NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

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Quarterly Research Performance Progress Report

(Period Ending 9/30/2017)

Characterizing Ocean Acidification and Atmospheric Emission caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin

Project Period (10/01/2016 to 09/30/2017)

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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Office of Fossil Energy

DISCLAIMER:

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1 Accomplishments

1.1 Summary of Progress Toward Project Objectives

Since the goals of this project remain the same and many tasks are conducted across quarters, some of the text from the Q1 – Q3 reports still applies and is repeated here. The major tasks during the first three quarters of year 1 were to prepare for the research cruise. During quarter 4, those preparations were completed and we also conducted this oceanographic research cruise.

The overall goal of this project is to investigate the fate of methane released at the seafloor either accidentally during the production of methane from a deep water gas hydrate well or the more natural decomposition of gas hydrate systems. This research is field-based, with investigations being conducted along the US Atlantic margin, in a geographic location where seafloor methane emission has been well documented near the upper boundary of methane hydrate stability. More specifically, this research expedition was conducted from 24 August to 7 September 2017 between Wilmington Canyon and Cape Hatteras using the Research Vessel (R/V) *Hugh Sharp*.

Main Objective 1: The first major objective of this project is to constrain the amount of methane released from gas hydrate systems that reaches the atmosphere between Wilmington Canyon and Cape Hatteras. The two major obstacles for determining this flux are (1) detecting and (2) fingerprinting regions where methane, once associated with gas hydrates, is being emitted to the atmosphere. Two new techniques were developed in the Kessler laboratory to solve these obstacles. First, an ultra-high resolution technique was established which enables the detection of isolated methane "hotspots" of emission from the surface waters to the atmosphere. Previous

techniques did not respond fast enough to changes in dissolved methane concentration nor did they enable samples to be collected at sufficient resolution to document such features. Our new technique circumvents both deficiencies by continually vacuum extracting the dissolved gases from a continuous feed of surface water. Second, we developed a technique to measure the natural radiocarbon content of methane dissolved in ocean waters. Methane released from gas hydrate systems in the ocean has been shown to be devoid of natural radiocarbon, yet methane sources from in-situ aerobic production, modern anoxic sediments, or the atmosphere has measurable levels of radiocarbon. This technique will help determine the source of methane evading to the atmosphere. Since the concentration of methane dissolved in seawater is relatively low, the major obstacle for this technique has been the collection of sufficient quantities of methane dissolved in seawater for a quantitative natural radiocarbon analysis. This problem was recently solved and methane can be extracted from >20,000 L of seawater in under 2 hours. During Q3, this technique was published (Sparrow and Kessler, L&O: Methods, 2017).

Main Objective 2: For methane that is not emitted to the atmosphere, but instead is dissolved in seawater, a major fate of that methane is oxidation (Ruppel and Kessler, 2017). The terminal product of this oxidation process is carbon dioxide, thus, the second major objective of this project is to constrain the amount of ocean acidification that can occur following the oxidation of the released methane.

Both of these main objectives, as well as several supporting objectives, were investigated during the two-week measurement campaign using the R/V *Hugh Sharp* along the US Atlantic margin.

Overall, this research project is being conducted in four stages: (1) prepare for the research cruise, (2) execute the research cruise, (3) analyze samples and interpret the results, and (4) disseminate the findings. During this reporting period, we finished stages (1) and (2), and began stage (3), analyzing the samples collected and interpreting the results.

Table 1. *Project milestones color-coded by the budget year in which the milestone (not the task) will be completed.*

Milestone Number.Title	Date	Verification Method
1. Task 1: Complete PMP (UR)	November 2016	Mutual acceptance by DOE and PIs
2. Task 2: Ship scoping document	November 2016	Go/no-go decision by DOE
3. Data Management Plan (USGS and UR)	January 2017	Mutual acceptance of revised plan by DOE and PIs
4. Subtask 3.2: Complete ship contracting (UR)	May 2017	Signed award documentation
5. Subtask 3.4: NEPA documentation (USGS)	June 2017	Final signatures by the USGS and then cognizant DOE officials
6. Subtask 3.2: Complete equipment leasing (USGS)	July 2017	Signed award documentation
7. Task 4: Complete research cruise—CRITICAL MILESTONE	October 2018	Cruise narrative not to exceed 5 pages provided in 4th quarter report
8. Task 4: Complete research cruise	January 2018	Submit *Fire in the Ice* article
9. Task 5: Geochemical analyses	September 2018	Submit first paper to peer-reviewed journal
10. Task 6: Geophysical analyses—CRITICAL MILESTONE	June 2019	Submit paper to peer-reviewed journal on updates to seeps database/intensity maps
11. Task 7: Interpretation of CH_4 and CO_2 distributions—CRITICAL MILESTONE	June 2019	Submit paper(s) to peer-reviewed journal on CH_4 fluxes and pH distributions
12. Task 8: Synthesis	September 2019	Release data and metadata

Complete

Informed by DOE in January 2017 that original data management submission is acceptable

The contract was signed and fully executed on 7 August 2017.

