Oil & Natural Gas Technology

DOE Award No.: DE-FE0024297

Quarterly Research Performance

Progress Report (Period Ending 3/30/2019)

Marcellus Shale Energy and Environment Laboratory (MSEEL)

Project Period (October 1, 2014 – September 30, 2019)

Submitted by:
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Executive Summary
Quarterly Progress Report

January 1 – March 30, 2019

The objective of the Marcellus Shale Energy and Environment Laboratory (MSEEL) is to provide a long-term field site to develop and validate new knowledge and technology to improve recovery efficiency and minimize environmental implications of unconventional resource development.

This quarter work focused on for MSEEL Phase 3 were presented to the technical advisory group and to DOE. Costs for various scenarios were evaluated. The wells spudded at the very end of 2018 and all the top holes were drilled in this quarter. The pilot hole for the 17H was started at the very end of this quarter. The Boggess pad in Monongalia County, West Virginia consists of six wells with various drilling and completion parameters.

We have worked to process the data from the downhole microseismic sensors and the fiber-optic data to better understand geomechanical properties and slow slip events during hydraulic fracture stimulation. Prepared manuscript for URTeC in July 2019/

Plans developed for MSEEL Phase 3 were are being executed at the Boggess Pad just west of Morgantown, WV. The Boggess pad consisting of six wells was selected.

Project Performance

This report summarizes the activities of Cooperative Agreement DE-FE0024297 (Marcellus Shale Energy and Environment Laboratory – MSEEL) with the West Virginia University Research Corporation (WVURC) during the second quarter of FY2019 (January 1 through March 30, 2019).

This report outlines the approach taken, including specific actions by subtopic. If there was no identified activity during the reporting period, the appropriate section is included but without additional information.

A summary of major lessons learned to this point of the project are provided as bullet points and will be added to as research is completed. New lessons listed below are:

Phase 3 Plans

A phase 3 of MSEEL is moving forward with drilling and completion through the next two quarters. Six 10,000+ foot horizontal Marcellus Shale wells off a single pad (Boggess) are being drilled very near the initial MIP pad (Figure 1.1). The pad will have at one permanent fiber optic (FO) cable installed that will provide digital acoustic sensing (DAS) during stimulation and distributed temperature sensing (DTS) during stimulation and long-term production monitoring along the lateral (Boggess 5H). Two deployable FO systems are also proposed (Boggess 1H and 17H). This will permit evaluation of stimulation effectiveness in near real-time and the 100's of terabytes of data to evaluate and model the reservoir across each individual stage, and at individual clusters within stages for 3 wells. The deployable fiber in parallel wells (skipping one adjacent) will allow excellent microseismic imaging, recognition and evaluation of long-period long-duration events in the test well. We will also be able to monitor adjacent wells to the test well during stimulation. We have developed techniques to use the permanent DAS and DTS monitoring in the 5H to determine production rates and changes at the stage level through the life of the well.

The cored and logged vertical pilot well is being evaluated to develop a high-resolution geomechanical model (stratigraphy) to type each 6 inches of the Marcellus. Logging while drilling (LWD) logs in each of the six laterals provide similar geomechanical logs and image logs to geomechanically type each foot of the laterals as the horizontal laterals move stratigraphically up and down through the Marcellus. This approach permits direct coupling and evaluation of cost-effective LWD technologies to the relatively high-cost permanent FO data and the basis for engineering stages in all wells.

The plan remains to undertake at least two of the laterals with the standard industrial geometrical completion practice (identical 200 feet stages with identical number of clusters in each stage). These will be the control wells. We will use the LWD and permanent FO in the one well (extremely large big data) and the LWD and microseismic only (relatively "thin" data) in the other wells to engineer stage and cluster spacing. Coupled with production data from all the wells including the control wells, this provides the basis to evaluate the reservoir through modeling and direct monitoring to develop a first ever, publicly available, multi-well unconventional fractured reservoir simulation.

MSEEL 2 will compare across the six wells and with the MIP pad (MSEEL 1) and use these data to form the basis for robust big data modeling. MSEEL 1 generated almost 10 terabytes of data and created approaches and capabilities to handle and process big data sets (i.e., volume, variety, velocity and veracity) from a single well to address the spacing between laterals and stage length, the importance of modeling at multiple scales from nanopores in kerogen to healed fractures spaced along the lateral, and the approaches to engineering stage and cluster design and stimulation processes. The multiple wells at MSEEL 2 and the new generation high resolution fiber and LWD tools will provide 100's of terabytes of data in a series of similar wells under controlled conditions to test and enhance the understanding of shale reservoirs, MSEEL 2 will test new technologies and approaches to provide robust models that can be modified in near real-time using "thick" relatively high-cost data sets limited to science wells, or when calibrated more cost-effective "thin" data sets that could be used in broader field development and basin evaluation.

Figure 1.1: Boggess Pad with new generation permanent fiber in the central well (Boggess 5H, red star)) and deployable fiber in adjoining wells skipping one (orange stars). We will be able to monitor in near-real time fracture stimulation in the central 3 wells (3H, 5H and 9H). A vertical pilot will be drilled, cored and logged.

Project Management Update

Approach

The project management team will work to generate timely and accurate reporting, and to maintain project operations, including contracting, reporting, meeting organization, and general oversight.

Results and Discussion

The project team is tracking eight (8) milestones in this budget period.

	Task	Milestone	Status	Due Date
1.	2.1.2	Develop kerogen models of shale from different zones of MSEEL well and compare them to shales from wells in other parts of the basin	Complete Kerogen samples extracted from sidewall cores covering the whole Marcellus formation (ranging from Marcellus Top to Marcellus-Onondaga transition) have been analyzed using 13C NMR. New schematic kerogen models are being developed using lattice parameters and being compared to models of kerogen derived from wells in less mature part of the basin. Plan to synthesize results and submit publications in Fall 2018.	9/30/2018
2.	2.1.8	Geostatistical Well Analysis	Complete A paper was presented at URTeC (July) on a predictive data-driven machine learning model to understand the MSEEL well's performance and forecast the gas production using DTS data and daily flowing time as dynamic inputs. Papers using image analysis and nitrogen adsorption to quantify nano-pores in the Marcellus have been submitted.	9/30/2018
3.	2.1.7	Improved Reservoir Simulation for field implementation	Complete but will continue to be enhanced with continued production monitoring, and will be presented at URTeC this summer An improved history match that incorporates the unconventional fracture model and how to use this knowledge to increase production, efficiently space laterals and reduce cost. A manuscript has been accepted for presentation to the	10/31/2018

			Society of Petroleum Engineers Annual Meeting.	
4.	2.1.5	Create a Comprehensive Fracture Model	Complete but will continue to be enhanced with continued production monitoring, and will be presented at URTeC this summer A provisional patent application for analysis of fiber-optic data is moving forward. Papers are accepted for fall meetings of SPE, URTeC and AAPG.	11/30/2018
5.	2.2.1	Completion of four additional methane audits to further assess temporal variability in methane emissions	Complete Four previous audits have shown significant temporal variability. Four or more (up to 8 more over 2 years) audits well help us understand (by increasing sample size) if variability correlates with temporal production, cumulative production, age, water production, or seasonal variability. Initial results are presented in Jan 2019 report, publications are possible.	12/31/2018
6.	2.1.2	Understanding the type, amount and origin of natural gas	Complete Data analysis and interpretations of pyrolysis data are currently underway. We expect to generate some preliminary data and make some conference presentations in Fall 2018 and submit publications by Spring 2019	3/30/2019
7.	2.2.1	Successful deployment of an open path methane monitoring system during site audits	Complete Industry seeks to reduce costs of audits and streamline greenhouse gas reporting programs. This will teach us if near-field, indirect quantification or detection methods are applicable to the Appalachia region, versus the well-established research in relatively flat and calm Barnett and Fayetteville plays.	3/30/2019
8.	2.2.1	Characterize chemical transformations during produced water storage from well 3H	Complete Will complete characterization of changes in produced water chemistry (specifically Fe, Sr, Ba, Ra 226, Ra 228) and biological activity (CO_2 and CH_4 production) that occur during short term storage (20 days). Measures of Ra	3/30/2019

			activity (Ra 226 and Ra 228) of the solid precipitate formed during short term storage of produced water will also be completed.	

