

# Radiocarbon DIC, DIC concentration, pH, and [CH<sub>4</sub>] in Hudson Canyon, northern US Atlantic Margin collected from R/V Endeavor cruise EN541 in July 2014

**Website:** <https://www.bco-dmo.org/dataset/737887>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2018-05-30

## Project

» [Investigating the chemical and isotopic kinetics of aerobic methane oxidation](#) (Aerobic methane oxidation)

Contributors	Affiliation	Role
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## Abstract

Radiocarbon DIC, DIC concentration, pH, and [CH<sub>4</sub>] in Hudson Canyon, northern US Atlantic Margin collected from R/V Endeavor cruise EN541 in July 2014.

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## Coverage

**Spatial Extent:** N:39.5668 E:-72.20012 S:39.2878 W:-72.42284

**Temporal Extent:** 2014-07-09 - 2014-07-13

## Dataset Description

Measurements of natural radiocarbon of DIC, DIC concentration, pH, and [CH<sub>4</sub>] in Hudson Canyon, northern US Atlantic Margin.

Methane concentration data was published by Weinstein et al. (2016) and Leonte et al., (2017).

The DIC and pH data are published as: Garcia-Tigreros, F. and Kessler, J.D. (2018)

Underway data for cruise EN541 was published and can be access at R2R: <https://doi.org/10.7284/903242>

## Methods & Sampling

### Methodology:

Dissolved inorganic carbon concentration ([DIC]) samples were measured by acidification and subsequent

release of CO<sub>2</sub> with a CO<sub>2</sub> cavity-ringdown spectrometer (CRDS; Picarro G1101-*i*) detector to an accuracy and precision better than  $\pm 3$   $\mu\text{mol}/\text{kg}$ . Precision is based on a set of 15 duplicates. Accuracy is based on certified reference materials prepared at the Scripps Institution of Oceanography of the University of California, San Diego.

Samples for pH were measured spectrophotometrically on board using an Agilent Cary 100 UV-Visible spectrophotometer and m-cresol purple dye (Clayton and Byrne, 1993; Liu et al., 2011). The pH values are reported on the total scale with a precision better than 0.0002 based on duplicate measurements. The estimated accuracy of spectrophotometric pH is better than 0.002.

Natural radiocarbon samples of DIC ( $\Delta 14\text{C-DIC}$ ) were analyzed at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California, Irvine. The accuracy and precision of the  $\Delta 14\text{C-DIC}$  measurements is 0.1‰ and 1.7‰, respectively.

### **Sampling and analytical procedures:**

Discrete seawater samples were collected inside Hudson Canyon, US Atlantic Margin aboard the R/V Endeavor from 9 - 13 of July 2014. A total 19 stations and 216 samples were collected along Hudson Canyon and another station was sampled outside the canyon (station E2-HC2). Samples were collected from a bottle Rosette following the procedures in SOP 1 and 6b in Dickson et al., (2007).

[DIC] samples were collected in acid washed and combusted 120 mL serum vials. Vials were allowed to overflow three times their volume, poisoned with 50  $\mu\text{L}$  of a 55  $\mu\text{M}$  HgCl<sub>2</sub>, capped, and store at 4 degrees C until analysis.

$\Delta 14\text{C-DIC}$  samples were collected in combusted 1L borosilicate bottles, poisoned with 200  $\mu\text{L}$  of a 55  $\mu\text{M}$  HgCl<sub>2</sub>, sealed and stored in the dark at room temperature until isotope analysis.

CH<sub>4</sub> concentration analyses were collected by filling 60, 120, or 160 mL glass serum vials. Vials were filled from the bottom with a length of 1/4" Tygon tubing. Vials were flushed with seven vial volumes of seawater to expel any bubbles and ensure collection of a clean sample, and then were sealed with butyl rubber stoppers taking care not to introduce bubbles during sealing. Immediately after sealing, a 10 mL headspace of ultrahigh purity nitrogen was introduced, displacing an equal volume of water, and the samples were preserved by adding 25  $\mu\text{L}$  of a saturated solution of mercuric chloride. The vials were stored inverted to minimize diffusive gas exchange through the butyl rubber stopper.

CH<sub>4</sub> concentration measurements were performed using an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID) following established protocols reported in Weinstein et al. (2016). The uncertainty associated with these measurements was 5.2% based on duplicate measurements.

## **Data Processing Description**

BCO-DMO Processing:

- modified parameter names to conform with BCO-DMO naming conventions;
- created date/time column formatted to ISO8601 standard.