USGS has approved NEPA documents that cover the cruise. The documentation was submitted to DOE, which has signed onto the USGS NEPA determination as a cooperating agency.

The USGS completed all equipment leasing.

Research cruise was successfully conducted from 24 August to 7 September 2017 and the narrative is submitted here.

1.2 Progress on Research Tasks

The main objectives during Q4 were to complete (1) Task 3 *Research Cruise Preparation*, Subtask 3.3 *Preparations*, (2) Milestone 4 *ship contracting*, (3) Milestone 5 *NEPA documentation*, (4) Milestone 6 *equipment leasing*, and (5) Milestone 7 *complete research cruise*. Also, during this reporting period, we began Milestone 8 *geochemical analyses*. The work completed and initiated during this report period is detailed below.

1.2.1. Subtask 3.3. Preparations

As detailed in the Project Narrative, several major analytical operations were planned for the research cruise. While all of these operations are established in the PIs' laboratories, the operations were nonetheless revisited during Q1 – Q4 to increase accuracy and precision, and to make them more efficient and effective for this specific research cruise. Detailed below are only the specific preparation activities investigated during Q4; all other activities were fully prepared in previous quarters.

Sea-Air flux

A new sea-air flux system was designed, developed, and tested in the laboratory and the field by Kessler's group prior to this award. Nonetheless, because this technique is relatively new, we performed further tests of this system in the laboratory and in the field for technique assessment. This system relies on the vacuum extraction of dissolved gases as seawater is rapidly pumped past a gas permeable membrane. During this reporting period, we assessed the precision, accuracy, and sensitivity of these techniques as a function of different membrane types, water and gas flowrates, pressure, and temperature (Figure 1). When components of the design that decreased the precision where identified, they were re-engineered during this report period.

