NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

DOE Award No.: DE-FE0028980

Quarterly Research Performance Progress Report

(Period Ending 3/31/2017)

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)

Submitted by:
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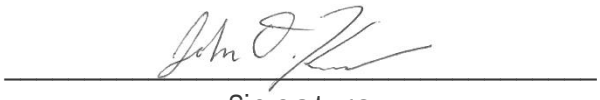

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1 Accomplishments

1.1 Summary of Progress Toward Project Objectives

Since the goals of this project remain the same and many tasks are conducted across quarters, much of the text from the Q1 report still applies and is repeated here.

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

Initiated but not completed in Q2.

1.2 Progress on Research Tasks

In Q1, the Project Management Plan was submitted and approved by DOE and the R/V *Hugh Sharp* was scoped and 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. Thus, the main objectives during Q2 were to continue progress towards completing Task 3 *Research Cruise Preparation*, Subtask 3.3 *Preparations*. Subtask 3.3 was initiated during Q1 and progress was continued during Q2 with emphasis placed on validating and publishing the analytical methods. The work being conducted and completed is detailed below. Also, a suitable candidate was identified for the research scientist position.

1.2.1. 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 Q1, 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. During this reporting period, we performed additional validations of this technique using previously collected samples along the US Atlantic

Margin and the US Beaufort Sea as well as DIC certified reference materials (CRM; i.e. Dickson seawater standards).

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). During Q1-Q3, we are evaluating our procedures with the goals of increasing accuracy and precision over the large dynamic range we anticipate to encounter. Part of this process is the automation of our analysis procedures.

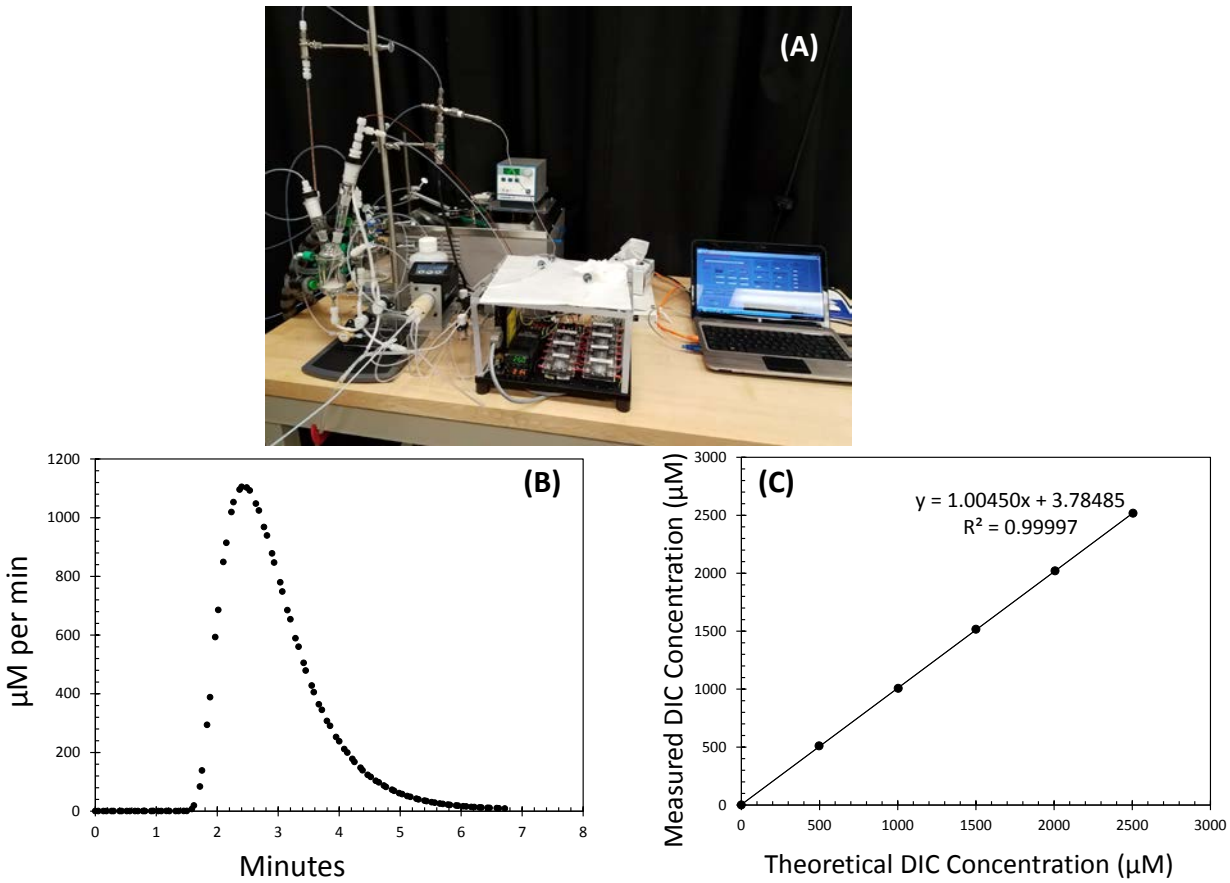

Figure 1. System to measure Dissolved Inorganic Carbon (DIC) and verification results. (a) Picture of the system to measure dissolved inorganic carbon concentration and $\delta^{13}C$ isotopes. (b) Example peak obtained when sparging CO_2 from seawater and measuring the resulting CO_2. (c) Calibration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

Sea-Air flux

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 are performing further tests of this system in the laboratory and analyzing data collected in the Summer and Fall of 2016 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.

