# Radiocarbon in methane from waters of the US Atlantic and Pacific margins as collected on R/V Hugh Sharp cruise HRS1713 and R/V Rachel Carson cruise RC0026 in 2017 and 2019

**Website**: https://www.bco-dmo.org/dataset/861576
**Data Type**: Cruise Results
**Version**: 1
**Version Date**: 2021-09-27

## Project
» Constraining Global Coastal Ocean Methane Emissions to the Atmosphere (Coastal Methane Emissions)
» Characterizing Ocean Acidification and Atmospheric Emission Caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin (Gas Hydrate Methane)

| Contributors | Affiliation | Role |
|---|---|---|
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| Gerlach, Dana Stuart | Woods Hole Oceanographic Institution (WHOI BCO-DMO) | BCO-DMO Data Manager |

## Abstract
Water column distribution of radiocarbon (14C) and concentrations of dissolved methane (CH4) collected from US-Atlantic and US-Pacific Margins in 2017 and 2019, respectively.

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## Coverage

**Spatial Extent**: **N**:48.486 **E**:-74.304 **S**:35.532 **W**:-125.06
**Temporal Extent**: 2017-08-25 - 2019-06-08

## Dataset Description

Data collection in 2017 was carried out under DOE Project Award DE-FE0028980: Characterizing Ocean Acidification and Atmospheric Emission Caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin

Data collection in 2019 was carried out under NSF Project Award OCE-1851402. Subsequent analyses and data compilation were also funded by this award: Constraining Global Coastal Ocean Methane Emissions to the Atmosphere

**Methods & Sampling**

Please see the Related Publications (Methods) section for references with additional acquistion and processing details.

**Radiocarbon Sample Collection at Sea:**
Gases dissolved in seawater were extracted following the procedures outlined in Sparrow and Kessler (2017) and Joung et al (2019 and 2020).  As detailed in these prior publications, waters were pumped through a suction hose with a discharge pump and were passed through multiple filters for removing particles. This water was then continuously passed through a gas-permeable membrane to vacuum extract the dissolved gases in the seawater.

**Radiocarbon Sample Preparation in the Laboratory:**
Extracted gas samples were purified and analyzed using vacuum line procedures and Accelerator Mass Spectrometry as previously detailed in Sparrow and Kessler, (2017).  The volume of the whole gas sample needed for processing in the laboratory using vacuum-line techniques was determined by the CH4 concentration and the amount of carbon necessary for the Accelerator Mass Spectrometry (AMS) analysis. Careful monitoring of standards and blanks was done to ensure efficiency of purification and combustion performance.

**Dissolved Methane Concentration Measurement:**
Dissolved methane concentration measurements were conducted using a headspace equilibration. The concentration of CH4 in the headspace was determined using an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID), which was then translated into the original dissolved gas concentration using headspace and water volumes, along with the gas solubility.

**Instrument notes:**
*All apparatus and their detail specifications for the 14C-CH4 measurements can be found in Sparrow and Kessler (2017) and Joung et al. (2019).
*GC-CH4 measurements references are Weinstein et al., (2016) and Leonte et al (2017)
*14C was measured by Accelerator Mass Spectrometer (AMS) at the Keck-Carbon Cycle AMS facility at UC Irvine
*Temperature, salinity, and dissolved oxygen were measured by the CTD sensors

**Data Processing Description**

**BCO-DMO Processing:**
- added columns for cruise and vessel name
- combined date and time fields into ISO8601 format
- added a conventional header with dataset name, PI names, version date
- adjusted parameter names to comply with database requirements
- units removed and added to Parameter Description metadata section

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# Data Files

| File |
| --- |
| **radiocarbon_methane_margins.csv**(Comma Separated Values (.csv), 9.60 KB)<br>MD5:d1bd2abf166fb8784d82bace27040b59<br><br>Primary data file for dataset ID 861576 |

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# Related Publications

Joung, D., Leonte, M., & Kessler, J. D. (2019). Methane Sources in the Waters of Lake Michigan and Lake