Topic 1 – Geologic Engineering

Approach

In addition to advances in improving our understanding of chemical evolution of produced water, methane emissions, microbiology and rock-fluid geochemistry, we worked to better understand the microseismic monitoring by downhole geophones, surface seismic, fiber-optic distributed acoustic sensing (DAS), and distributed temperature sensing (DTS) observations made during the hydraulic fracture stimulation of the MIP-3H well. DAS and DTS data measure the fiber strain and temperature, respectively, along a fiber-optic cable cemented behind the casing of the well. The presence of long-period long-duration (LPLD) events as picked up on surface sensor employed by NETL (Kumar et al. 2017) were evaluated in the borehole geophones, DAS data, and surface seismic data of one of the MIP-3H stimulated stages. LPLD events are generally overlooked during the conventional processing of microseismic data, but they represent significant nonbrittle deformation produced during hydraulic fracture stimulation. In a single stage that was examined, 160 preexisting fractures and two faults of suboptimal orientation are noted in the image logs. We identified two low-frequency (<10 Hz) events of large temporal duration (tens of seconds) by comparing the surface seismic data, borehole geophone data, and DAS amplitude spectra of one of the MIP-3H stages. Spectrograms of DAS traces in time and depth reveal that the first low-frequency event might be an injection noise that has footprints on all DAS channels above the stimulated stage. However, the surface seismic array indicates an LPLD event concurrent with the first low-frequency event on DAS. The second LPLD event on DAS data and surface seismic data is related to a local deformation and does not have footprints on all DAS channels. The interpreted events have duration less than 100 s with frequencies concentrated below 10 Hz and accompanied by microseismic events. We will test these results in the advanced fiber deployed at the Boggess pad.

Kumar, A., E. V. Zorn, R. Hammack, and W. Harbert, 2017a, Seismic monitoring of hydraulic fracturing activity at the Marcellus shale energy and environment laboratory (MSEEL) Site, West Virginia: Presented at the Unconventional Resources Technology Conference, Paper 2670481.

Results and Discussion

Analysis of the DAS, downhole geophone data for LPLD events, and surface seismic data of stage 10 brings the following concluding remarks:

- Spectrograms of the DAS and borehole geophone data reveal different frequency content. The DAS spectrogram showed lower frequency content than the borehole geophone data. This unusual finding is attributed to the poor signal-to-noise ratio for the DAS data.
- The initial scan of the DAS and borehole geophones suggested the presence of three LPLD events: one at approximately 3000 s, close to formation breaking pressure, one at

approximately 4200 s, and the last one at approximately 7000 s. Further analysis of the geophone data revealed that events on geophone data are swarms of MSEs and are not LPLDs. These MSEs may be accompanied by lower frequency LPLD events. Events at 7000 s seemed to have a source at the surface because of the reverse moveout from the surface toward the reservoir. In addition, surface seismograms suggest a local surface source close to FRAC1, which is closest to the wellpad.

- The low-frequency (0.1–5 Hz) DAS data suggested that the event at 3000 s is affected by injection noise. However, a surface seismic array recorded an event at approximately 3000 s on all three seismograms. The duration of the event is around a minute and has LPLD characteristics. The low frequency (0.1–5 Hz) DAS data also revealed an event at approximately 4200 s. Unlike the 3000 s event, it is not visible on all DAS channels. It is also recorded by the surface seismic array three seismometers. We suggest that this event is likely an LPLD event as well.
- The DTS data show a warming effect in stage 9 during hydraulic fracture stimulation of stage 10. The temperature response appears to coincide with the LPLD events in the DAS spectrogram. This temperature change recorded by the DTS system likely suggests hydraulic connections between two consecutive stages, particularly due to the reactivation of preexisting fractures that triggered LPLD events.
- The instantaneous frequency of DAS data shows some temporal correlation with the DTS data in low frequencies. However, we show that low frequency patches that are interpreted as LPLDs are accompanied with high microseismic activity. This could suggest that during stimulation of stage 10, preexisting fractures undergo shear failure and establish cross-stage flow that pushes back warmed fracturing fluid toward stage 9.
- Regional earthquakes are very unlikely to have any effect on the local temperature variation, as measured by DTS data. Thus, LPLD events observed in the current study in the DAS and surface seismic array and contemporaneous variation in temperature recorded by DTS are most likely related to local deformation in the reservoir during hydraulic fracturing rather than an overprint of a known or unknown regional earthquake in the distant area.

Products

The results are being published in the Journal *Interpretation* as:

Kavousi Ghahfarokhi, P., Wilson, T.H., **Carr, T.R.**, Kumar, A., Hammack, R. and Di, H., 2019. Integrating distributed acoustic sensing, borehole 3C geophone array, and surface seismic array data to identify long-period long-duration seismic events during stimulation of a Marcellus Shale gas reservoir. Interpretation, *7*(1), pp. SA1-SA10. https://doi.org/10.1190/INT-2018-0078.1.

Plan for Next Quarter

Will be working to interpret geomechanical properties derived from the drilling of the laterals at the Boggess Pad to design fracture stimulation which will occur in the next quarter.

Topic 2 – Geophysical & Geomechanical

Approach

Geophysical and Geomechanical

During this quarterly period, the influence of a discrete fracture network on the growth of hydraulic fractures was investigated through the use of numerical modeling. The numerical model updated in a previous quarter was used to compute hydraulic fracture dimensions for stage 26 through stage 30 of well MIP-5H.

During this quarterly period, the influence of a discrete fracture network on the growth of hydraulic fractures was investigated through the use of numerical modeling. All numerical modeling results were synthesized along with microseismic data results.

Microseismic data was available for stages 7 through 28 at well MIP-3H and stages 2 and 5 through 30 at well MIP-5H. Microseismic, well, and hydraulic fracture geometry data were visualized in three dimensions. Figure 1 shows a side-view of well MIP-3H with all numerically modeled hydraulic fractures with available microseismic data. Figure 2 shows a side-view of well MIP-5H with all numerically modeled hydraulic fractures with available microseismic data. Figure 3 shows a top view of well MIP-3H with all numerically modeled hydraulic fractures with available microseismic data. Figure 4 shows a top view of well MIP-5H with all numerically modeled hydraulic fractures with available microseismic data. Figure 5 shows a top view of both wells MIP-3H and MIP-5H with all numerically modeled hydraulic fractures with available microseismic data.

The match between numerical model calculated fracture heights and lengths and microseismic estimated height and length data is not currently considered to be excellent. The current modeling study will be continued to evaluate the influence of geomechanical properties on fracture geometries in comparison to microseismic estimates. A statistical methodology is being explored to better reconcile numerical model calculated fracture heights and lengths, and microseismic height and length estimates.

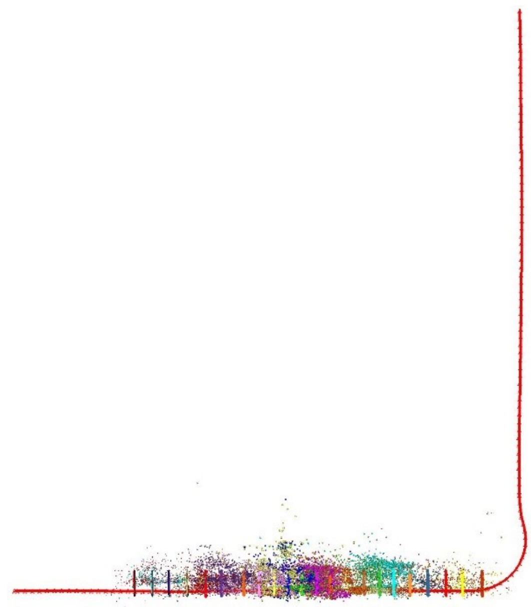


Figure 2.1: Side View of Calculated Hydraulic Fractures with Available Microseismic Data and Wellbore – Well MIP-3H

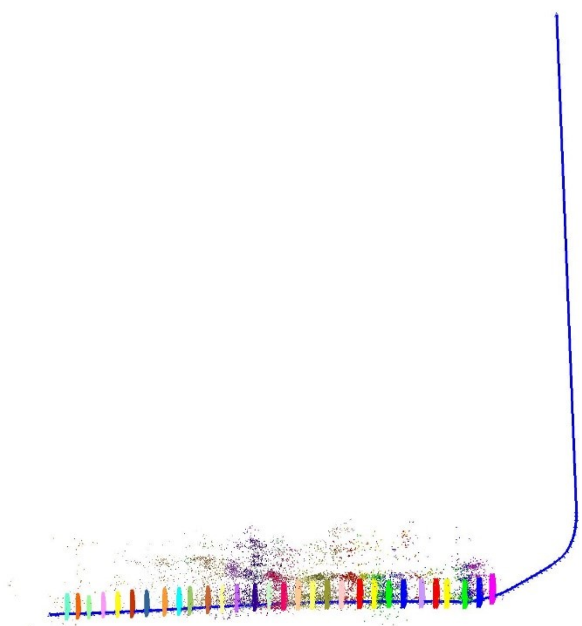


Figure 2.2: Side View of Calculated Hydraulic Fractures with Available Microseismic Data and Wellbore – Well MIP-5H