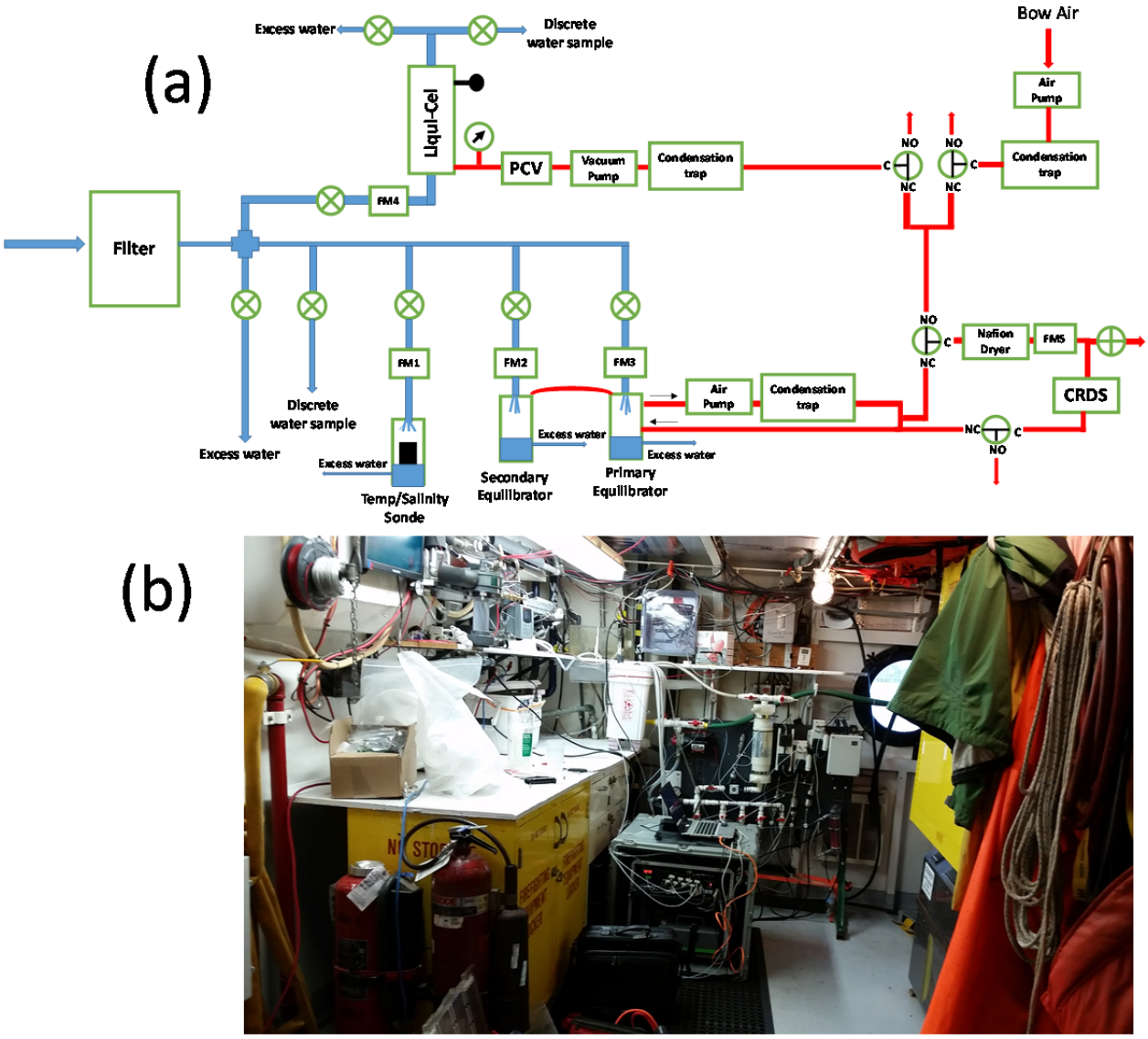

Figure 1. (a) Schematic and (b) Photograph of the system operating on the R/V *Blue Heron* used for the ultra-fast analysis of dissolved methane and carbon dioxide concentrations and isotopes in surface waters. The blue and red lines on the schematic indicate directions of water and gas flow, respectively. ⊗ = Two-way manual ball valve. ⊕ = Two-way solenoid valve. ⊖ = Three-way solenoid valve. ⊘ = Pressure gauge. PCV = Proportional Control Valve. FM = Flow Meter. NO = Normally open. NC = Normally closed. C = Common.

Radiocarbon Methane

This system was also previously established in the Kessler laboratory prior to funding this project. However, additional modifications and validations were conducted during this reporting period to increase the efficiency of this analysis and to be able to sample deeper waters. The

challenge with measuring the natural radiocarbon content of methane dissolved in seawater is that typical concentrations of dissolved methane are low and require the extraction of methane from tens of thousands of liters of water for a single analysis. We developed a new procedure where water is pumped onboard at a rate of 220 liters per minute and the dissolved gases are vacuum extracted continuously. Then, the degassed water is returned overboard, while the extracted gases are compressed into a small cylinder to return to the home laboratory for further preparations and analysis. During Q3, a manuscript of this method was formally published in Limnology & Oceanography: Methods (Figure 2) acknowledging DOE support. Also during Q3-4, we investigated how to further increase this pumping rate to over 300 liters per minute to decrease the sample collection time and how to efficiently collect these samples not only in the surface ocean, but also the deep waters. These increased flow rate and deep water sampling operations were tested on the R/V *Blue Heron* in June 2017 and where conducted effectively on the R/V *Hugh Sharp* in August/September 2017.

