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Quarterly Research Performance Progress Report (Period Ending 6/30/2018)

Characterizing Ocean Acidification and Atmospheric Emission caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin Project Period (10/01/2017 to 09/30/2018)

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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 previous reports still applies and is repeated here. 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 conducted along the US Atlantic margin in FY17 Q4, 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. Published values of methane in oceanic gas hydrates and released from seafloor seeps have shown the methane to be devoid of natural radiocarbon, yet methane sources from in-situ aerobic production, modern anoxic sediments, or the atmosphere have measurable levels of radiocarbon. This technique will help determine what fraction of methane in surface waters and evading to the atmosphere was originally released from the seafloor from decomposing gas hydrates and seeps. Since the concentration of methane dissolved in seawater is relatively low, the major obstacle for this measurement 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.

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 FY17, stages (1) and (2) were completed. During FY18 Q1, stage (3) was initiated, focusing on the measurements of CH₄ concentration, high precision pH, CH₄ stable isotopes ($\delta^{13}\text{C-CH}_4$), and natural CH₄ radiocarbon ($^{14}\text{C-CH}_4$), and natural radiocarbon of dissolved inorganic carbon ($^{14}\text{C-DIC}$). These geochemical analyses were continued during FY18 Q2 and were completed slightly ahead of schedule during this quarter, FY18 Q3, on 1 June 2018.

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) informed by DOE in January 2017 that original data management submission is acceptable	January 2017	Mutual acceptance of revised submission is acceptable
4. Subtask 3.2: Complete ship contracting (UR)	May 2017 The contract was signed and fully executed on 7 August 2017.	Signed award documentation
5. Subtask 3.4: NEPA documentation (USGS)	June 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.	Final signatures by the USGS and then cognizant DOE officials
6. Subtask 3.2: Complete equipment leasing (USGS)	July 2017 The USGS completed all equipment leasing.	Signed award documentation
7. Task 4: Complete research cruise--CRITICAL MILESTONE	October 2018 Research cruise was successfully conducted from 24 August to 7 September 2017.	Cruise narrative not to exceed 5 pages provided in 4th quarter report
8. Task 4: Complete research cruise	January 2018 Research cruise was successfully conducted from 24 August to 7 September 2017. The Fire in the Ice article was fully submitted on July 31, 2018.	Submit Fire in the Ice article
9. Task 5: Geochemical analyses	September 2018 The geochemical analyses were completed on 1 June 2018 and the three publications from this cruise are in preparation.	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—	June 2019	Submit paper(s) to peer-reviewed journal on CH ₄ fluxes and pH

CRITICAL MILESTONE		distributions
12. Task 8: Synthesis	September 2019	Release data and metadata

1.2 Progress on Research Tasks

The main objective during FY18, Q3 was to complete Task 5 *Geochemical Analyses*, which occurred on 1 June 2018.

1.2.1. Task 5. Geochemical Analyses

The research expedition on the U.S. Atlantic Margin was successfully completed during FY 17, Q4, during which time samples and data were collected. Our major effort during FY 18, Q3 was to continue and complete the analysis of collected samples and begin processing the data collected at sea. During this quarter, we began and completed the geochemical analysis of dissolved inorganic carbon concentration, thus completing our geochemical analyses.

Dissolved Inorganic Carbon Concentration ([DIC])

Samples were collected on the research cruise to analyze for DIC dissolved in seawater. After the cruise, these samples were returned to the Kessler laboratory at the University of Rochester for analysis, following our research plan. The sample collection and analysis procedures are previously published in Garcia-Tigreros and Kessler (2018). During this reporting period, these

analyses were initiated and completed. In addition, we began the interpretation of this data in the context of all the other data collected.

1.2.2. Task 7. Interpretation of CH₄ and CO₂ distributions

Since all the analyses were completed during this reporting period, we began the interpretation of this data focusing on (1) the sea-to-air flux and coordination with seafloor emissions, (2) fingerprinting the source emitted to the atmosphere and determining what fraction of that emission was originally released from the seafloor, (3) the extent of aerobic methane oxidation in the water column, and (4) the influence that CO₂, produced from aerobic methane oxidation, has on ocean acidification and inorganic carbon chemistry. Drafts of three manuscripts containing these interpretations were assembled during this reporting period.