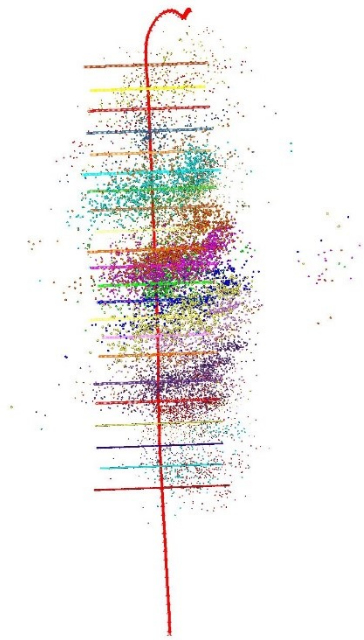


Figure 2.3: Top View of Calculated Hydraulic Fractures with Available Microseismic Data and Wellbore – Well MIP-3H

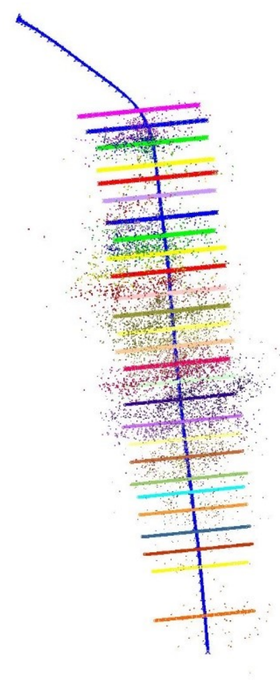


Figure 2.4: Top View of Calculated Hydraulic Fractures with Available Microseismic Data and Wellbore – Well MIP-5H

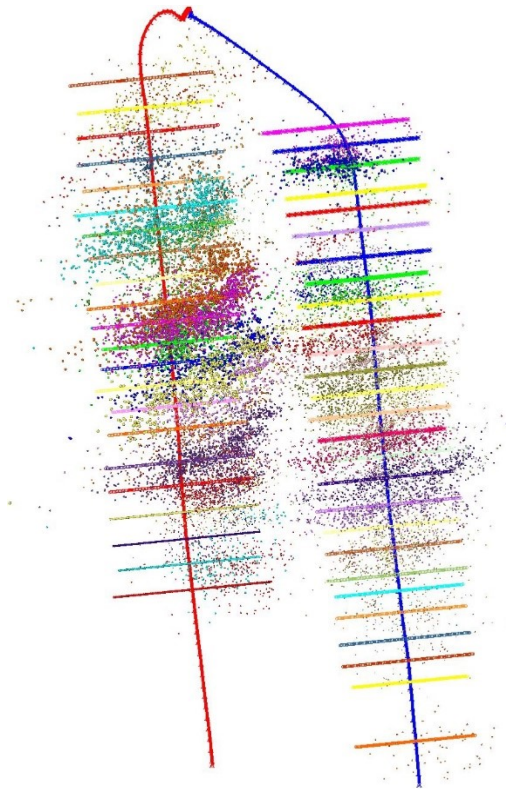


Figure 2.5: Top View of Calculated Hydraulic Fractures with Available Microseismic Data and Wellbores – Wells MIP-3H and MIP-5H

Plan for Next Quarter:

The current modeling study will be continued to evaluate the influence of geomechanical properties on fracture geometries in comparison to microseismic estimates. Also, an effort will be undertaken to explore a statistical methodology which may reconcile discrepancies between numerical model fracture height and length calculations and microseismic height and length estimates.

Topic 3 – Deep Subsurface Rock, Fluids, & Gas

Approach

The approach is to work across a broad spectrum of detailed geochemical and biogeochemical investigations that could have significant impact on completion and production.

1. Experiments to understand kerogen-frac fluid and interaction. The manuscript on understanding the effect of maturity and mineralogy on shale fracturing fluid interactions was accepted and published. We completed the extraction of kerogen from all the shale samples used in these high P-T experiments to understand the effect on frac fluid interaction on kerogen molecular structure. The extracted kerogen samples will be submitted for the 13C NMR analysis.

Deliverables: 1) A manuscript summarizing key findings is published in journal *Environmental Science: Processes & Impacts.* 2) Completed extraction of kerogen samples 3) Finish analysis of all kerogen samples using ^{13}C solid-state NMR by summer 2019

2. Understanding the type, amount and origin of the gas. Results from the open and closed pyrolysis experiments are being interpreted by V. Agrawal. Using this analysis, the composition and kinetics of petroleum generated in Marcellus shale at different maturity (including MSEEL samples) were determined. Major findings of this study are 1) it provides evidence that Marcellus shale has the potential to generate "late gas," composed mainly of methane, at higher maturity at VRo >3 (Figure. 1). 2) artificial maturation data can be compared with the pyrolysis data from natural shale maturity series to decipher the fluctuations in sources of OM and paleo-redox. We are in the process of submitting a manuscript summarizing results in the journal *Fuel*.

Deliverable: Submit a manuscript to the journal *Fuel* by Summer 2019.

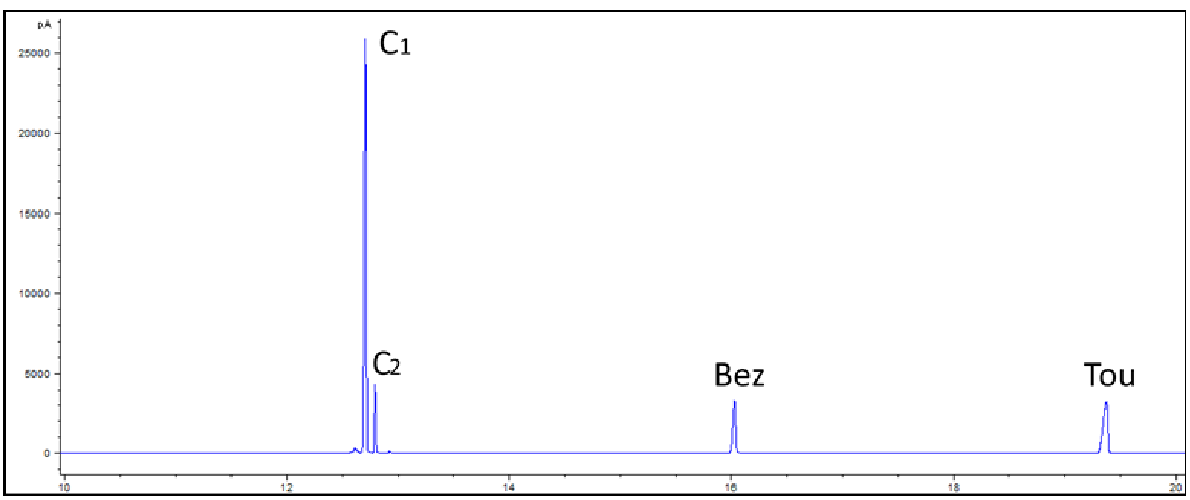


Figure 3.1: Late gas generated by kerogen pyrolysis using micro-scale sealed vessel (MSSV). C_1, C_2, Bez, Tou stands for methane, ethane, benzene, and toluene respectively.

3. Microbial lipid analysis of sidewall cores from MSEEL: Ph.D. student Rawlings Akondi is working on a manuscript that characterizes the effects of sampling and long term storage on microbial lipid biomarker distribution in deep subsurface Marcellus Shale cores. The manuscript uses membrane ester-linked phospholipid (PLFA) and diglyceride fatty acid (DGFA) analyses to examine the effects of sampling and surface storage conditions on the microbial community structure and composition of deep subsurface black shale cores. We collected the core samples

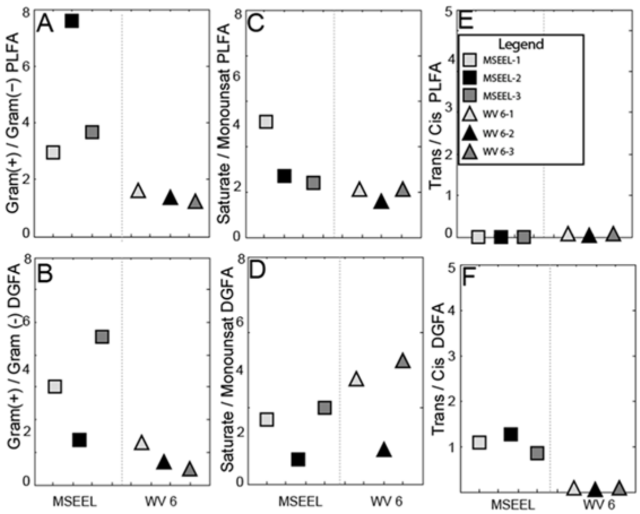


Figure 3.2: Biomass yields showing ratio of Gram (+)/Gram (-) (A, B), ratio of saturated/unsaturated (C, D), and trans/cis lipid biomarkers (E, F) for the PLFA and DGFA in the MSEEL and WV 6 core samples.