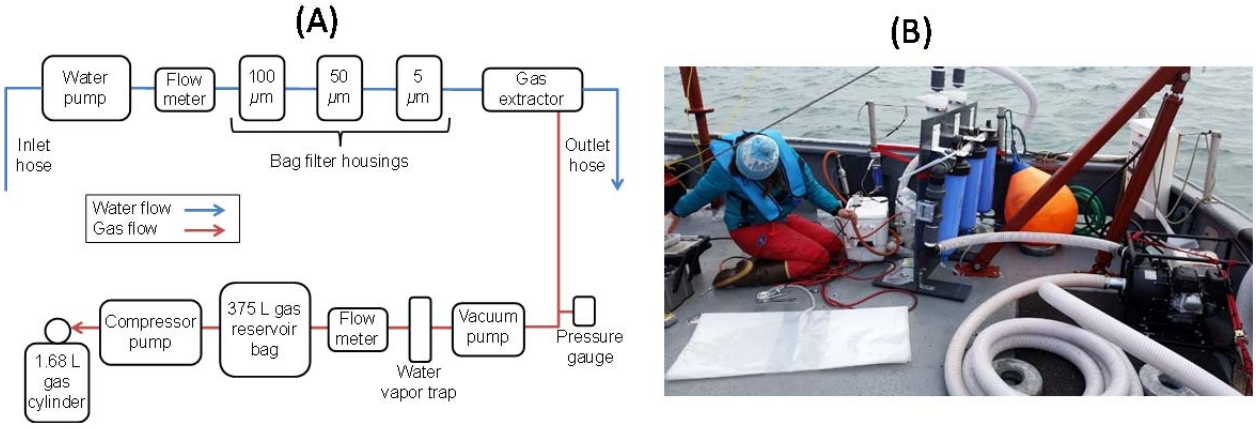

Figure 2. Measurement system for natural radiocarbon abundance of methane in seawater. (a) Schematic of the shipboard extracted gas sample collection system for collecting dissolved methane. Water flow: Seawater is pumped up from depth at rates of 220-230 L/min using a non-submersible pump. The seawater is filtered to 5 µm before flowing through the gas extractor. The dissolved gases are vacuum extracted as the water flows continuously through the gas permeable membrane of two gas extractors in parallel. The degassed water is returned overboard. Gas flow: An oil-free vacuum pump continuously extracts the dissolved gases from the water flowing

across the gas permeable membrane. Water vapor is removed from the gas stream before it is deposited in a 400 L gas reservoir bag. Once it is filled with gas, the reservoir bag is compressed into a 1.68 L high-pressure aluminum gas cylinder using an oil-free compressor pump. (b) Sample collection operations in Prudhoe Bay, AK. Photo taken onboard the R/V *Ukpik* just prior to beginning a sample collection. The gas reservoir bag has just been evacuated after flushing with ultra-zero air contained in a cylinder that the extracted gas sample was compressed into after collection (Sparrow and Kessler, L&O Methods, 2017).

Isotopic models

During this research cruise, we collected data on $\delta^{13}C\text{-}CH_4$ dissolved in seawater. This data will be used to constrain the extent of methane oxidation in seawater. The $^{12}CH_4$ isotope oxidizes at a slightly faster rate than the $^{13}CH_4$ isotope. This leads to a gradual enrichment in the $^{13}CH_4$ isotope in the remaining methane. Our approach is to exploit these isotopic changes to constrain the total extent of the released methane that was oxidized. We investigated this kinetic isotope effect in the Hudson Canyon, US Atlantic margin and used it to constrain the extent of methane oxidation. During the Q2 reporting period, this Hudson Canyon manuscript was published (Leonte et al., Geochim. et Cosmochim. Acta, 2017). A similar procedure is being used to constrain the total integrated extent of methane oxidation between Wilmington Canyon and Cape Hatteras for data collected during our research cruise.

Our exploration of methane stable isotope fractionation also led to the realization that the solubility of $^{12}CH_4$ is slightly different from $^{13}CH_4$. We realized that for a methane bubble released from the seafloor, a shift in the natural isotopic ratios should be observed as more methane dissolves. During the Q2 – Q4 reporting periods, we used data collected in the Gulf of Mexico during April 2015, on a cruise led by Scott Socolofsky at TAMU, to constrain the

fraction of seafloor released methane that had dissolved out of the bubble. The results suggested a rapid rate of methane dissolution into the deep waters. We then compared our results against what Socolofsky's bubble model predicts, finding agreement. Those results are currently in the final stages of preparation for submission to a peer-reviewed journal.

1.2.2. Task 4. Complete Research Cruise

Narrative for the Research Cruise: During this reporting period, we completed the research cruise, which is Milestone 7 and Task 4. The verification method of this critical milestone is the cruise narrative, not to exceed 5 pages, submitted here.

During August and September of 2017, the fate of methane released from gas hydrates systems, be those releases natural or accidental from gas hydrate production, was investigated along the US Atlantic margin by PIs Kessler and Ruppel. These investigators jointly led a team of eight scientists from the University of Rochester and five scientists from the US Geological Survey on a research expedition aboard the research vessel (R/V) *Hugh Sharp*. The vessel was modelized with scientific equipment on August 24 and departed Lewes, Delaware on August 25, 2017. Data, seawater, and dissolved gas samples were collected along the continental shelf and slope between approximately Wilmington Canyon (offshore of Delaware) and Keller Canyon (offshore of Cape Hatteras, North Carolina) (Figure 3). The vessel returned to port in Lewes, Delaware on September 6 and the scientific equipment was demobilized on September 7, 2017. In total this expedition covered approximately 1000 nautical miles.