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## **Data Files**

File
<b>Hudson_Canyon_DIC_pH.csv</b> (Comma Separated Values (.csv), 29.13 KB) MD5:f8f9fe56c708b13f3153777126f844ed
Primary data file for dataset ID 737887

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## **Related Publications**

Clayton, T. D., & Byrne, R. H. (1993). Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep Sea Research Part I: Oceanographic Research Papers*, 40(10), 2115–2129. doi:[10.1016/0967-0637\(93\)90048-8](https://doi.org/10.1016/0967-0637(93)90048-8)

*Methods*

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO<sub>2</sub> measurements. PICES Special Publication 3, 191 pp. ISBN: 1-897176-07-4. URL: [https://www.nodc.noaa.gov/ocads/oceans/Handbook\\_2007.html](https://www.nodc.noaa.gov/ocads/oceans/Handbook_2007.html) <https://hdl.handle.net/11329/249>

*Methods*

Garcia-Tigreros, F., & Kessler, J. D. (2018). Limited Acute Influence of Aerobic Methane Oxidation on Ocean Carbon Dioxide and pH in Hudson Canyon, Northern U.S. Atlantic Margin. *Journal of Geophysical Research: Biogeosciences*, 123(7), 2135–2144. doi:10.1029/2018jg004384 <https://doi.org/10.1029/2018JG004384>

*Results*

Leonte, M., Kessler, J. D., Kellermann, M. Y., Arrington, E. C., Valentine, D. L., & Sylva, S. P. (2017). Rapid rates of aerobic methane oxidation at the feather edge of gas hydrate stability in the waters of Hudson Canyon, US Atlantic Margin. *Geochimica et Cosmochimica Acta*, 204, 375–387. doi:[10.1016/j.gca.2017.01.009](https://doi.org/10.1016/j.gca.2017.01.009)

*Related Research*

Liu, X., Patsavas, M. C., & Byrne, R. H. (2011). Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements. *Environmental Science & Technology*, 45(11), 4862–4868. doi:[10.1021/es200665d](https://doi.org/10.1021/es200665d)

*Methods*

Weinstein, A., Navarrete, L., Ruppel, C., Weber, T. C., Leonte, M., Kellermann, M. Y., Arrington, E. C., Valentine, D. L., Scranton, M. I., & Kessler, J. D. (2016). Determining the flux of methane into Hudson Canyon at the edge of methane clathrate hydrate stability. *Geochemistry, Geophysics, Geosystems*, 17(10), 3882–3892. <https://doi.org/10.1002/2016gc006421> <https://doi.org/10.1002/2016GC006421>

*Results*

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## Parameters

Parameter	Description	Units
Cruise_ID	Cruise identifier (EN = R/V Endeavor)	unitless
Station_ID	Cruise station identifier	unitless
CTD_hex_file	CTD hex file name	unitless
ISO_DateTime	Date and time formatted to ISO8601 standard: yyyy-mm-ddTHH:MM:SS	unitless
GMT_Date	Date GMT (yyyy-mm-dd)	unitless
GMT_Time	Time GMT (HH:MM:SS)	unitless
Latitude	Latitude North at start of CTD cast	decimal degrees
Longitude	Longitude West at start of CTD cast	decimal degrees
depth	Niskin bottle depth (m) at sample collection	meters (m)
pressure	Pressure at sample collection	Digiquartz (db)
temp	Temperature at sample collection	Degrees Celsius
sal	Salinity at sample collection	Practical (PSU)
Density	Density at sample collection	kilograms per cubic meter (Kg/m <sup>3</sup> )
pH	Spectrophotometric pH measured at 25 C using the total hydrogen ion scale	Unitless; pH scale
DIC	Dissolved Inorganic Carbon concentration	micromoles per kilogram (umol/kg)
CH3	Dissolved methane concentration	nanomolar (nM)
d14C_DIC	Natural radiocarbon of DIC	Per mil (‰)
C14_DIC_age	Age of DIC	Years before present

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## Instruments

<b>Dataset-specific Instrument Name</b>	W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory
<b>Generic Instrument Name</b>	Accelerator Mass Spectrometer
<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 1x10 <sup>15</sup> (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>	Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID)
<b>Generic Instrument Name</b>	Flame Ionization Detector
<b>Generic Instrument Description</b>	A flame ionization detector (FID) is a scientific instrument that measures the concentration of organic species in a gas stream. It is frequently used as a detector in gas chromatography. Standalone FIDs can also be used in applications such as landfill gas monitoring, fugitive emissions monitoring and internal combustion engine emissions measurement in stationary or portable instruments.