References from this section

F. Garcia-Tigreros and J. D. Kessler (2018), "Limited acute influence of aerobic methane oxidation on ocean carbon dioxide and pH in Hudson canyon, northern U.S. Atlantic margin." *Journal of Geophysical Research: Biogeosciences*, 123, <https://doi.org/10.1029/2018JG004384>

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 and dispersion in the water column. During this reporting period, Leonte was the lead author on a manuscript submitted to a peer-reviewed journal that acknowledged this support. Joung is championing the natural radiocarbon analyses of dissolved methane. In addition to advancing the sampling and analysis techniques for radiocarbon methane analyses, Joung also analyzed the dissolved inorganic carbon concentration samples during this reporting period and assembled a first draft of a manuscript identifying the source of methane emitted to the atmosphere across our study area.

1.4 Dissemination of Results to Communities of Interest

During this reporting period, one manuscript was accepted for publication (20 June 2018) in the *Journal of Geophysical Research: Biogeosciences*, although the final published version did not appear online until FY18, Q4 (14 July 2018). This manuscript describes our analyses investigating what influence aerobic methane oxidation has on pH and the CO₂ content of seawater in Hudson Canyon, US Atlantic Margin.

In addition, two other manuscripts were submitted for publication to peer-reviewed journals. One manuscript was submitted to *Geochemistry, Geophysics, Geosystems* and describes our stable isotope technique whereby measurements of natural $\delta^{13}\text{C-CH}_4$ are used to determine the fraction of methane which dissolves out of a bubble released from the seafloor. The other manuscript was submitted to *Nature: Scientific Reports* and describes how the oxidation of methane and organic carbon released from hydrates and thawed permafrost in the U.S. Beaufort Sea influences seawater pH and oceanic CO_2 . While the samples reported in this manuscript were not from the U.S. Atlantic margin, the work conducted on this DOE project helped interpret these results, and thus the DOE is acknowledged in this manuscript. 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. During this reporting period, work was conducted on Milestones 8 and 9.

1.6 Plans for the Next Reporting Period

During the next reporting period, the data resulting from the research cruise will continue to be interpreted and prepared for publication. Specifically, we will continue our interpretation of the $^{14}\text{C-CH}_4$, $\delta^{13}\text{C-CH}_4$, $[\text{CH}_4]$, $^{14}\text{C-DIC}$, $[\text{DIC}]$, pH, and sea-to-air flux data. We are also assembling and editing manuscripts detailing (1) the source of methane emitted to the atmosphere, (2) the extent of aerobic oxidation and dispersion of methane in the water column following seafloor release, and (3) how ocean acidification is influenced by seafloor methane release and subsequent oxidation.

The USGS is in the process of compiling all seep location data from this project's cruise, as well as other cruises, to support the release of a preliminary updated seeps database to NOAA's Office of Ocean Exploration and Research (Task 6/Milestone 10).

2. PRODUCTS

2.1 Publications, Conference Papers, and Presentations (Included here is a tally of all the products acknowledging this support without regard to the quarter it was produced.)

Publications

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

- 1) C. D. Ruppel and J. D. Kessler (2017), "The Interaction of Climate Change and Methane Hydrates." *Reviews of Geophysics*, 55, <https://doi.org/10.1002/2016RG000534>
- 2) 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*, <https://doi.org/10.1002/lom3.10184>
- 3) 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 (2018), "Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf." *Science Advances*, 4, <https://doi.org/10.1126/sciadv.aao4842>

- 4) F. Garcia-Tigreros and J. D. Kessler (2018), "Limited acute influence of aerobic methane oxidation on ocean carbon dioxide and pH in Hudson canyon, northern U.S. Atlantic margin." *Journal of Geophysical Research: Biogeosciences*, 123, <https://doi.org/10.1029/2018JG004384>

Submitted Manuscripts Currently In Review

- 1) M. Leonte, B. Wang, S. A. Socolofsky, S. Mau, J. A. Breier, and J. D. Kessler (2018), "Using Carbon Isotope Fractionation to Constrain the Extent of Methane Dissolution Into the Water Column Surrounding a Natural Hydrocarbon Gas Seep in the Northern Gulf of Mexico." *Geochemistry, Geophysics, Geosystems*, *Submitted*.
- 2) F. Garcia-Tigreros, K. J. Sparrow, K. M. Schreiner, J. D. Kessler (2018), "Assessing acidification from the remineralization of dissolved organic carbon and methane in the coastal Beaufort Sea, Alaska." *Nature: Scientific Reports*, *Submitted*.

Conference Presentations

Conference: Gordon Research Conference on Natural Gas Hydrate Systems, Galveston, TX USA, February 25 - March 2, 2018.