from lithologic units of the same depth in two Marcellus Shale wells (WV 6 and MSEEL) in Monongalia County, West Virginia. The PLFAs and DGFAs were extracted, trans-esterified, and analyzed as fatty acid methyl esters (FAMEs) using the gas chromatography-mass spectrometry (GC-MS). We reported higher lipid biomarker concentration and diversity in all the MSEEL core samples compared to the WV 6 core samples. Stress indicative biomarkers like oxiranes, keto, and dimethyl lipid fatty acids were only present in the MSEEL core samples. Gram (+) microbial lipid biomarkers were also more dominant in the MSEEL compared to WV 6 core samples (Figure 4). Other lipid profiles such as normal saturate, terminal branched, monounsaturates, and polyunsaturates were shared across the WV 6 and MSEEL core samples. The absence of some stress biomarkers after storage could suggest the transformation of the subsurface adapted biomarkers to relatively more stable structures in response to low temperatures and pressures in the surface. The similarity of some microbial biomarkers in MSEEL and WV 6 core samples after decades of storage indicates the potential persistence of subsurface microbial communities in surface environmental conditions for extended durations. This study highlights the adaptive ability of subsurface shale microbes and emphasizes the necessity of efficient sample storage for deep subsurface ecological studies.

Deliverables: The manuscript reporting the results will be submitted in *Frontiers in Microbiology* in this spring 2019 Semester.

4. Stable Carbon Isotope Ratios of Lipid Biomarkers in Deep Subsurface Formations of the Marcellus Shale. Ph.D. student Rawlings Akondi is also working in submitting a manuscript that assesses the bulk carbon isotopic composition of organic matter ($\delta^{13}C_{TOC}$), and compound-specific isotope analysis (CSIA) of membrane lipid fatty acids ($\delta^{13}C_{lipids}$) to examine the potential role microbes play in carbon cycling in deep subsurface ecosystems. The study samples were acquired from a ~2.2 km. deep Marcellus Shale well drilled as part of a Marcellus Shale Energy and Environmental Laboratory (MSEEL) project in Morgantown, West Virginia. With the exception of lipids like c13:0, br16:1, c21:0, and c22:0, for which the $\delta^{13}C_{lipids}$ were enriched compared to $\delta^{13}C_{TOC}$, all other lipid biomarkers were depleted in relation to $\delta^{13}C_{TOC}$; the greatest depletion occurring in 20:5ω3. The average isotopic composition of all the lipids ($\delta^{13}C_{av.\ lipids}$) was depleted compared to average $\delta^{13}C_{TOC}$ by ~0.7 ‰. These results are important for providing insight into the study of carbon flux and interpreting the biogeochemical cycling of carbon/substrate in deep subsurface environments.

Deliverables: The manuscript reporting the results will be submitted in *Frontiers in Microbiology* in the summer 2019 Semester.

PUBLICATIONS

1. Agrawal, V., and S. Sharma, 2019, Pitfalls in modeling physicochemical properties of shales using kerogen type: Scientific Reports, no. (in review).
2. Pilewski, J., S. Sharma, V. Agrawal, J. A. Hakala, and M. Y. Stuckman, 2019, Effect of maturity and mineralogy on fluid-rock reactions in the Marcellus Shale: Environmental Science: Processes & Impacts, doi:10.1039/C8EM00452H.
3. Phan, T. T., J. A. Hakala, C. L. Lopano, and S. Sharma, 2019, Rare earth elements and radiogenic strontium isotopes in carbonate minerals reveal diagenetic influence in shales and limestones in the Appalachian Basin: Chemical Geology, v. 509, p. 194–212, doi: 10.1016/j.chemgeo.2019.01.018.

Wrighton's Lab (OSU-CSU); Wilkins Lab (OSU-CSU)

Milestone 1: Compare the numerous strains of *Halanaerobium* across shales, many isolated from the MSEEL project. We will investigate how strains persist and co-exist in the shales.

Deliverable 1: A manuscript will be in advanced preparation in March 2019 for anticipated submission to a high-impact journal.

The manuscript from Booker et al. titled 'Deep Subsurface Pressure Stimulates Metabolic Plasticity in Shale-Colonizing *Halanaerobium*' has been published in Applied and Environmental Microbiology. The full citation is provided below:

Booker AE, Hoyt DW, Meulia T, Eder E, Nicora CD, Purvine SO, Daly RA, Moore JD, Wunch K, Pfiffner SM, Lipton MS, Mouser PJ, Wrighton KC, and Wilkins MJ (2019) Deep Subsurface Pressure Stimulates Metabolic Plasticity in Shale-Colonizing *Halanaerobium*. *Applied and Environmental Microbiology*. doi:10.1128/AEM.00018-19

It is available at the following link:

https://aem.asm.org/content/early/2019/04/08/AEM.00018-19

Mouser Lab (OSU-UNH)

Approach

This quarter involved finalizing PhD student Morgan Evan's dissertation, Evens carrying out her PhD defense, and Evans submitting her dissertation chapters for review.

Additionally, Mouser co-edited a themed issue (with Plata, Jackson and Vengosh) on environmental geochemistry and biology of hydraulic fracturing in the Royal Society of Chemistry journal Environmental Science: Processes & Impacts, (21), 2, 185-398. The publication below summarizes the state-of-the-research in the field, and introduces the articles collected in this special topic.

Results & Discussion

The following progress has occurred for the milestones outlined in the Mouser lab.

Milestone 1: (from Dec 2018): Characterization of intact polar lipids in MSEEL core and fluid samples.

This paper is still in the final stages of editing based on co-author feedback. We expect to submit the paper for review by May 2019.

Milestone 2: (from Dec 2018): Characterization of dehalogenation pathways in MSEEL fluid samples.

Evans submitted this paper in March 2019; we received feedback for "minor revisions" by three reviewers, and expect to submit revisions by May 2019.

Milestone 3: (from March 2019): OSU student associated with MSEEL project (Evans) to defend thesis Feb/March 2019.

Evans defended her dissertation on 4/8/2019. She will submit her dissertation associated with MSEEL project to the OSU document bank and make all data/text publically available within the next 6 months.

Deliverables

PUBLICATIONS & PRESENTATIONS

Peer Reviewed Publications associated with MSEEL:

1. Plata DL, Jackson RB, Vengosh A, **Mouser PJ.** (2019). More than a decade of hydraulic fracturing and horizontal drilling research. *Environmental Sciences: Processes & Impacts* 21 (2), 193-194.

Papers in Review/Preparation

Evans MV, Daly RA, *Luek JL, Wrighton KC, **Mouser PJ.** (Accepted with revisions). Hydraulically fractured natural-gas well microbial communities contain genomic (de)halogenation potential. *Environmental Science & Technology Letters*.

We have two additional papers in preparation that involve MSEEL related samples/topics that we expect to submit in May/June/July 2019.

Presentations

Luek J, Murphy C, Wrighton KC, **Mouser PJ.** (2019). Detection of antibiotic and metal resistance genes in deep shale microbial community members. ACS annual conference, Orlando, FL, Mar 31-Apr 4, 2019.

Evans M, Luek J, Daly R, Wrighton KC, **Mouser PJ**. (2019). Microbial (de)halogenation in hydraulically fractured natural-gas wells in the Appalachian Basin. ACS annual conference, Orlando, FL, Mar 31-Apr 4, 2019.

Cole Lab (OSU)

Milestone 1: Complete laser ablation inductively coupled plasma mass spectrometry (ICP-MS) analysis on polished thick section of hydraulic fracturing target (Lower Marcellus) to track distribution of trace elements in the rock.

Deliverable 1: Preparation of a manuscript that compares/contrasts the Lower Marcellus with Lower Point Pleasant.

Deliverable 2: Preparation of a manuscript that couples flowback geochemistry to the distribution of major and trace elements in a hydraulic fracturing target (Lower Marcellus), fluid and rock collected from the same well (MIP 3H).

Analysis of the MSEEL core sample in preparation for detailed analysis for trace metal characterization by electron microscopy and laser ablation ICP-MS has been ongoing. A review of SEM backscattered electron (BSE) and QEMSCAN imagery has been done in order to select regions of interest for laser ablation ICP-MS of the Lower Marcellus, depth 7543′. **Figure 1** shows a silt-sized organic matter maceral (center of image) partially replaced by multiple bright BSE phases (including sulfides, sulfates, and potentially uranium or REE-bearing minerals). Variation in gray scale of the grains results from variations in average atomic number contrast and therefore differences in mineral chemistry. Clay-sized and nanoscale particles intercalated with phyllosilicates and organic matter (yellow arrow) also are examples of areas hypothesized to be potentially important sources of Ba, Sr, and trace elements (transition metals other than Fe, U, REE). This effort will help answer the question of which minerals/OM are solubilized to release these elements in produced waters, and contribute to the manuscript comparing geochemistry and mineralogy of hydraulic fracturing targets with contrasting mineralogy and OM preservation.