Superior as Revealed by Natural Radiocarbon Measurements. Geophysical Research Letters, 46(10), 5436–5444. doi:10.1029/2019gl082531 https://doi.org/10.1029/2019GL082531
*Methods*

Joung, D., Leonte, M., Valentine, D. L., Sparrow, K. J., Weber, T., & Kessler, J. D. (2020). Radiocarbon in Marine Methane Reveals Patchy Impact of Seeps on Surface Waters. Geophysical Research Letters, 47(20). doi:10.1029/2020gl089516 https://doi.org/10.1029/2020GL089516
*Methods*

Joung, D., Ruppel, C., Southon, J., & Kessler, J. D. (2021). Elevated levels of radiocarbon in methane dissolved in seawater reveal likely local contamination from nuclear powered vessels. Science of The Total Environment, 150456. doi:10.1016/j.scitotenv.2021.150456
*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
*Methods*

Sparrow, K. J., & Kessler, J. D. (2017). Efficient collection and preparation of methane from low concentration waters for natural abundance radiocarbon analysis. Limnology and Oceanography: Methods, 15(7), 601–617. doi:10.1002/lom3.10184
*Methods*

Sparrow, K. J., Kessler, J. D., Southon, J. R., Garcia-Tigreros, F., Schreiner, K. M., Ruppel, C. D., Miller, J. B., Lehman, S. J., & Xu, X. (2018). Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf. Science Advances, 4(1), eaao4842. https://doi.org/10.1126/sciadv.aao4842
*General*

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
*Methods*

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## Related Datasets

### IsRelatedTo

Joung, D., Kessler, J. D. (2020) **Carbon isotopes (13C and 14C) and concentrations of dissolved methane (CH4) in surface waters sampled in June 2019 at the Coal Oil Point seep field of the Santa Barbara Basin.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2020-09-10 doi:10.26008/1912/bco-dmo.823720.1 [view at BCO-DMO]

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## Parameters

| Parameter | Description | Units |
|---|---|---|
| Location | Ocean body | unitless |
| Vessel | Cruise vessel | unitless |
| Cruise | Cruise identification | unitless |
| Station | Station identification | unitless |
| Latitude | Latitude of sample collection | decimal degrees |
| Longitude | Longitude of sample collection | decimal degrees |
| ISO_DateTime_UTC | Date and Time in ISO8601 format | unitless |
| StnDepth | Depth of water column at the station | meters (m) |
| SamDepth | Water depth where sample was collected | meters (m) |
| Temperature | Temperature measured by CTD | degrees Celsius |
| Salinity | Salinity measured by CTD | practical salinity unit (psu) |
| DO | Dissolved oxygen measured by CTD | micromole per liter (umol/L) |
| Water_filtered | Volume of water filtered | liter (L) |
| CH4 | Dissolved methane concentrations measured by GC-FID | nanoMolar (nM) |
| C14_in_CH4 | Radiocarbon in methane measured by Accelerator Mass Spectrometry | percent modern (pMC) |
| Std_Dev_C14_in_CH4 | Standard deviation of 14C in CH4 | percent modern (pMC) |
| D14C | Radiocarbon in methane measured by Accelerator Mass Spectrometry | per mil |
| Std_Dev_D14C | Standard deviation of 14C in CH4 | per mil |

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## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | UC-Irvine Keck-Carbon Cycle AMS |
| **Generic Instrument Name** | Accelerator Mass Spectrometer |
| **Dataset-specific Description** | 14C was measured by Accelerator Mass Spectrometer (AMS) at the Keck-Carbon Cycle AMS facility at UC Irvine |
| **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** | CTD sensors |
| **Generic Instrument Name** | CTD - profiler |
| **Dataset-specific Description** | Temperature, salinity, and dissolved oxygen were measured by the CTD sensors |
| **Generic Instrument Description** | The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934. |

| | |
|---|---|
| **Dataset-specific Instrument Name** | Agilent 6850 GC-FID |
| **Generic Instrument Name** | Flame Ionization Detector |
| **Dataset-specific Description** | Methane concentration measurements were performed in the Kessler laboratory at the University of Rochester using an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID). |
| **Generic Instrument Description** | 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. |

