NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

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Quarterly Research Performance Progress Report

(Period Ending 12/31/2017)

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

Project Period (10/01/2017 to 09/30/2018)

Submitted by:
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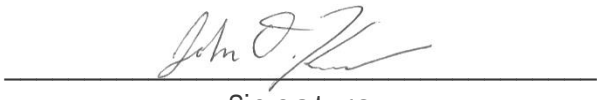

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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

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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 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 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 have 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.

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 CH_4 concentration, high precision pH,

CH_4 stable isotopes ($\delta^{13}C$-CH_4), and natural CH_4 radiocarbon (^{14}C-CH_4), and natural radiocarbon of dissolved inorganic carbon (^{14}C-DIC).

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 PI
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.

1.2 Progress on Research Tasks

The main objective during FY18, Q1 was to commence Task 5 *Geochemical Analyses*.

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, Q1 was to begin the analysis of collected samples. During this quarter, we began and completed the analysis of dissolved methane concentration and high precision pH, and began the analyses of methane stable isotopes ($\delta^{13}C\text{-}CH_4$), methane natural radiocarbon ($^{14}C\text{-}CH_4$), and dissolved inorganic carbon natural radiocarbon ($^{14}C\text{-}DIC$).

Methane Concentration

Seawater samples for dissolved methane concentration were collected during the research expedition on the U.S. Atlantic Margin and were analyzed on the ship, shortly after recovery. The procedure used is detailed in two previous publications (Leonte et al., 2017; Weinstein et al., 2016). While all analyses were performed at sea, the data and calibrations were quality checked back at our home institution during this quarter.

High Precision pH

Seawater samples for high precision pH were collected during the research cruise. All analyses of high precision pH were performed using a spectrophotometric technique on the research vessel shortly after sample collection following standardized procedures (Clayton and Byrne, 1993; Dickson et al., 2007). During this quarter, the results were reinvestigated back at our home institution for quality assurance.

Methane Stable Isotopes ($\delta^{13}C\text{-}CH_4$)

Samples were collected on the research cruise to analyze for $\delta^{13}C\text{-}CH_4$ dissolved in seawater. After the cruise, these samples were shipped to the Woods Hole Isotope Laboratories for analysis, following our research plan. The sample collection and analysis procedures are previously published in Leonte et al., (2017). During this reporting period, these analyses was started.

Methane Natural Radiocarbon ($^{14}C\text{-}CH_4$)

These analyses will be used to fingerprint if seafloor released methane is present in the surface waters and being emitted to the atmosphere. During the research expedition, samples were collected to measure natural $^{14}C\text{-}CH_4$ dissolved in seawater. During this reporting period, the samples were prepared in the Kessler laboratory for natural radiocarbon analysis via accelerator mass spectrometry (AMS), a procedure that involves sample purification and oxidation. The samples were fully prepared during this reporting period and sent to the Keck Carbon Cycle-

AMS (CCAMS) facility at the University of California, Irvine for analysis. The procedures for the at-sea sample collection and the laboratory sample preparation were formally published during FY1 Q3, acknowledging this DOE support (Sparrow and Kessler, 2017).

Dissolved Inorganic Carbon Natural Radiocarbon (^{14}C-DIC)

During the research expedition, 127 samples were collected for ^{14}C-DIC. During this reporting period, these samples were transferred to the Keck CCAMS facility at UC Irvine for analysis. These sample collection and analysis protocols have been previously published and produce results with precisions <2 ‰ (Gao et al., 2014).

References from this section

T. D. Clayton and R. H. Byrne (1993), "Spectrophotometric Seawater pH Measurements - Total Hydrogen-Ion Concentration Scale Calibration of M-Cresol Purple and at-Sea Results." Deep-Sea Research Part I-Oceanographic Research Papers 40, 2115.

A. G. Dickson, C. L. Sabine, J. R. Christian (2007), "Guide to best practices for ocean CO2 measurements." PICES Special Publication 3, 191.

P. Gao et al. (2014), "Rapid sample preparation of dissolved inorganic carbon in natural waters using a headspace-extraction approach for radiocarbon analysis by accelerator mass spectrometry." Limnology and Oceanography-Methods 12, 174.

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.

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

Weinstein, A., L. Navarrete, C. Ruppel, T. C. Weber, M. Leonte, M. Y. Kellermann, E. C. Arrington, D. L. Valentine, M. I. Scranton, and J. D. Kessler (2016), “Determining the flux of methane into Hudson Canyon at the edge of methane clathrate hydrate stability.” Geochem. Geophys. Geosyst., 17, doi:10.1002/2016GC006421.

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.

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, the work conducted on this DOE project helped interpret these results, and thus the DOE is acknowledged in this manuscript. This manuscript was formally accepted for publication in Science Advances during this reporting period, but was not formally published until FY 18, Q1. The second publication is in the final stages of preparation prior to submission and describes our newly developed technique whereby measurements of natural $\delta^{13}C\text{-}CH_4$ are used 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. During this reporting period, work was conducted on Milestone 9.

1.6 Plans for the Next Reporting Period

During the next reporting period, the data and samples collecting during the research cruise will continue be analyzed. Specifically, the following analyses will be completed: natural radiocarbon content of dissolved methane ($^{14}C\text{-}CH_4$), natural radiocarbon content of dissolved inorganic carbon (^{14}C-DIC), and the stable isotopes of dissolved methane ($\delta^{13}C\text{-}CH_4$). We will begin preparing for the analysis of [DIC] but may not begin those analyses until FY18, Q3. In

addition to the analysis of these samples, we will begin to process and interpret the ultra-high resolution sea-to-air flux data collected at sea.

2. PRODUCTS

2.1 Publications, Conference Papers, and Presentations

Publications.

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 (2018), "Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf." Science Advances, Accepted during FY18 Q1.

Presentations

Departmental Seminar

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

2.2 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, began 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

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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:** During this reporting period, Ruppel helped lead this project and began processing the collected data geophysical 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 Task 5: *Geochemical analyses* by preparing and analyzing samples and data for methane concentration and stable carbon isotopes ($\delta^{13}C\text{-}CH_4$). He also analyzed existing data from the Gulf of Mexico 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.

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 leading 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 the quarterly reports from FY17.

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 invoice for our use of the R/V *Hugh Sharp* during FY17, Q4 was received during FY18, Q1 in the amount of $198,283.50 and was processed for payment. 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

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)

Table 3. Budget Report

	Budget Period 2							
Baseline Reporting	**Q1**		**Q2**		**Q3**		**Q4**	
Quarter	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						
Non-Federal Share	$ 28,446.00	$ 28,446.00						
Total Incurred Cost	$ 302,367.00	$ 302,367.00						
Variance over the entire project								
Federal Share	$ (64,320.00)	$ (64,320.00)						
Non-Federal Share	$ 467.00	$ 467.00						
Total Variance	$ (63,853.00)	$ (63,853.00)	$ -	$ -	$ -	$ -	$ -	$ -