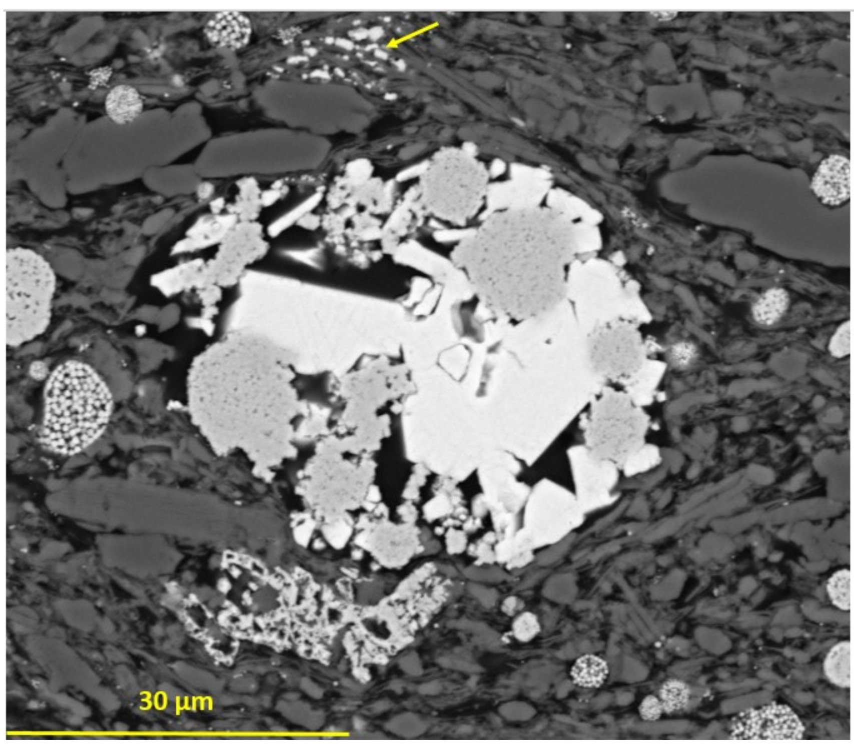


Figure 3.3: BSE image of Lower Marcellus, core depth 7543′ demonstrating minerals with variable gray scale, crystal habit, and grain size. Example targets for laser ablation ICP-MS are the central grain with silt-sized bright BSE candidates, and regions with few or no visible bright phases, to help determine which minerals solubilize to produce major and trace elements measured in produced fluids.

Bulk rock geochemistry of major and trace metals has been obtained and analyzed to better target regions of interest for analysis for trace metal geochemistry within the core samples. The results show that the target zones for the UPP and Marcellus formation have very different lithology and geochemistry (Table 1). In particular, elevated concentrations of Zn in the bulk geochemical analysis and in the fluids are consistent with the SEM observations of Zn-rich trace minerals (Figure 1). In addition, the Marcellus middle and lower core samples had elevated U which is consistent with the high levels of NORM described for these samples.

Table 3.4: Major and trace element composition of the UPP and the Marcellus formation close to the depth interval of the hydraulic fracturing target. Concentrations have been normalized to 100% after the loss on ignition.

Normalized Major Elements (Weight %):						
formation	UPP	UPP	UPP	Marc Top	Marc Mid	Lower Marc
depth	8492	8529	8550	7451.5	7509	7543
SiO2	38.35	51.95	34.45	65.69	71.84	63.77
TiO2	0.53	0.71	0.45	0.71	0.64	0.44
Al2O3	10.20	13.39	9.37	17.56	14.91	11.08
FeO*	4.05	3.65	3.05	9.14	4.91	7.64
MnO	0.07	0.05	0.05	0.03	0.01	0.02
MgO	2.07	2.18	2.87	1.49	1.45	1.13
CaO	**41.02**	**23.75**	**46.61**	0.76	1.86	12.30
Na2O	0.62	0.93	0.66	0.45	0.55	0.52
K2O	2.34	3.03	2.07	4.09	3.70	2.98
P2O5	0.76	0.36	0.42	0.09	0.13	0.11
LOI %	25.93	20.26	29.47	11.65	18.08	19.47
Normalized Trace Elements ppm:						
BaO ppm	218.1	273.3	204.0	**1108.1**	**1038.8**	**1167.6**
SrO ppm	**1320.3**	**979.4**	**1964.3**	132.8	148.1	417.2
ZnO	57.9	79.7	48.5	**140.8**	**481.7**	**373.2**
La2O3	36.6	36.2	27.0	39.1	35.8	47.5
CeO2	69.1	74.1	43.9	79.2	83.0	78.5
ThO2	5.7	7.5	6.1	10.9	7.5	6.8
Nd2O3	30.9	32.5	18.8	34.5	47.2	49.3
U2O3	5.2	4.2	3.5	7.1	**70.2**	**74.3**

Fluid Chemistry and Water-Rock Interaction.

Interpretation of flowback fluid geochemistry in light of the MSEEL hydraulic fracturing target rock mineralogy and microtexture continues. The rock focus is on Lower Marcellus core, depth 7543′, together with input, flowback, and produced fluid measurements obtained from wells MIP 3H and 5H. These fluids were analyzed in support of biogeochemical studies. In addition, we are leveraging fluid and rock measurements from an additional hydraulically fractured well in the Appalachian Basin (Utica-Point Pleasant) with strongly contrasting rock and input fluid geochemistry. The comparison of these two systems clarifies the behavior of frac fluid/rock/native brine during ongoing hydrocarbon production.

Analysis of trends in fluid species over time shows that, overall, the TDS and major solubilized elements in the Marcellus and Utica-Point Pleasant (UPP) brines (Na, Ca, Cl) are remarkably similar over time (Figure 2). With the exception of flowback samples collected in the first few days which were affected by the heavy brines in the well during the shut in period, the UPP brines exhibit a systemic increase in concentration over time that reflects the volume of water that returns to the surface. The changes in concentrations in the MSEEL wells varied but in general increased over time.   In addition, behavior of Na, Br, and Cl suggest that the produced water signatures (with the exception of early-obtained flowback samples more indicative of input fluids) are derived from the native rock brines. Major exceptions to this “similar behavior” of major elements from contrasting rocks are Ba and Sr. Measurements of these elements are very different when comparing Marcellus produced waters to Point Pleasant produced waters. Interpretations of the differences include 1) a high sulfate input fluid used in the Point Pleasant well studied resulted in most of the Ba precipitating from solution 2) recycled flowback used in one of the two Point Pleasant wells studied 3) different concentrations of Sr and Ba in the hydraulic fracturing target rocks.

