OIL & GAS

DOE Award No.: DE-FE0028980

Quarterly Research Performance Progress Report

(Period Ending 12/31/2016)

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)

Submitted by:
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Signature

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Office of Fossil Energy

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1 Accomplishments

1.1 Summary of Progress Toward Project Objectives

The overall goal of this project is to investigate the fate of methane released at the seafloor from decomposing gas hydrate systems along the US Atlantic margin. 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. A major obstacle for determining this flux is both detecting and 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. Second, a technique to measure the natural radiocarbon content of methane in surface waters was established. Since the concentration of methane dissolved in seawater is relatively low, the major obstacle for this analysis has been the collection of sufficient quantities of methane dissolved in seawater. This problem was recently solved and methane can be extracted from >20,000 L of seawater in under 2 hours (Sparrow and Kessler, 2017). 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 processes will be investigated during a 2-week measurement campaign using the R/V *Hugh Sharp* along the US Atlantic margin. Overall, this research project will be conducted in four stages: (1) prepare for the research cruise, (2) execute the research cruise, (3) analyze and interpret the samples and results, and (4) disseminate the findings.

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

1.2 Progress on Research Tasks

As displayed in Table 1, the Project Management Plan has been submitted to and approved by DOE. The R/V *Hugh Sharp* was been scoped and was determined to be the most appropriate vessel for the research in terms of proximity to the region being studied, facilities to support the planned research, and cost. In addition, Task 3 *Research Cruise Preparation*, Subtask 3.3 *Preparations* was partially completed during this reporting period. The work being conducted and completed is detailed below.

1.2.1. Task 1.0: Project Management and Planning

The Project Management Plan (PMP) was completed and submitted to the program officer on November 1, 2016. The plan was fully accepted on November 8, 2016.

1.2.2. Task 2.0: Scoping of R/V Hugh Sharp for 2017 Research Cruise

Through conversations with the operator of the R/V *Hugh Sharp*, and based on past experience working on this specific vessel by PI Ruppel, we assessed whether this research vessel would be able to support our planned operations. The vessel's laboratory and deck space, as well as the vessel's equipment and infrastructure, were carefully considered and determined to be both the most suitable and cost effective option for our planned research. Kessler plans to visit the *Hugh Sharp* in early May (Q3) during Ruppel's mobilization of another cruise to establish the most efficient operating structure for our scientific activities during the August/September 2017 cruise.

1.2.3. Subtask 3.3. Preparations

As detailed in the Project Narrative, several major analytical operations are planned for the research cruise. While all of these operations are established in the PIs' laboratories, the operations are nonetheless being revisited during this reporting period to increase accuracy and precision, and to make them more efficient and effective for this specific research cruise.

DIC measurement system

A system is established in the Kessler laboratory at the University of Rochester to measure the dissolved inorganic concentration in seawater. This system precisely acidifies a seawater sample and sparges the CO_2 into a Picarro G1101-i Cavity Ringdown Spectrometer (CRDS). During this reporting period, the system design was updated slightly to more precisely control sample temperature and volume, as well as gas flow rate. This increased the precision of our system by roughly a factor of 3, and precisions of 0.3 % or less are typical. This system also has the ability to constrain $\delta^{13}C$ and we are currently quantifying and optimizing the accuracy and precision of this analysis (Figure 1).

System to measure dissolved methane concentration in seawater

A conventional analysis in the Kessler laboratory is the measurement of dissolved methane concentration in seawater. However, during this research expedition, we anticipate to have highly variable concentrations ranging from background to >10,000 times background. Our normal analysis procedure involves collecting seawater samples in glass vials, equilibration with a headspace, and analysis of the headspace on a gas chromatograph with a flame ionization detector (Weinstein et al., 2016). Our procedures are being evaluated to increase accuracy and precision over the large dynamic range we anticipate to encounter.