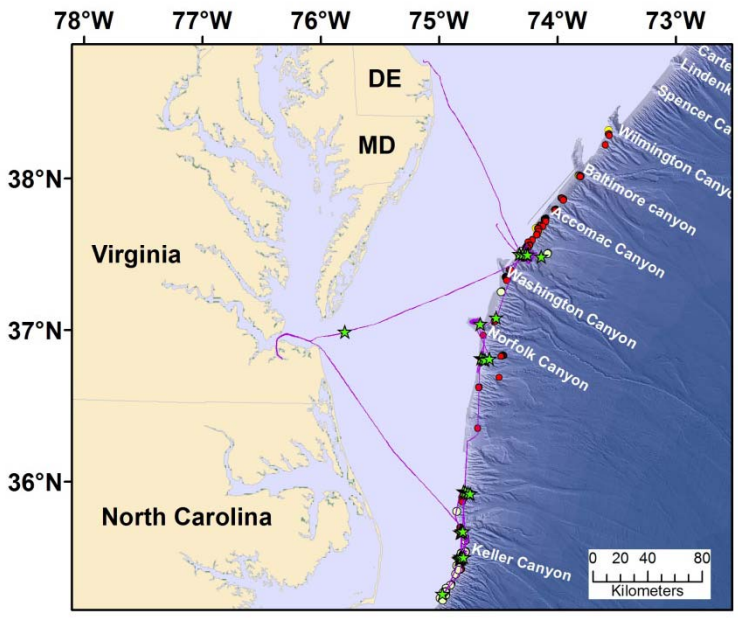

Figure 3. Cruise tracks (purple) for the oceanographic research expedition on the R/V *Hugh Sharp* from August 25 – September 7, 2017. The circles represent methane seeps reported in Skarke et al., (2014) (red) and discovered by PI Ruppel during a 2016 cruise on the R/V *Armstrong* (white). Green stars are the locations of the CTD water column sampling stations during this expedition.

This research expedition had two overarching scientific objectives. Objective 1 was to investigate if methane released at the seafloor from gas hydrates systems was reaching the atmosphere, and if so, to quantify those emission rates. Objective 2 was to quantify any ocean acidification that may have occurred as the released methane was biodegraded to carbon dioxide by aerobic bacteria.

To accomplish these two main objectives, first we identified methane bubble plumes being emitted from the seafloor and the height above the seafloor when the bubbles fully dissolved in the water. The USGS team used two acoustic systems to locate and characterize methane plumes in the water column. The first was a Kongsberg EM2040p 200-400 kHz single-swath high-resolution multibeam with water column imaging capabilities. Because multibeam echosounders (MBES) record data in a strip, instead of within a narrow cone, they are far more effective than split-beam sonars in merely locating plumes. The EM2040p nominally images to 550 m water

depth, which is the approximate maximum depth of the updip limit of gas hydrate stability on the US Atlantic margin, and produces a swath up to 760-m-wide. After bubble plumes were identified with the MBES, a second acoustic system was used to obtain more quantitative data on plume characteristics. A broadband EK80 transceiver that drives a split-beam sonar operated with a single 38 kHz transducer was used for this operation. The EK80 produced an image of gas bubbles in the water column and quantitative information was obtained that can be used to infer plume characteristics and estimate flow rates. These acoustic surveys were typically conducted during nighttime operations.

While the acoustic survey was underway, the surface water concentration of dissolved methane and the associated sea-to-air flux were mapped continuously with ultra-high spatial resolution. The Kessler laboratory at the University of Rochester has developed a system that continually pumps surface water through a system that continually vacuum extracts the dissolved gases and continually pumps the extracted dissolved gases through a cavity-ringdown spectrometer for concentration analysis. Since this system does not rely on dissolved gases equilibrating with a gaseous headspace, as is more commonly conducted, but instead vacuum extracts the dissolved gases, relatively long (>30 minutes) equilibration times are eliminated enabling surface water methane concentrations to be mapped with high spatial resolution. This operation was conducted successfully while acoustic surveys were conducted. The acoustically imaged bubbles plumes emanating from the seafloor are currently being correlated with surface water methane concentration data.