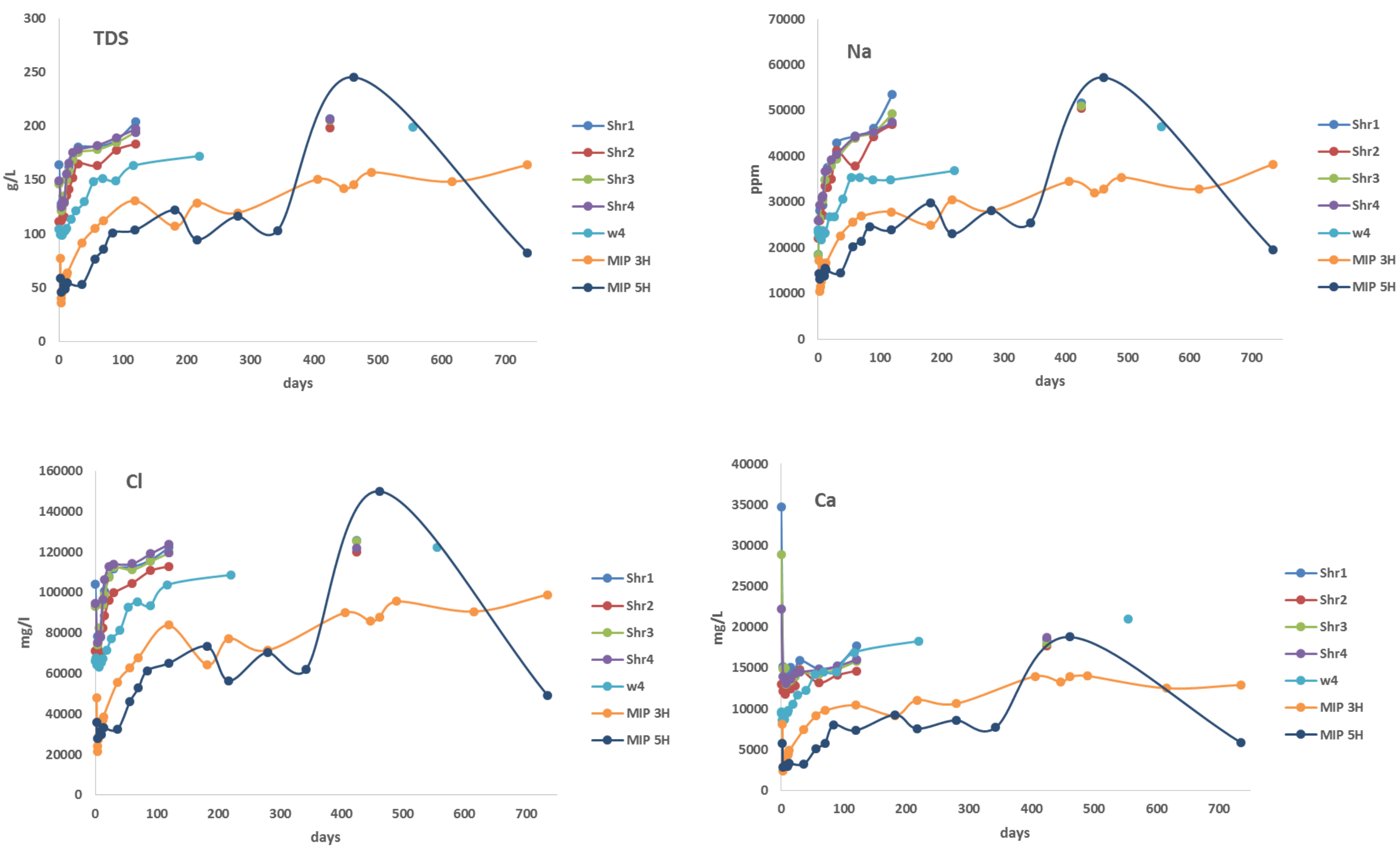


Figure 3.5: Time series showing the evolution of flowback geochemistry of MSEEL (MIP 3H and 5H) and Utica-Point Pleasant hydraulic fracturing wells.

Deliverable 2: Produce a draft of a manuscript comparing geochemistry of flowback fluids between Utica and Marcellus wells.

SAW, JMS, and DRC are drafting a paper comparing the geochemistry of flowback fluids from Utica-Point Pleasant Shale to the geochemistry of fluids from the MSEEL site.

Flowback fluid signals from the Appalachian Basin: Focus on the Marcellus and Utica-Point Pleasant. Susan A. Welch, Julia M. Sheets, Rebecca A. Daly, Andrea J. Hanson, **more authors** and David R. Cole

Darrah Lab (OSU)

Milestone 1: Characterization of water and gas samples for noble gas (He, Ne, Ar, Kr, and Xe), fixed gas (N_2, H_2, CO_2) and hydrocarbon gas (C1-C5, C6+) composition (11 samples remain).

Deliverable 1: Completed final data report for remaining noble gas, hydrocarbon, and fixed gas measurements of water and gas samples. This includes the completion of 63 samples for noble gas isotope (He, Ne, Ar, Kr, and Xe) and bulk gas geochemistry (C_1-C_5, CO_2, N_2, H_2).

This work represents the completion of the funded portion of the MSEEL project and brings the total of noble gas samples to n=89 combined natural gas (n=40) and produced water (n=49) samples that have been analyzed and reported.

Update 1: Completed.

Milestone 2: Characterization of fluid inclusion gas compositions for noble gas and hydrocarbons.

Deliverable 2: Data report for remaining noble gas and hydrocarbon composition of fluid inclusions is complete.

Update 2: Data processing and reporting in progress.

Milestone 3: Characterization of hydrocarbon residence time and hydrocarbon generation time using He, Ne, and Ar isotopes.

Deliverable 3: Submit manuscript about hydrocarbon generation time and fluid residence time in various reservoirs.

Update 3: Analyses completed. Data has been processed, residence time modeling completed, and manuscript in preparation.

Milestone 4. Complete noble gas manuscript of gas composition through time.

Deliverable 4. Manuscript to report data about changes in the hydrocarbon, fixed, and noble gas composition throughout time.

Update 4: Analyses completed. Data interpretation completed. Manuscript draft in progress.

Project Title	Milestone Name	Milestone Description	Estimated Completion Date
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Compare the numerous strains of *Halanaerobium* across shales (Wrighton/Wilkins)	The manuscript from Booker et al. titled 'Deep Subsurface Pressure Stimulates Metabolic Plasticity in Shale-Colonizing *Halanaerobium*' has been published in Applied and Environmental Microbiology. The full citation is provided below: Booker AE, Hoyt DW, Meulia T, Eder E, Nicora CD, Purvine SO, Daly RA, Moore JD, Wunch K, Pfiffner SM, Lipton MS, Mouser PJ, Wrighton KC, and Wilkins MJ (2019) Deep Subsurface Pressure Stimulates	March 31, 2019

		Metabolic Plasticity in Shale-Colonizing *Halanaerobium*. *Applied and Environmental Microbiology*. doi:10.1128/AEM.00018-19	
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Characterization of intact polar lipids in MSEEL core and fluid samples. (Mouser)	This paper is still in the final stages of editing based on co-author feedback. We expect to submit the paper for review by May 2019.	April 30, 2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Characterization of dehalogenation pathways in MSEEL fluid samples. (Mouser)	Evans submitted this paper in March 2019; we received feedback for "minor revisions" by three reviewers, and expect to submit revisions by May 2019.	05/01/2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	OSU student associated with MSEEL project (Evans) to defend thesis Feb/March 2019. (Mouser)	Evans defended her dissertation on 4/8/2019. She will submit her dissertation associated with MSEEL project to the OSU document bank and make all data/text publically available within the next 6 months.	04/08/2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Complete laser ablation inductively coupled plasma mass spectrometry (ICP-MS) analysis on polished thick section of hydraulic fracturing target (Lower Marcellus) to track distribution of trace elements in the rock. (Cole)	Draft manuscript nears completion that compares/contrasts the Lower Marcellus with Lower Point Pleasant. Preparation of a manuscript that couples flowback geochemistry to the distribution of major and trace elements in a hydraulic fracturing target (Lower Marcellus), fluid and rock collected from the same well (MIP 3H).	05/30/2019

Marcellus Shale Energy and Environment Laboratory (MSEEL)	Complete assessment of comparison of Marcellus and Utica flowback fluids (Cole)	A manuscript is partially completed on a comparison of geochemistry of flowback fluids between Utica and Marcellus.	06/30/2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Characterization of water and gas samples for noble gas (Darrah)	Completed final data report for remaining noble gas, hydrocarbon, and fixed gas measurements of water and gas samples. This includes the completion of 63 samples for noble gas isotope (He, Ne, Ar, Kr, and Xe) and bulk gas geochemistry (C_1-C_5, CO_2, N_2, H_2). A paper is in preparation that summarizes these noble gas data from the rock characterization.	05/31/2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Characterization of fluid inclusion gas compositions for noble gas and hydrocarbons. (Darrah)	Data report for remaining noble gas and hydrocarbon composition of fluid inclusions is complete Data processing and reporting in progress.	03/31/2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Characterization of hydrocarbon residence time and hydrocarbon generation time using He, Ne, and Ar isotopes. (Darrah)	Submit manuscript about hydrocarbon generation time and fluid residence time in various reservoirs. Analyses completed. Data has been processed, residence time modeling completed, and manuscript in preparation.	06/30/2019
Marcellus Shale Energy and Environment Laboratory (MSEEL)	Complete noble gas manuscript of gas composition through time series. (Darrah)	Manuscript to report data about changes in the hydrocarbon, fixed, and noble gas composition throughout time. Analyses completed. Data interpretation completed. Manuscript draft in progress.	07/31/2019

Topic 4 – Produced Water and Solid Waste Monitoring –

Approach

Over three years into the post completion part of the program, the produced water and solid waste component of MSEEL has continued to systematically monitor changes in produced water quality and quantity. During year one of the study, hydraulic fracturing fluid, flowback, produced water, drilling muds and drill cuttings were characterized according to their inorganic, organic and radio chemistries. In addition, surface water in the nearby Monongahela River was monitored upstream and downstream of the MSEEL drill pad. Toxicity testing per EPA method 1311 (TCLP) was conducted on drill cuttings in both the vertical and horizontal (Marcellus) sections to evaluate their toxicity potential. Sampling frequency has been slowly scaled back following well development. **Error! Reference source not found.** shows an "X" for sample collection dates. Wells 4H and 6H were brought back online in late 2016. Other blank sample dates in **Error! Reference source not found.** indicate that samples were not collected, due to lack of availability of produced water from the well(s).