- 1) Author: John Kessler. Title: (Invited Talk) High Resolution Measurements of the Sea-to-Air Flux of Methane Released from Hydrates

2) Author: Carolyn Ruppel. Title: (Invited Talk) Interaction of Deepwater and Permafrost-Associated Gas Hydrates with Climate Since the Last Glacial Maximum

3) Author: Mihai Leonte. Title: (Poster) Determination of Methane Sources and Sinks Using Stable Isotopes in Areas of Active Gas Seepage

4) Author: DongJoo Joung. Title: (Poster) Radiocarbon Measurements of Methane Dissolved in Seawater Near the Upper Edge of Methane Hydrate Stability

Presentations

1) Departmental Seminar (John Kessler)

University of North Carolina Chapel Hill

Department of Marine Sciences

October 11, 2017

Title: The Briny Blue Bubble Bender: Investigations of the chemical and isotopic kinetics of aerobic methane oxidation

2) Departmental Seminar (Carolyn Ruppel)

University of New Hampshire

Center for Coastal and Ocean Mapping

February 16, 2018

Title: An Update on the U.S. Northern Atlantic Margin Seep Province: Five Years Later

2.2 Websites or Other Internet Sites

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

2.3 Technologies or Techniques

While updating and improving various technologies is an essential component of this research project and was done during previous reporting periods (for example, one of our publications acknowledging support from this project is a technique paper – Sparrow and Kessler, 2017), no technology or technique improvements were conducted during this reporting period.

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, continued processing the collected data, helped analyze the collected samples, and wrote and edited the publications acknowledging this project for support.
 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:** During this reporting period, Ruppel helped lead this project, continued processing the collected data geophysical data, and generated maps of the various geochemical datasets and their spatial relationship to seeps.
 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 began interpreting the methane concentration and stable carbon isotope ($\delta^{13}\text{C-CH}_4$) data to determine the extents of aerobic methane oxidation and dispersion in the water column along the U.S. mid-Atlantic margin. He also submitted a manuscript to a peer-reviewed scientific journal describing how changes in $\delta^{13}\text{C-CH}_4$ can be used to constrain dissolution of methane from bubbles into the water column following seafloor release.

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

2. **Project Role:** Research Scientist

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

4. **Contribution to Project:** During this reporting period, Dr. Joung contributed to Task 5: *Geochemical analyses* by completing the analyses of the dissolved inorganic carbon concentration samples. He also interpreted the natural radiocarbon content of methane data and assembled a first draft of a manuscript describing these results.

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 one example of the accomplishments from those communications is a coauthored publication which was submitted during this quarter.

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 Tables 2 (FY17) and 3 (FY18). The expenses to date are less than anticipated due to the delay in hiring Dr. DongJoo Joung. However, his salary is slightly higher than was originally budgeted, so this deficit is anticipated to be utilized during the remainder of this project.

Table 2. Budget Report

Baseline Reporting Quarter	Budget Period 1							
	Q1		Q2		Q3		Q4	
	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)

Table 3. Budget Report

Baseline Reporting Quarter	Budget Period 2							
	Q1		Q2		Q3		Q4	
	10/1/2017- 12/31/2017		1/1/2018 - 3/31/2018		4/1/2018 - 6/30/2018		7/1/2018 - 9/30/2018	
DE-FE0028980	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	\$ 76,402.00	\$ 76,402.00	\$ 81,402.00	\$ 157,804.00	\$ 41,677.00	\$ 199,481.00	\$ 60,033.00	\$ 259,514.00
Non-Federal Share	\$ 28,446.00	\$ 28,446.00	\$ 28,446.00	\$ 56,892.00	\$ 7,928.00	\$ 64,820.00	\$ -	\$ 64,820.00
Total Planned	\$ 104,848.00	\$ 104,848.00	\$ 109,848.00	\$ 214,696.00	\$ 49,605.00	\$ 264,301.00	\$ 60,033.00	\$ 324,334.00
Actual Incurred Cost								
Federal Share	\$ 273,921.00	\$ 273,921.00	\$ 116,061.00	\$ 389,982.00	\$ 54,022.00	\$ 444,004.00		
Non-Federal Share	\$ 28,446.00	\$ 28,446.00	\$ 28,446.00	\$ 56,892.00	\$ 8,251.00	\$ 65,143.00		
Total Incurred Cost	\$ 302,367.00	\$ 302,367.00	\$ 144,507.00	\$ 446,874.00	\$ 62,273.00	\$ 509,147.00		
Variance over the entire project								
Federal Share	\$ 197,519.00	\$ (64,320.00)	\$ 34,659.00	\$ (29,661.00)	\$ 12,345.00	\$ (17,316.00)		
Non-Federal Share	\$ -	\$ 467.00	\$ -	\$ 467.00	\$ 323.00	\$ 790.00		
Total Variance	\$ 197,519.00	\$ (63,853.00)	\$ 34,659.00	\$ (29,194.00)	\$ 12,668.00	\$ (16,526.00)	\$ -	\$ -