| | |
|---|---|
| **Dataset-specific Instrument Name** | Digital flowmeter |
| **Generic Instrument Name** | Flow Meter |
| **Dataset-specific Description** | Seawater is pumped through a digital flowmeter then on to filter housings before flowing through gas extractors |
| **Generic Instrument Description** | General term for a sensor that quantifies the rate at which fluids (e.g. water or air) pass through sensor packages, instruments, or sampling devices. A flow meter may be mechanical, optical, electromagnetic, etc. |

| Dataset-specific Instrument Name | Agilent 6850 GC-FID |
|---|---|
| Generic Instrument Name | Gas Chromatograph |
| Dataset-specific Description | Methane concentration measurements were performed in the Kessler laboratory at the University of Rochester using an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID). |
| Generic Instrument Description | 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) |

| Dataset-specific Instrument Name | Water pump |
|---|---|
| Generic Instrument Name | Pump |
| Dataset-specific Description | Seawater is pumped up to the deck by a gasoline-powered, chemical-resistant water pump A high-performance discharge pump was used to pump water onto the vessel |
| Generic Instrument Description | A pump is a device that moves fluids (liquids or gases), or sometimes slurries, by mechanical action. Pumps can be classified into three major groups according to the method they use to move the fluid: direct lift, displacement, and gravity pumps |

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## Deployments

### RC0026

| Website | https://www.bco-dmo.org/deployment/854591 |
|---|---|
| Platform | R/V Rachel Carson |
| Start Date | 2019-05-27 |
| End Date | 2019-06-08 |
| Description | Location: US-Pacific Margin (48N, 122 W) See more information from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RC0026 Cruise DOI: 10.7284/908687 |

### HRS1713

| Website | https://www.bco-dmo.org/deployment/854589 |
|---|---|
| Platform | R/V Hugh R. Sharp |
| Start Date | 2017-08-25 |
| End Date | 2017-09-06 |
| Description | As of 2021-06-24, not yet in R2R (www.rvdata.us).  As of 2021-09-28, information and DOI there.  Location: US-Atlantic Margin  bewteen 38N, 74W and 35N, 75W |

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# Project Information

## Constraining Global Coastal Ocean Methane Emissions to the Atmosphere (Coastal Methane Emissions)

**Coverage**: US Pacific Margin, US Atlantic Margin, Gulf of Mexico, Arctic Ocean

*NSF Award Abstract:*
This project will determine global methane emissions from coastal marine environments, one of the most uncertain natural sources of methane to the atmosphere. Methane is a greenhouse gas whose impact on future climate warming will depend on emissions from both human sources and the changing natural environment. It is therefore critical to understand the baseline emission rates of natural methane sources to the atmosphere as well as their sensitivity to change. While the open ocean environment is thought to emit only minor amounts of methane to the atmosphere, concentrations and emission rates of methane increase substantially approaching coastlines. Coastal ocean methane emissions are potentially significant at the global scale but remain highly uncertain due to a lack of observations that accurately capture coastal distributions. Furthermore, the source of methane emitted from coastal surface waters is not well known, limiting our ability to predict how emissions will change in the future. This project will determine the source and global emission rate of methane from the coastal ocean to the atmosphere, and establish a framework to predict future emission rates in a warming climate. In addition to these scientific and societal impacts, this project will have strong educational impacts as it will provide undergraduate students the opportunity to experience the entire scientific process from idea conception to publication of the final results. A sequence of classes has been established by the PI at the University of Rochester to guide students through this process from an ocean science perspective. This project will serve as the focus for the next iteration of the class sequence, and participating students will be vital contributors to the research. When conducted previously, this educational outreach has empowered undergraduates to pursue their own scientific interests and has led to significant numbers of students pursuing graduate careers in the ocean sciences. This project will also support a Ph.D. student in a truly unique experience whereby she/he will have the opportunity to conduct meaningful research in both sea-going measurement as well as modeling laboratories, and thus integrate into two often disparate communities.