Table 4.1: MIP sampling events are indicated with an "X".

Year	2015			2016												
Day/Month	10-Dec	17-Dec	22-Dec	6-Jan	20-Jan	3-Feb	2-Mar	23-Mar	20-Apr	18-May	2-Jul	17-Aug	21-Jun	19-Oct	16-Nov	14-Dec
3H	X		X	X	X	X		X	X	X	X	X	X	X		X
4H															X	X
5H	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
6H															X	X

Year	2017									2018					
Day/Month	13-Jan	14-Feb	13-Mar	7-Apr	5-May	12-Jul	20-Dep	3-Nov	20-Dec	22-Jan	23-Feb	16-May	2-Aug	16-Oct	15-Dec
3H	X	X	X	X	X	X	X	X	X	X	X	X	X		X
4H	X	X	X	X	X					X	X	X	X	X	X
5H		X			X				X	X		X		X	X
6H	X	X	X	X	X							X	X		

Year	2019	
Day/Month	24-Jan	5-Mar
3H	X	X
4H	X	X
5H	X	X
6H		X

Results & Discussion

Trends in produced water chemistry

Major ions

While makeup water was characterized by low TDS (total dissolved solids) and a dominance of calcium and sulfate ions, produced water from initial flowback is essentially a sodium/calcium chloride water (Figure 4.2). While produced water TDS (total dissolved solids) increased by an order of magnitude from initial flowback to the present, the ionic composition of produced water changed very little through 1181 days post completion. Produced water TDS was affected by shut-in/turn-in cycles at individual wells. For example, upon turn-in TDS was invariably very low but reached pre-shut-in concentrations within a month. MIP 3H was shut-in sometime after day 966 and turned back in just prior to sampling on day 1101. While concentrations are magnitudes lower, the proportion of ionic compounds is consistent with previous samples.

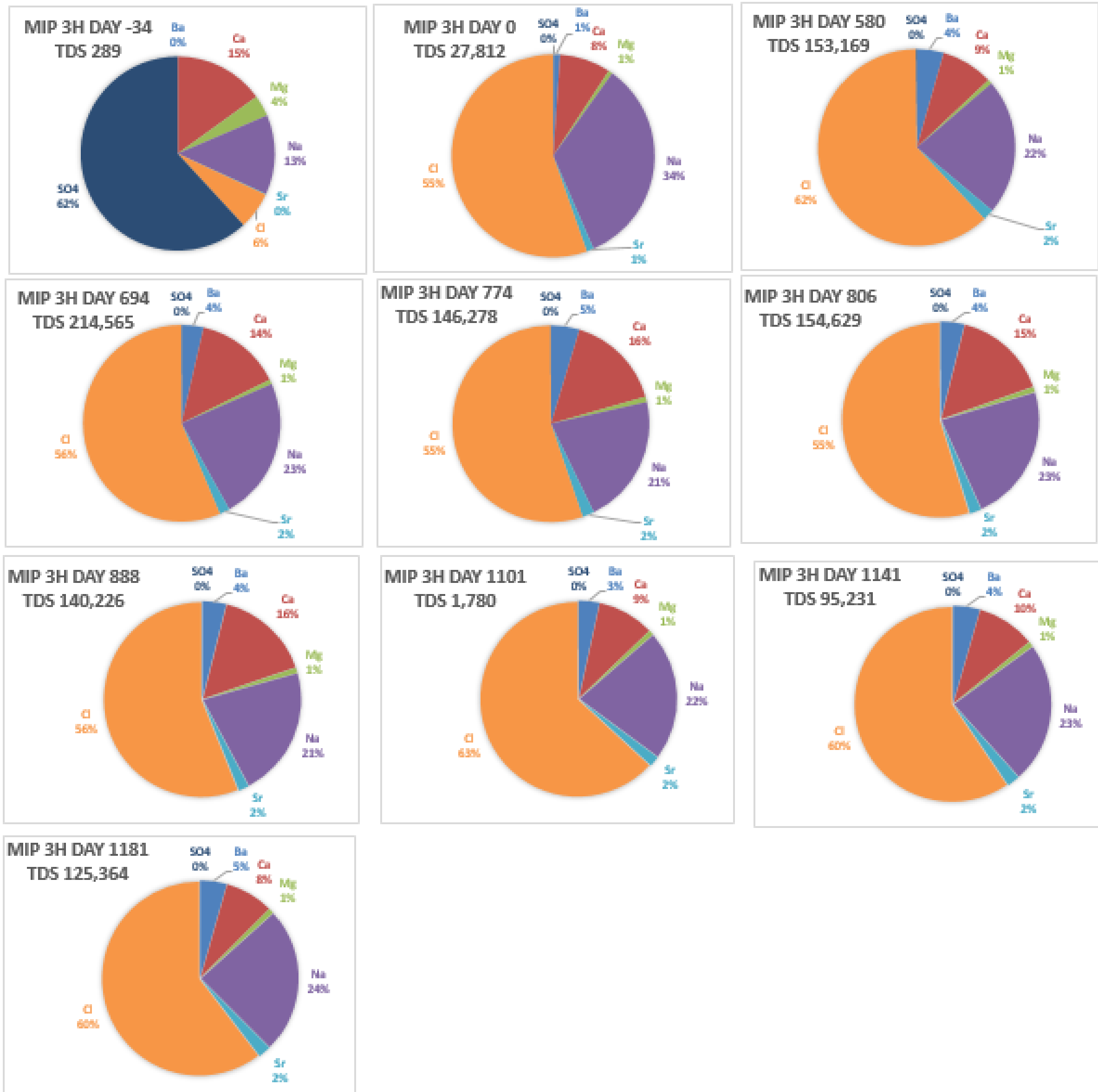


Figure 4.2: Changes in major ion concentrations in produced water from well MIP 3H. Top left Day -34 represents makeup water from the Monongahela River, top center is produced water on the first day (Day 0) and the remainder of pie charts show flow back and produced water on sampling dates through the 1181th day post completion.

In wells 3H and 5H, TDS increased rapidly over the initial 90 days post completion while TDS stabilized between 100,000 and 200,000 mg/L through day 1181(3H) (Figure). Note that 3H and 5H were both shut-in near day 966 and brought back online prior to sampling on day 1101. 3H and 5H are showing an upward trend following day 1101.

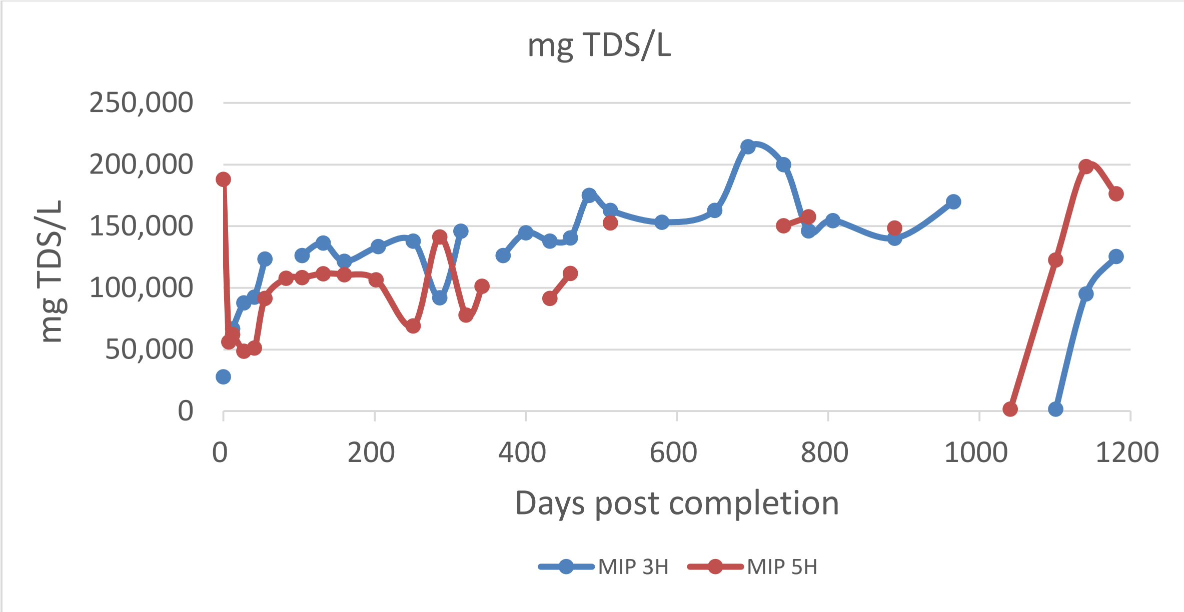


Figure 4.3: Changes in produced water TDS sdc (sum of dissolved constituents) through the first 1181 days post completion (3,5H).