While the colocation of methane concentration "hot spots" in the surface waters with bubble plumes suggests that methane emitted from the seafloor is ultimately being emitted to the atmosphere, it does not provide a fingerprint connecting these different methane pools. For this reason, we also measured the natural radiocarbon content of methane dissolved in seawater. Methane emitted from gas hydrates has previously been shown to be devoid of natural radiocarbon, however, methane formed from more modern carbon, either anaerobically in surface sediments or aerobically in the subsurface ocean, contains modern levels of radiocarbon. A previous study above seafloor seep emissions displayed low radiocarbon contents of methane dissolved in deep waters contrasted against methane in the surface waters with modern levels of radiocarbon (Kessler et al., 2008). Thus, samples were collected at several stations to measure the natural radiocarbon content of methane throughout the water column so that the source of methane in the surface waters could be better constrained. The challenge with this technique is that, due to the relatively low concentration of methane dissolved in seawater, dissolved methane must be extracted from greater than 20,000 L of seawater for a quantitative analysis. In order to accomplish this task, seawater was continually pumped up to the ship at a rapid rate, the dissolved gases were continually extracted, and the degassed water was continually discarded overboard. In total, 14 samples were successfully collected and are currently being processed for analysis via accelerator mass spectrometry.

After the bubble plumes were identified and the surface water concentration mapped, CTD hydrocasts were conducted guided by the EK80. The hydrocasts collected seawater samples used to investigate if methane oxidation was producing carbon dioxide at high enough levels to influence ocean acidification. From the seawater samples collected, the following measurements

were conducted: dissolved methane concentration, $\delta^{13}C$-CH_4, dissolved inorganic carbon (DIC) concentration, $\delta^{13}C$-DIC, natural radiocarbon of DIC, and high-precision pH via a spectrophotometric method. The measurements of dissolved methane concentration and high-precision pH were both conducted onboard the R/V *Hugh Sharp* shortly after the samples were collected. All other samples were preserved and returned to the home laboratory for later analysis. The samples of dissolved methane concentration and $\delta^{13}C$-CH_4 were collected to constrain the extent of aerobic methane oxidation in the water column using an approached described in Leonte et al., [2017]. The samples of DIC concentration, $\delta^{13}C$-DIC, natural radiocarbon of DIC, and high-precision pH were all used to constrain the influence of the oxidation of gas hydrate-released methane on ocean acidification. More specifically, the measurements of high-precision pH and DIC concentration are used to determine changes in dissolved CO_2 concentrations as well as acidification. The measurements of $\delta^{13}C$-DIC and natural radiocarbon DIC are used to constrain the source of any CO_2 perturbation, relying on the observations that methane released from gas hydrates is devoid of natural radiocarbon and background DIC has more modern radiocarbon values. In total, five transects running perpendicular to the continental slope were conducted between Cape Hatteras and Wilmington Canyon. Each transect contained four to five stations, sampling water from twelve different depths. In total, over one thousand samples were collected. Despite an active hurricane season in the Atlantic Ocean, this was a highly successful research expedition. We accomplished or exceeded all of the goals proposed for this expedition with regards to sample and data collection.

Upon returning to shore, the samples for natural radiocarbon and $\delta^{13}C$ of DIC as well as $\delta^{13}C$-CH_4 were sent to the appropriate analytical facilities for analysis (Keck CCAMS facility at Univ.

of California Irvine and the Woods Hole Isotope Labs, respectively). The natural radiocarbon methane samples are currently being prepared in the Kessler laboratory for analysis. The dissolved inorganic carbon concentration samples are awaiting analysis in the Kessler laboratory with an anticipated start date in early 2018. All data collected at sea (acoustic, high-resolution surface water CH_4 concentration mapping, dissolved methane concentration, and high-resolution pH), are currently being investigated and interpreted.

1.3 Training and Professional Development

During the reporting period, this project supported Ph.D. student Mr. Mihai Leonte and research scientist Dr. DongJoo Joung. Leonte is being trained in isotope geochemistry, and he is gaining skills on how to collect samples, conduct concentration and isotope analyses, interpret the isotope geochemical results to determine the fate of released methane, and present and publish the results. Leonte is being trained on how to use natural isotopic measurements to specifically determine the extent that methane dissolves in seawater following a seafloor bubble release as well as the extent of methane oxidation in the water column. Joung is championing the natural radiocarbon analyses of dissolved methane. He has already optimized this technique by increasing the rate at which these samples are collected by 50% and developing the means to sample deep water. Both Leonte and Joung participated in, and were essential components of, the research cruise on the R/V *Hugh Sharp*.

