earth's various reservoirs.

#### **Resources:**

Ramped pyrolysis oxidation (RPO) data is currently accessible through the RPO database maintained on GitHub by Jordon Hemingway ([http://github.com/FluvialSeds/RPO\\_Database](http://github.com/FluvialSeds/RPO_Database)).

J.D. Hemingway et al. A compiled database of published ramped pyrolysis/oxidation results, 2018- , [http://pypi.python.org/pypi/RPO\\_Database](http://pypi.python.org/pypi/RPO_Database), doi:10.5281/zenodo.1158742 [online; accessed 2022-07-10]

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## **Funding**

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1736656</a>

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