<b>Dataset-specific Instrument Name</b>	Agilent 6850 gas chromatograph
<b>Generic Instrument Name</b>	Gas Chromatograph
<b>Generic Instrument Description</b>	Instrument separating gases, volatile substances, or substances dissolved in a volatile solvent by transporting an inert gas through a column packed with a sorbent to a detector for assay. (from SeaDataNet, BODC)

<b>Dataset-specific Instrument Name</b>	bottle Rosette
<b>Generic Instrument Name</b>	Niskin bottle
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	CO2 cavity-ringdown spectrometer (CRDS; Picarro G1101-i)
<b>Generic Instrument Name</b>	Spectrometer
<b>Generic Instrument Description</b>	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

<b>Dataset-specific Instrument Name</b>	Agilent Cary 100 UV-Visible spectrophotometer
<b>Generic Instrument Name</b>	Spectrophotometer
<b>Generic Instrument Description</b>	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

## Deployments

### EN541

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/737792">https://www.bco-dmo.org/deployment/737792</a>
<b>Platform</b>	R/V Endeavor
<b>Start Date</b>	2014-07-08
<b>End Date</b>	2014-07-13
<b>Description</b>	Additional data from this cruise are available from the Rolling Deck to Repository (R2R): <a href="http://www.rvdata.us/catalog/EN541">http://www.rvdata.us/catalog/EN541</a>

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## Project Information

### Investigating the chemical and isotopic kinetics of aerobic methane oxidation (Aerobic methane oxidation)

#### *NSF Award Abstract:*

Roughly 8 billion moles of methane (CH<sub>4</sub>) were emitted in 83 days during the Deepwater Horizon disaster in the northern Gulf of Mexico in 2010. Interestingly, none of this CH<sub>4</sub> was emitted to the atmosphere, but instead stayed dissolved and suspended as "plume" or "intrusion" layers approximately 1000m below the ocean surface. Based on measurements of CH<sub>4</sub> concentration and oxidation rates, dissolved oxygen anomalies, and microbial community structure as well as a CH<sub>4</sub> geochemical model, it was determined that all the CH<sub>4</sub> emitted during this disaster was respired within 120 days of the initial well blowout. In addition, the methanotrophic bacteria responsible for the oxidation of this CH<sub>4</sub> appeared to experience all stages of microbial growth, limited only by the availability of CH<sub>4</sub>. This finding suggests that releases of CH<sub>4</sub> into deepwater, be them anthropogenic or natural, will have minimal direct influence on the radiative budget of the atmosphere.

The major weakness in these previous investigations is that CH<sub>4</sub> related parameters were only measured at the beginning (May - June 2010) and end (September - October 2010) of this massive CH<sub>4</sub> feast, primarily because the rapid demise of CH<sub>4</sub> was unanticipated. Thus, the time- and growth phase-dependent understanding of the kinetics of this bloom response is only based on model interpolation between endpoints. A more complete, and measurement-based, understanding of the chemical kinetics is necessary to predict an oceanographic environment's ability to respire large CH<sub>4</sub> perturbations. And while measurements of CH<sub>4</sub> stable isotopes in theory can be used to assess the extent that the released CH<sub>4</sub> has been oxidized, this kinetic isotope effect can only be used in a quantitative fashion if it is known how the isotopic fractionation factor changes with varying chemical and temperature conditions and throughout all stages of the microbial bloom.

In this study, researchers at the Texas A & M University will test two fundamental hypotheses relating to aerobic CH<sub>4</sub> oxidation and ultimately produce a thorough characterization of the time-, growth phase-, and temperature-dependency of CH<sub>4</sub> oxidation rates, oxidation rate constants, and isotopic fractionation factors. Hypothesis 1: Excluding mixing processes, the bacterial response to a large CH<sub>4</sub> perturbation will be limited primarily by the availability of CH<sub>4</sub> or dissolved oxygen. Hypothesis 2: Without knowing the stage of microbial growth, measurements of natural stable isotopes of CH<sub>4</sub> and dissolved carbon (organic and/or inorganic) cannot be used to assess the extent of CH<sub>4</sub> oxidation in situations of large CH<sub>4</sub> perturbations. In order to test these hypotheses, with the goal of disproving hypothesis 2, a suite of mesocosm and pure culture incubations will be conducted. Throughout these incubations, concentrations of CH<sub>4</sub> and dissolved inorganic carbon as well as their <sup>13</sup>C isotopes will be measured in extremely high resolution with new equipment and experimental designs. In addition, dissolved oxygen, nutrient concentrations, trace metals, CH<sub>4</sub> oxidation rates, and microbial community structure will be measured.

Broader Impacts. In addition to the normal dissemination of results in publications, meeting presentations, and on a project web site, this work will have strong educational and research impacts with close interactions between the PIs, postdoctoral scholar, graduate student, and undergraduate researchers with collaborations between Texas A&M University and the University of California Santa Barbara. The students will have extended visits at each lab for skill development, knowledge transfer, and general academic growth. During 2010, an

informal collaboration was established with Ms. Vicki Soutar, a high school science teacher in Watkinsville, GA, to develop high school science laboratory exercises using real scientific data. This proposed project will involve Ms. Soutar to formalize, enhance, extend, and disseminate the products of this collaboration

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1318102</a>

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