1.4 Dissemination of Results to Communities of Interest

During this reporting period, work was conducted on two publications. The first publication describes results obtained using our methane radiocarbon technique to determine the source of methane in the Arctic Ocean. While the samples were not from the US Atlantic margin, this work conducted on this DOE project helped interpret these results, and thus the DOE is acknowledged in this manuscript. This manuscript is currently in review at Science Advances. The second publication is in the final stages of preparation prior to submission and describes our newly developed technique of using natural measurements of $\delta^{13}C\text{-}CH_4$ to determine the fraction of methane which dissolves out of a bubble released from the seafloor. A list of all publications resulting from this work to date can be found below in section 2.1.

1.5 Milestones Log

Table 1 displays the milestones for this project. Milestone 4, 6, and 7 were completed during this reporting period.

1.6 Plans for the Next Reporting Period

During the next reporting period, the data and samples collecting during the research cruise will be analyzed. Specific analyses to be conducted are the natural radiocarbon content of methane and dissolved inorganic carbon (DIC) and $\delta^{13}C\text{-}CH_4$. We will begin preparing for the analysis of [DIC] but will likely not begin those analyses until Y2, Q2. In addition to the analysis of these samples, the data collected at sea for $[CH_4]$, high precision pH of seawater, and the ultra-high

resolution sea-to-air flux data will be processed and quality control/quality assurance analyses will be conducted.

2. PRODUCTS

2.1 Publications, Conference Papers, and Presentations

Publications.

This publication establishes a technique which will be used on our August research expedition.

M. Leonte, J. D. Kessler, M. Y. Kellermann, E. C. Arrington, D. L. Valentine, S. P. Sylva (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, doi:10.1016/j.gca.2017.01.009.

The following peer-review publications acknowledge this DOE project for support.

C. D. Ruppel and J. D. Kessler (2017), "The Interaction of Climate Change and Methane Hydrates." Reviews of Geophysics, 55, doi: 10.1002/2016RG000534.

K. J. Sparrow and J. D. Kessler (2017), "Efficient collection and preparation of methane from low concentration waters for natural radiocarbon analysis." L&O: Methods, doi: 10.1002/lom3.10184.

K. J. Sparrow, J. D. Kessler, J. R. Southon, F. Garcia-Tigreros, K. M. Schreiner, C. D. Ruppel, J. B. Miller, S. J. Lehman, and X. Xu (2017), "Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf." Science Advances, In Review.

Presentations

No presentations were made during this reporting period.

2.2 Websites or Other Internet Sites

A project website is currently under design but is not currently public.

2.3 Technologies or Techniques

Part of Subtask 3.3. *Preparations* is to test and validate new techniques which were used on the research expedition on the R/V *Hugh Sharp*. During Q3-Q4, the methane radiocarbon technique was updated to make it more efficient and able to sample deeper waters and the technique was formally published. The ultra-high resolution technique for surface water dissolved methane concentration mapping was also updated during this reporting period to make the results higher precision.

2.4 Inventions, Patent Applications, and/or Licenses

Nothing to report.

2.5 Other Products

Nothing to report.

3. PARTICIPANTS AND OTHER COLLABORATING ORGANIZATIONS

3.1 Project Personnel

1. **Name:** John D. Kessler

2. **Project Role:** Principal Investigator

3. **Nearest person month worked:** 1

4. **Contribution to Project:** During this reporting period, Kessler led this project, contributed to reviewing the ship contract, wrote and edited the publications acknowledging this project for support, prepared, tested, and validated the analytical equipment necessary for the field and laboratory research associated with this project, led the research cruise on the R/V *Hugh Sharp*, and began processing the collected data.

5. **Collaborated with individual in foreign country:** No

6. **Travelled to foreign country:** No

1. **Name:** Carolyn D. Ruppel

2. **Project Role:** Principal Investigator

3. **Nearest person month worked:** 0.5

4. **Contribution to Project:** Completed the NEPA documentation and contributed ship specifications for UR ship contracting; completed leasing for large equipment; helped lead the research expedition on the R/V *Hugh Sharp*; began processing the collected data.