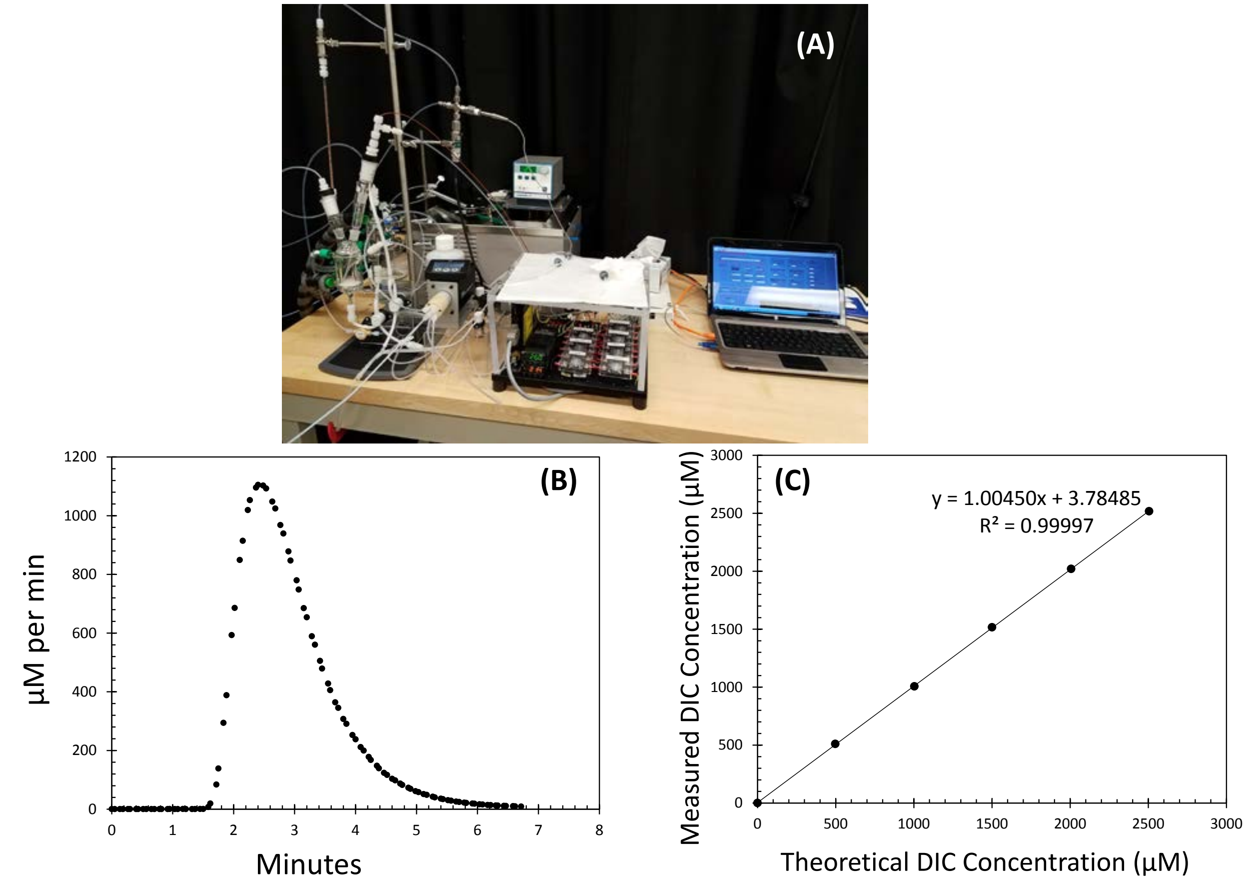

Figure 1. System to measure Dissolved Inorganic Carbon (DIC) and verification results. (a) Picture of the system to measure dissolved inorganic carbon concentration and $\delta^{13}C$ isotopes. (b) Example peak obtained when sparging CO_2 from seawater and measuring the resulting CO_2. (c) Calibration curve from prepared standards.

Sea-Air flux

As detailed in the project narrative, a new sea-air flux system was designed, developed, and tested in the laboratory and the field by Kessler's group over the past year. Further testing of the system has been conducted in the laboratory during this reporting period. This system relies on the vacuum extraction of dissolved gases as seawater is rapidly pumped past a gas permeable membrane. During this reporting period, different membranes were tested in both the laboratory as well as on Lake Superior as part of a separate project funded by the NSF.

