NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

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Quarterly Research Performance Progress Report

(Period Ending 6/30/2017)

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)

Submitted by:
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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 and Q2 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 deepwater gas hydrate well or the more natural decomposition of gas hydrate systems. These investigations will be conducted along the US Atlantic margin between Wilmington Canyon and Cape Hatteras, where methane emission has been documented on the upper continental slope near the upper boundary of hydrate stability.

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. Two major obstacles for determining this flux are 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. 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 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 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).

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 samples and interpret the 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
Complete		
3. Data Management Plan (USGS and UR)	January 2017	Mutual acceptance of revised plan by DOE and PIs
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
The contract has been approved by the General Counsel and signatures are being obtained from university administration.		
5. Subtask 3.4: NEPA documentation (USGS)	June 2017	Final signatures by the USGS and then cognizant DOE officials
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.		
6. Subtask 3.2: Complete equipment leasing (USGS)	July 2017	Signed award documentation
The USGS completed all equipment leasing.		
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

1.2 Progress on Research Tasks

The main objectives during Q3 were to continue progress towards completing Task 3 *Research Cruise Preparation*, Subtask 3.3 *Preparations* as well as to largely complete the ship contracting, the NEPA documentation, and the equipment leasing. Even though PIs Kessler and Ruppel are in regular contact, during this reporting period they conducted 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). Subtask 3.3 was initiated during Q1 and progress was continued during Q2. During Q3, many of the techniques were field tested during a separate project on the R/V *Blue Heron*. In addition, one of the techniques was fully published. The work being conducted and completed is detailed below. Also, a suitable candidate was hired for the research scientist position, and he has been a significant contributor to the research cruise preparation efforts.

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 and Q2, the system design was updated slightly to increase precision and the final validations were conducted. Thus, no new validations were necessary to conduct during Q3.

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. In anticipation for a research cruise in August 2017, these techniques were tested in the field on the R/V *Blue Heron* in June 2017.

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 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. We also conducted a final field trial of this technique on the R/V *Blue Heron* in June 2017 (Figure 1).

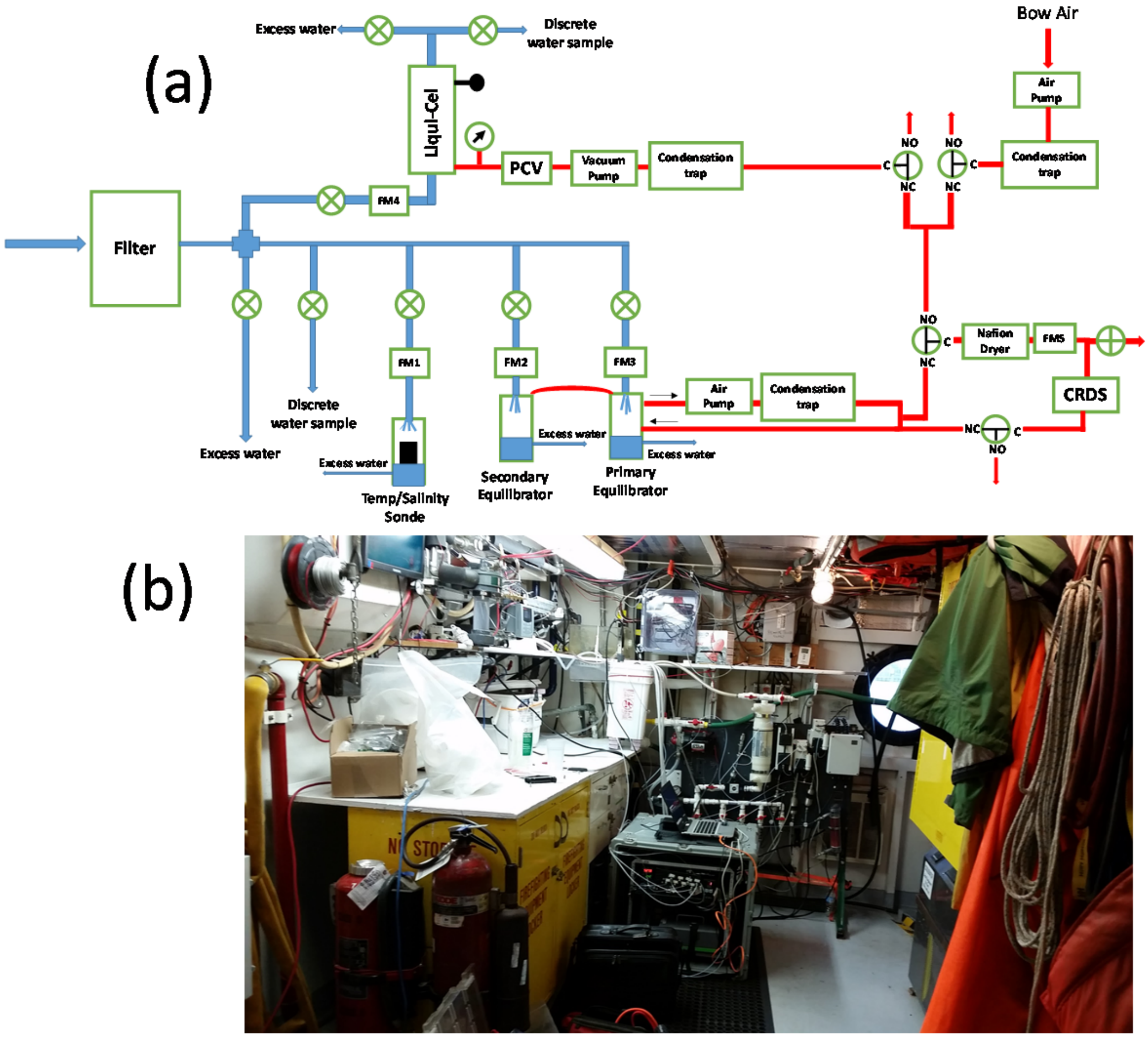

Figure 1. (a) Schematic and (b) Photograph of the system operating on the R/V *Blue Heron* used for the ultra-fast analysis of dissolved methane and carbon dioxide concentrations and isotopes in surface waters. The blue and red lines on the schematic indicate directions of water and gas flow, respectively. ⊗ = 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 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 published in Limnology & Oceanography: Methods (Figure 2) acknowledging DOE support. 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. These increased flow rate operations and deepwater sampling were also tested on the R/V *Blue Heron* in June 2017.