This project will be accomplished through a unique and equal combination of observational and statistical modeling work, leveraging methodologies that are well established in the PI and co-PI's laboratories to make rapid progress over the 2.5-year duration of the project. In total, surface methane concentrations in four coastal regions "spanning three different ocean basins and subtropical to subpolar latitude ranges" will be measured using an ultra-fast vacuum extraction method, yielding coastal data coverage that is unparalleled in previous datasets. Additionally, the radiocarbon content of surface methane will be measured to fingerprint its provenance between fossil and microbial sources, and biogeochemical data including chlorophyll, nutrient, and dissolved oxygen concentrations will be collected. Initial cruise data (year 1) will be used to train Artificial Neural Network models to predict surface methane supersaturation as a function of biogeochemical variables, and later cruises (year 2) will allow for independent model validation in regions that were not used for training. Having established the fidelity with which this model can generalize between coastal environments, it will be applied to extrapolate maps of methane supersaturation and estimate regional and global scale coastal methane emissions while quantifying their uncertainty. Overall, this work will close these gaps in our knowledge of the natural methane budget, yielding the most robust estimates to date of coastal ocean emissions and a new understanding of the mechanisms that sustain them.

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.

## Characterizing Ocean Acidification and Atmospheric Emission Caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin (Gas Hydrate Methane)

**Website**: https://netl.doe.gov/node/2084

**Coverage**: U.S. Atlantic margin

**Goal**

## Goal

The primary objective of this project is to determine how methane seepage from the US Atlantic Margin (USAM) upper continental slope near the up-dip limit of gas hydrate stability affects ocean chemistry and sea-to-air greenhouse gas flux in three-dimensions and how this seepage interacts with oceanographic phenomena (e.g., southwardly flowing currents) to create hypothesized hotspots of decreased pH (i.e., acidification potential). A complementary objective is to collect physical data to constrain the location of the methane seeps, the height of plumes above the seafloor, the intensity of seepage, and the estimated volumetric flow rate of methane. Synthesizing the data required to meet these objectives will elucidate the sources and sinks for seep methane and track the flow of methane carbon through the ocean-atmosphere system once released at the seafloor.


## Background

Gas hydrate is known to exist widely within shallow marine sediments where ocean depths exceed ~500m. Gas hydrate that may occur along the landward edge of the zone of gas hydrate occurrence is particularly susceptible to destabilization in response to natural environmental changes, including changes in bottom water temperature. The methane emitted during destabilization can have a range of implications, including the potential transmission of methane to atmosphere, the conversion of methane to carbon dioxide in ocean waters, which may then be transmitted to the atmosphere and contribute to acidification of seawater.

In recent years, surveys of the Atlantic Margin have revealed the presence of numerous, previously-undocumented methane seeps in locations that appear to coincide with the landward edge of hydrate stability. This project will conduct targeted acquisition of field data during a 13-day research cruise from the University-National Oceanographic Laboratory System's (UNOLS) R/V Hugh R. Sharp to acquire water column samples and complete thorough surveys of sea-to-air greenhouse gas flux and seafloor gas emissions on the upper continental slope between Cape Hatteras and Wilmington Canyons. These data will then be analyzed to address the key questions related to the environmental impact of methane seeping from the margin near the up-dip limit of gas hydrate stability. The project will also continue to develop and refine laboratory procedures to help determine whether sampled methane was derived from recently dissociated gas hydrate or was perhaps generated by another source.

### Impact

The resulting data will 1) advance our understanding of the sources, source strengths, and distribution of methane emission from deepwater gas hydrate systems; 2) measure the concentration of methane near the seafloor and in the water column; and 3) assess the vigor of aerobic methane oxidation in ocean waters and the linked change in seawater buffering capacity and acidification along the edge of gas hydrate stability on the U.S. Atlantic Margin. The project will also characterize ocean currents that transport emitted methane and its byproducts southward toward Cape Hatteras, the amount of water column methane carbon derived from gas hydrate dissociation, and the emission intensity of methane derived from gas hydrate to the atmosphere.

**Final Report:** https://doi.org/10.2172/1634089

## Funding

| Funding Source | Award |
|---|---|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1851402 |
| US Department of Energy (DOE) | DE-FE0028980 |