Radiocarbon Methane

This system was also previously established in the Kessler laboratory prior to funding this project. However, additional validations were conducted during this reporting period and confirmed our ability to quantitatively prepare methane for radiocarbon analysis. 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 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 this reporting period, final validation tests were conducted and a manuscript of this procedure was submitted. Conditional acceptance for publication has since occurred, but after this reporting period (Figure 2).

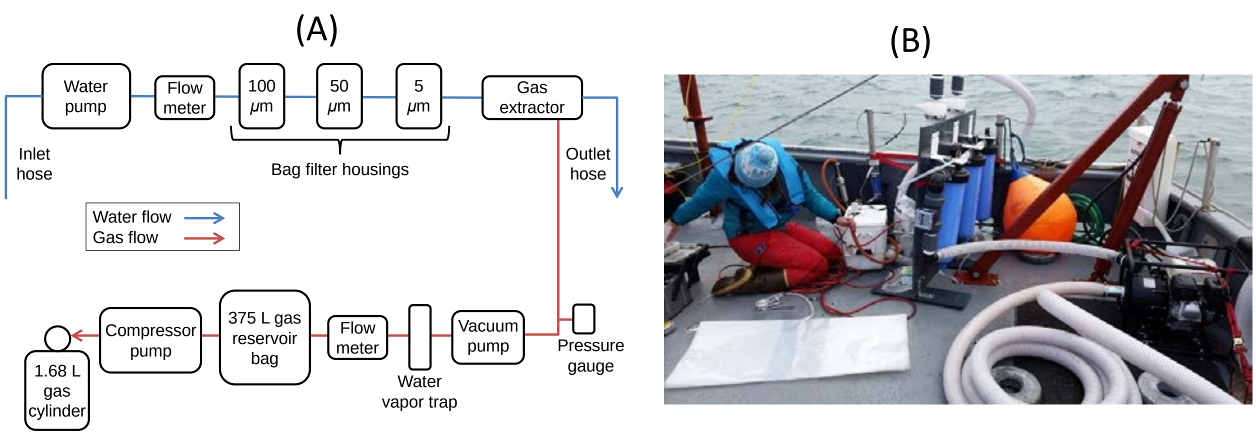

Figure 2. Measurement system for natural radiocarbon abundance of methane in seawater. (a) Schematic of the shipboard extracted gas sample collection system for collecting dissolved methane. Water flow: Seawater is pumped up from depth at rates of 220-230 L/min using a non-submersible pump. The seawater 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, Conditional Acceptance).

Isotopic models

This research cruise will collect 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 this reporting period, this Hudson Canyon manuscript was revised and accepted for publication (Leonte et al., Geochim. et Cosmochim. Acta, 2017, Accepted). A similar procedure will be used to constrain the total integrated extent of methane oxidation between Wilmington Canyon and Cape Hatteras for data collected during our upcoming 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 $^{13}CH_4$. During this reporting period, we realized that for a methane bubble released from the seafloor, a shift in the natural isotopic ratios should be observed and can be used to constrain the fraction of seafloor released methane that has dissolved out of the bubble. We tested this hypothesis with data collected in the Gulf of Mexico during April 2015, on a cruise led by Scott Socolofsky at TAMU. 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 preparation for submission to a peer-reviewed journal.

1.3 Training and Professional Development

During the reporting period, this project supported Ph.D. student Mr. Mihai Leonte. Leonte is being trained in isotope geochemistry and he is gaining skills on how to collect samples, conduct concentration and isotope analyses, and interpret the isotope geochemical results to determine the fate of released methane. Leonte is being trained on how 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; Leonte is being trained how to make these determinations with natural isotopic measurements.

1.4 Dissemination of Results to Communities of Interest

Two peer-reviewed scientific publications acknowledging this support were accepted during this reporting period. These publications can be found below in section 2.1. Also, a relationship was established with a local Rochester city elementary school (James P.B. Duffy School # 12, Rochester, NY) and Kessler will give a presentation to a 5th grade class during the next reporting period.

1.5 Milestones Log

Table 1 displays the milestones for this project. Accomplished during this reporting period are Milestones 1 and 2.