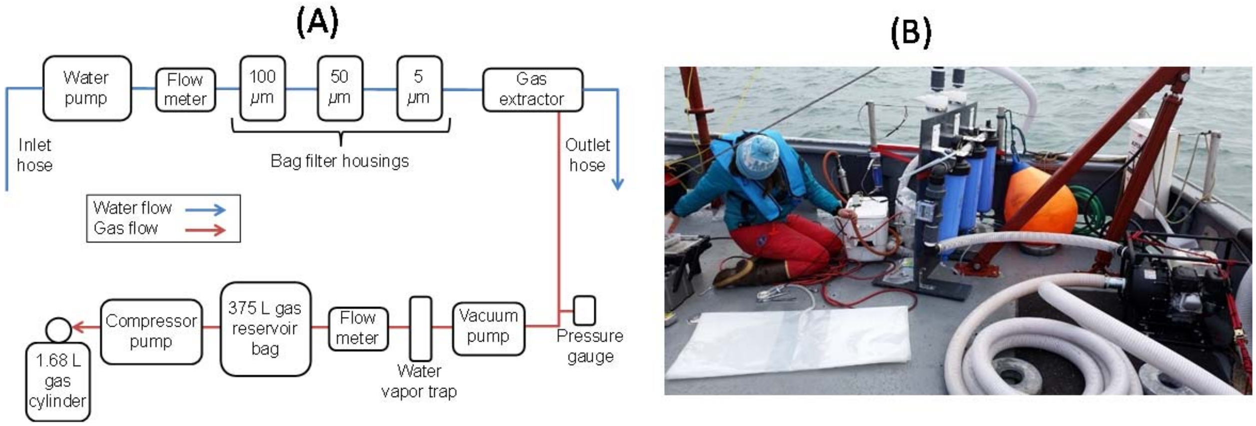

Figure 2. Measurement system for natural radiocarbon abundance of methane in seawater. (a) Schematic of the shipboard extracted gas sample collection system for collecting dissolved methane. Water flow: Seawater is pumped up from depth at rates of 220-230 L/min using a non-submersible pump. The seawater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

This research cruise will collect data on $\delta^{13}C$-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 the Q2 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 as more methane dissolves. During the Q2 and Q3 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 has 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.

1.3 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 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. 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 deepwater. Both Leonte and Joung participated in the research cruise on the R/V *Blue Heron* during this reporting period to further test these techniques.

1.4 Dissemination of Results to Communities of Interest

One publication acknowledging this support was formally published during this reporting period. 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 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*. 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 research scientist. The sampling equipment for the [CH_4], $\delta^{13}C$-CH_4, [DIC] and $\Delta^{14}C$-DIC analyses will be prepared.

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.

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

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 will be used on the research expedition on the R/V *Hugh Sharp*. During this reporting period, the methane radiocarbon technique was updated to make it more efficient and able to sample deeper waters, it was tested in the Great Lakes on the R/V *Blue Heron*, 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 it more robust, and it was also field tested on the R/V *Blue Heron*.

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 *Blue Heron* to test much of this equipment, and conducted a pre-cruise meeting with Carolyn Ruppel on the R/V *Hugh Sharp*.

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:** Completed the NEPA documentation and contributed ship specifications for UR ship contracting; conducted a pre-cruise meeting with Kessler on the R/V *Hugh Sharp*; completed leasing for large equipment; participated in pre-cruise

meeting with Kessler and R/V Sharp marine operations personnel in July 2017 and ran a meeting with USGS operational personnel in July 2017; arranged for availability of USGS equipment and appropriate software for the upcoming cruise; coordinated with USGS engineer for CTD-mounted camera.

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. Finally, Mr. Leonte participated in the technique validation cruise on the R/V *Blue Heron*.

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*, by making the technique to collect samples for natural radiocarbon analysis of methane more efficient. Dr. Joung's modifications to this technique reduced the time necessary to collect a sample by 50% and he developed the ability to sample at different depths throughout the water column. Finally, Dr. Joung validated these new technique modifications in both the laboratory as well as on the Great Lakes during a cruise on the R/V *Blue Heron*.

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 a new 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 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 candidate for the research scientist position was formally hired (Dr. DongJoo Joung). Dr. Joung 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 is a highly skilled and welcome addition to this project.

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 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		
Non-Federal Share	$ 46,345.34	$ 46,345.34	$ 36,571.00	$ 82,916.34	$ 16,644.98	$ 99,561.32		
Total Incurred Cost	$ 52,427.95	$ 52,427.95	$ 54,937.37	$ 107,365.32	$ 50,521.19	$ 157,886.51		
Variance								
Federal Share	$ (17,140.39)	$ (17,140.39)	$ (21,377.63)	$ (38,518.02)	$ (9,867.79)	$ (48,385.81)		
Non-Federal Share	$ -	$ -	$ (546.33)	$ (546.33)	$ 444.65	$ (101.68)		
Total Variance	$ (17,140.39)	$ (17,140.39)	$ (21,923.96)	$ (39,064.35)	$ (9,423.14)	$ (48,487.49)		