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 to increase the efficiency of this 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 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 this reporting period, a manuscript of this method was formally accepted in Limnology & Oceanography: Methods (Figure 2). Also during this reporting period, we began investigating 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.

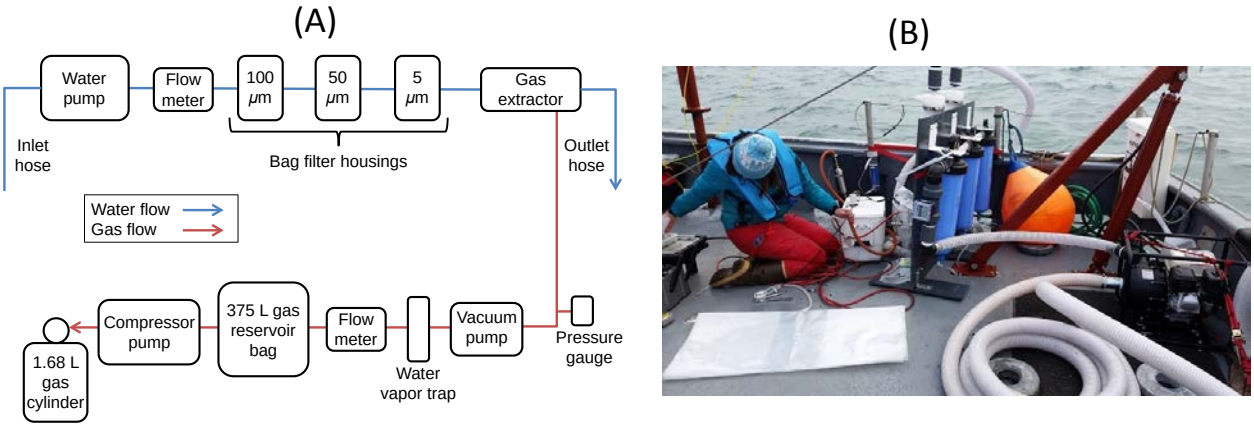

Figure 2. Measurement system for natural radiocarbon abundance of methane in seawater. (a) Schematic of the shipboard extracted gas sample collection system for collecting dissolved methane. Water flow: Seawater is pumped up from depth at rates of 220-230 L/min using a non-submersible pump. The seawater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

This research cruise will collect data on δ^{13}C-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 published (Leonte et al., Geochim. et Cosmochim. Acta, 2017). 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 using natural isotopic measurements.

1.4 Dissemination of Results to Communities of Interest

Two peer-reviewed scientific publications relevant to this project were fully published during this reporting period; one additional paper was accepted during this reporting period. Two of these three publications acknowledge this support. These publications can be found below in section 2.1.

1.5 Milestones Log

Table 1 displays the milestones for this project. Milestone 3 was completed and Milestone 4 was initiated during this reporting period.

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) Milestone 4. Subtask 3.2: Complete ship contracting (UR). This will formally completed by the UR with assistance from the USGS. (2) Even though PIs Kessler and Ruppel are in regular contact, they will conduct a formal pre-cruise PI meeting (Subtask 3.1) at the R/V Hugh Sharp in early May to discuss both logistics (Subtask 3.2 Ship Contracting, Subtask 3.4 NEPA Review Documentation) and science (establish a cruise plan, Subtask 3.3. Preparations). (3) Milestone 5. Subtask 3.4: NEPA documentation will be completed by the USGS with input from the UR. (4) 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 [CH_4], δ^{13}C-CH_4, [DIC] and Δ^{14}C-DIC analyses will be prepared.

2. PRODUCTS

2.1 Publications, Conference Papers, and Presentations

Publications.

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 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.

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

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 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 and accuracy of this technique was increased during this reporting period and validated against a DIC certified reference material. The ability to concurrently measure reliable δ^{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 visited the University of Rochester during this reporting period and he began his transition to the team.

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 he is transitioning to the University of Rochester during the next reporting period.

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				
Non-Federal Share	$ 46,345.34	$ 46,345.34	$ 36,571.00	$ 82,916.34				
Total Incurred Cost	$ 52,427.95	$ 52,427.95	$ 54,937.37	$ 107,365.32				
Variance								
Federal Share	$ (17,140.39)	$ (17,140.39)	$ (21,377.63)	$ (38,518.02)				
Non-Federal Share	$ -	$ -	$ (546.33)	$ (546.33)				
Total Variance	$ (17,140.39)	$ (17,140.39)	$ (21,923.96)	$ (39,064.35)				

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