1.6 Plans for the Next Reporting Period

During the next reporting period, the PIs will continue to prepare for the oceanographic research expedition, which will occur along the US Atlantic margin in August and September 2017 on the R/V *Hugh Sharp*. To this end, the PIs will complete the following objectives. (1) The Data Management Plan will be finalized by the PIs and submitted to DOE for approval. (2) Even though PIs Kessler and Ruppel are in regular contact, they will conduct a formal pre-cruise PI meeting (Subtask 3.1) using a web-based conferencing tool such as WebEx, Skype, and Google Hangouts. Topics to be discussed at this meeting will include both logistics (Subtask 3.2 Ship Contracting, Subtask 3.4 NEPA Review Documentation) and science (establish a cruise plan, Subtask 3.3. Preparations). (3) The PIs will continue to prepare for the research cruise (Subtask 3.3. Preparations). The ultra-high spatial resolution technique used to measure sea-to-air flux will be tested and updated to make it more portable and efficient during our at-sea investigations. The new technique to be used for natural radiocarbon measurements of methane will be practiced by the Ph.D. students and postdoc. The sampling equipment for the [DIC] and $\Delta^{14}C$-DIC analyses will be prepared.

2. PRODUCTS

2.1 Publications, Conference Papers, and Presentations

Publications.

The following peer-review publications acknowledge this 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.

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.

Sparrow and Kessler (2017), “Efficient collection and preparation of methane from low concentration waters for natural radiocarbon analysis.” L&O: Methods, Conditional Acceptance.

Presentations

Drs. Kessler and Ruppel made a presentation to the Project Kick-Off via WebEx to DOE/NETL on November 14, 2016. No other 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 a new technique which has been developed in the Kessler laboratory to measure the concentration of dissolved inorganic carbon ([DIC]). In a controlled and automated system, seawater is acidified and the resulting CO_2 is stripped into a Picarro G1101-i Cavity Ringdown Spectrometer (CRDS) for analysis. The precision of this technique was increased during this reporting period and the ability to concurrently measure reliable $\delta^{13}C$-DIC results was also assessed during this reporting period. The details of this technique are currently being prepared for publication.

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 establishing the project management plan, wrote and edited the publications acknowledging this project for support, and has prepared, tested, and validated the analytical equipment necessary for the field and laboratory research associated with this project.

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

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

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

2. **Project Role:** Principal Investigator

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

4. **Contribution to Project:** Contributed to project management plan and participated in kickoff meeting; interacted with DOE program officers on data management plan; scoping of vessel, preliminary plans for NEPA approval, planning of lease options in contracts for geophysical cruise instrumentation being used on both her

May 2017 cruise and the Aug/Sept cruise funded by this award, design of fantail mount for multibeam sonar equipment, preparation of computer program to convert raw split-beam methane imaging data from broadband EK80 transceiver to format readable by community-based programs for EK60, preparations for automating outriggers for EK80 calibration during planned cruise. Some of these activities are needed for Ruppel's upcoming May 2017 cruise, but do double-duty in providing basic work needed for the cruise funded by this award.

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 will be used on the research cruise in Year 1.

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

This project collaborates closely with Professor Scott Socolofsky at Texas A&M University, who is the PI of a new projected 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 Section *1.2.3.,* Subtask *3.3. Preparations, Isotope Models.*

4. IMPACT

None at this point.

5. CHANGES/PROBLEMS

During this reporting period, a suitable postdoctoral candidate was identified. The candidate has experience working with Kessler as well as experience working in oceanographic environments containing natural seepage in both the US Atlantic Margin and the Gulf of Mexico. He has a planned visit to the University of Rochester shortly and we anticipate his transition to the team shortly thereafter.

6. SPECIAL REPORTING REQUIREMENTS

None require.

7. BUDGETARY INFORMATION

The expenses through the end of this reporting period are summarized in Table 2. The expenses to date are less than anticipated due to the delay in hiring a postdoctoral research assistant for this project. A suitable candidate was identified during this reporting period and we anticipate he will transition to the University of Rochester shortly.

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							
Non-Federal Share	$ 46,345.34							
Total Incurred Cost	$ 52,427.95							
Variance								
Federal Share	$ (17,140.39)							
Non-Federal Share	$ -							
Total Variance	$ (17,140.39)							

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