5. **Collaborated with individual in foreign country:** No

6. **Travelled to foreign country:** No

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1. **Name:** Mihai Leonte

2. **Project Role:** Ph.D. student

3. **Nearest person month worked:** 3

4. **Contribution to Project:** During this reporting period, Mr. Leonte contributed to Subtask 3.3. *Preparations*, by analyzing existing data from the Gulf of Mexico and Hudson Canyon, US Atlantic Margin to test and validate the isotopic models which will be used in this project to determine the extent of methane (1) dissolution from bubbles into the water column and (2) oxidation. In addition, Mr. Leonte contributed to this subtask by testing the analytical equipment and validating the methods to measure

dissolved methane concentration and isotopes, which were used on the research cruise. Finally, Mr. Leonte participated in the research cruise on the R/V *Hugh Sharp* and analyzed dissolved methane concentrations and collected samples for the analysis of $\delta^{13}C\text{-}CH_4$.

1. **Name:** Dr. DongJoo Joung

2. **Project Role:** Research Scientist

3. **Nearest person month worked:** 2

4. **Contribution to Project:** During this reporting period, Dr. Joung contributed to Subtask 3.3. *Preparations* and Task 4 *Complete Research Expedition*. Dr. Joung has led our efforts to measure the natural radiocarbon content of methane, which is being used as an isotopic fingerprint for methane sources.

5. **Collaborated with individual in foreign country:** No

6. **Travelled to foreign country:** No

3.2 Partner Organizations

None to report.

3.3 External Collaborators or Contacts

We collaborate closely with Professor Scott Socolofsky at Texas A&M University, who is the PI of another project funded by DOE/NETL entitled "Dynamic Behavior of Natural Seep Vents: Analysis of Field and Laboratory Observations and Modeling." PIs Kessler, Ruppel, and Socolofsky communicate regularly and accomplishments from those communications can be found in Subtask *3.3. Preparations, Isotope Models.*

4. IMPACT

None at this point.

5. CHANGES/PROBLEMS

None to report.

6. SPECIAL REPORTING REQUIREMENTS

None required.

7. BUDGETARY INFORMATION

The expenses through the end of this reporting period are summarized in Table 2. The expenses to date are significantly less than anticipated due to a delay in receiving an invoice for our use of the R/V *Hugh Sharp*. The invoice has since been received in the amount of $198,283.50 and is being processed for payment.

Table 2. Budget Report

	Budget Period 1							
Baseline Reporting	**Q1**		**Q2**		**Q3**		**Q4**	
Quarter	10/1/2016 - 12/31/2016		1/1/2017 - 3/31/2017		4/1/2017 - 6/30/2017		7/1/2017 - 9/30/2017	
DE-FE0028980	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	$ 23,223.00	$ 23,223.00	$ 39,744.00	$ 62,967.00	$ 43,744.00	$ 106,711.00	$ 285,025.00	$ 391,736.00
Non-Federal Share	$ 46,345.34	$ 46,345.34	$ 37,117.33	$ 83,462.67	$ 16,200.33	$ 99,663.00		$ 99,663.00
Total Planned	$ 69,568.34	$ 69,568.34	$ 76,861.33	$ 146,429.67	$ 59,944.33	$ 206,374.00	$ 285,025.00	$ 491,399.00
Actual Incurred Cost								
Federal Share	$ 6,082.61	$ 6,082.61	$ 18,366.37	$ 24,448.98	$ 33,876.21	$ 58,325.19	$ 71,572.00	$ 129,897.00
Non-Federal Share	$ 46,345.34	$ 46,345.34	$ 36,571.00	$ 82,916.34	$ 16,644.98	$ 99,561.32	$ 569.00	$ 100,130.00
Total Incurred Cost	$ 52,427.95	$ 52,427.95	$ 54,937.37	$ 107,365.32	$ 50,521.19	$ 157,886.51	$ 72,141.00	$ 230,027.00
Variance								
Federal Share	$ (17,140.39)	$ (17,140.39)	$ (21,377.63)	$ (38,518.02)	$ (9,867.79)	$ (48,385.81)	$ (213,453.00)	$ (261,839.00)
Non-Federal Share	$ -	$ -	$ (546.33)	$ (546.33)	$ 444.65	$ (101.68)	$ 569.00	$ 467.00
Total Variance	$ (17,140.39)	$ (17,140.39)	$ (21,923.96)	$ (39,064.35)	$ (9,423.14)	$ (48,487.49)	$ (212,884.00)	$ (261,372.00)