The older 4H and 6H wells offer insight into the longer-term TDS trend. Those wells only came back on line during this quarter after a shut-in period of 315 days and those results vary but they are much lower than the current values for wells MIP 3H and 5H. Both 4H and 6H were shut down during late 2017. TDS was very low at MIP 4H during the first sampling event of early 2018. Calculated TDS was 2,455 mg/L and lab reported TDS was 2,300 mg/L. A similarly low TDS trend was noted when well 4H went back online around 1,793 days post-completion (after being shut-in for 315 days) and again when 6H went online around day 2,417 A rise in TDS subsequently follows the initial return to online status with TDS on an upward trend, reaching 160,000 for 6H. MIP 6H has been offline during this quarter's sampling events. MIP 4H is on a downward trend after peaking at around 140,000 at day 2552 (Figure 3).

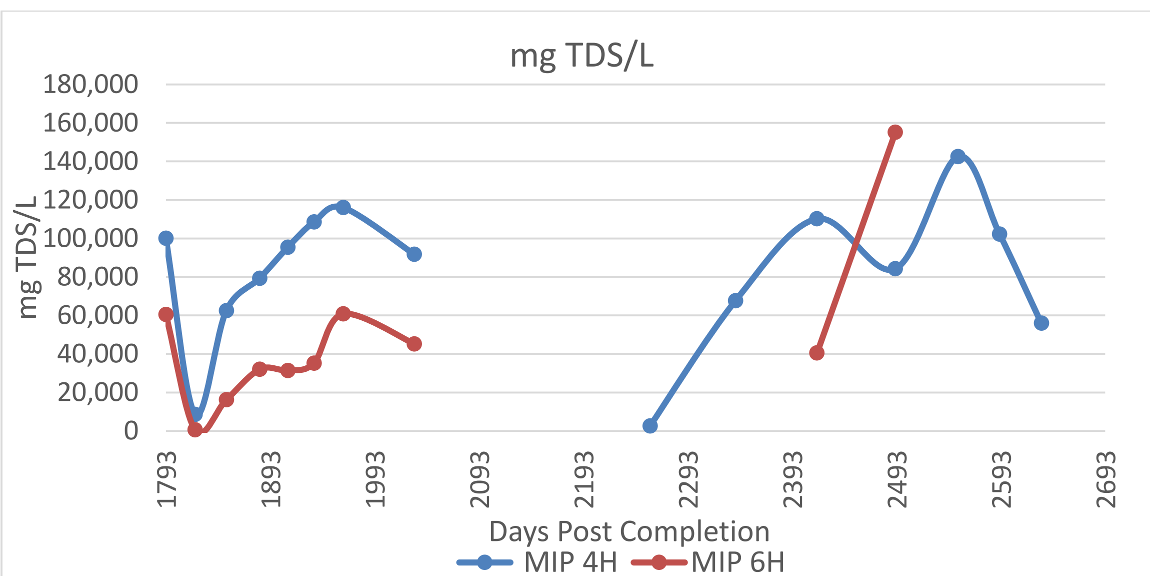


Figure 4.4: Changes in produced water TDS sdc (sum of dissolved constituents) through the days 1793 to 2632 post completion (4,6H).

Water soluble organics

The water soluble aromatic compounds in produced water: benzene, toluene, ethylbenzene and xylene were never high. With two exceptions at post completion day 321 and 694, benzene has remained below 30 µg/L (Figure 1). This seems to be a characteristic of dry gas geologic units. After five years, benzene has declined below the drinking water standard of 5 µg/L.

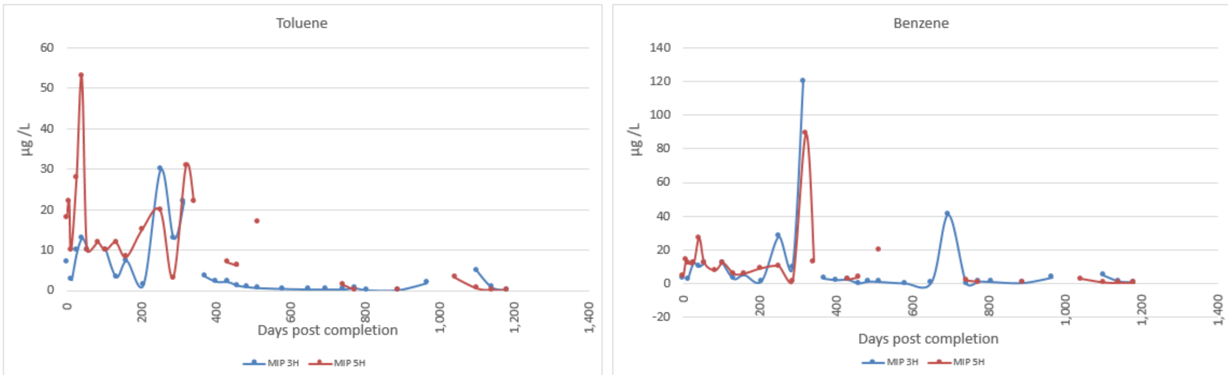


Figure 1.5: Changes in benzene and toluene concentrations. The figure shows data from well both 3H and 5H.

Radium isotopes

The radiochemical concentrations were determined by Pace Analytical in Greensburg PA, a state certified analytical lab. Radium concentrations generally increased through 800 days post completion at wells MIP 3H and 5H. Maximum levels of the radium isotopes reached about 21,800 pCi/L at the unchoked 3H well and about half that amount at 5H. After returning online prior to day 966, both wells are on a general upward trend, except for 3H on day 1101. (Figure 4.6).

<u>Radioactivity in produced water</u>

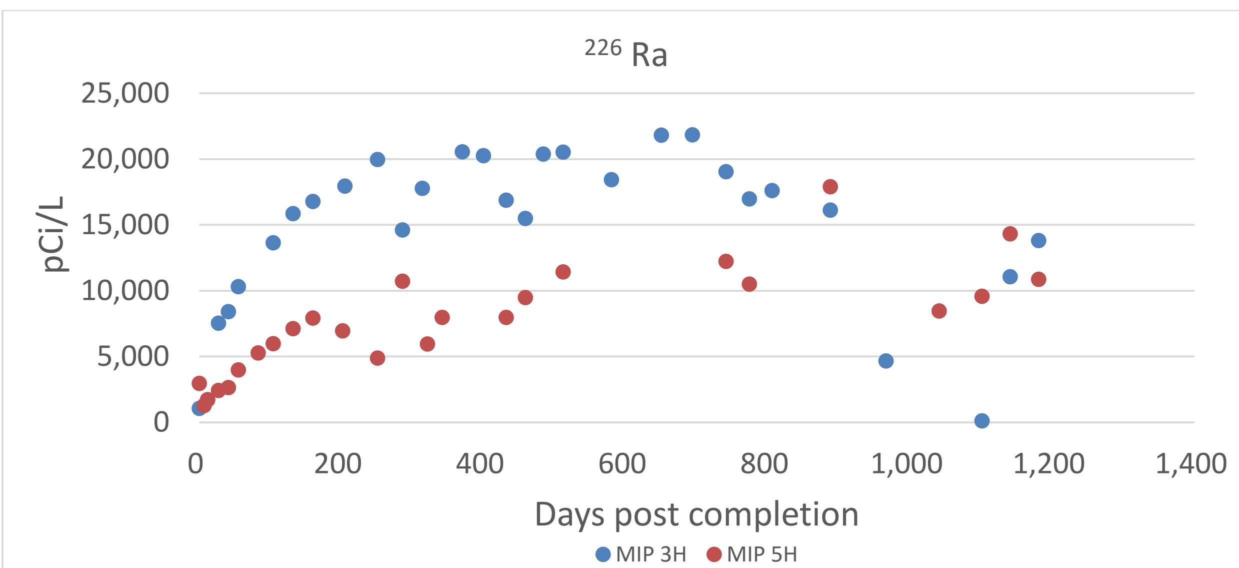


Figure 4.6: The radium isotopes are plotted against days post well completion. Well 5H was choked more periodically the 5H. 3H produced less water and lower concentrations of radium.

Radium concentrations at wells 4H and 6H were below 9,000 pCi/L during all sampling periods. Both wells were choked at day 1963. Well 4H was reopened at day 2225, radium was 58 pCi/L on the first sampling after the reopening and 3719 pCi/L at day 2257, a month later (Figure) peaked at 5,127 pCi/L then returned to 3,892 pCi/L. The same trend is noted at day 2492 when 4H returned online with 57 pCi/L then peaked at day 2632 with 8,197 pCi/L. Additional data is needed to capture long-term trends.

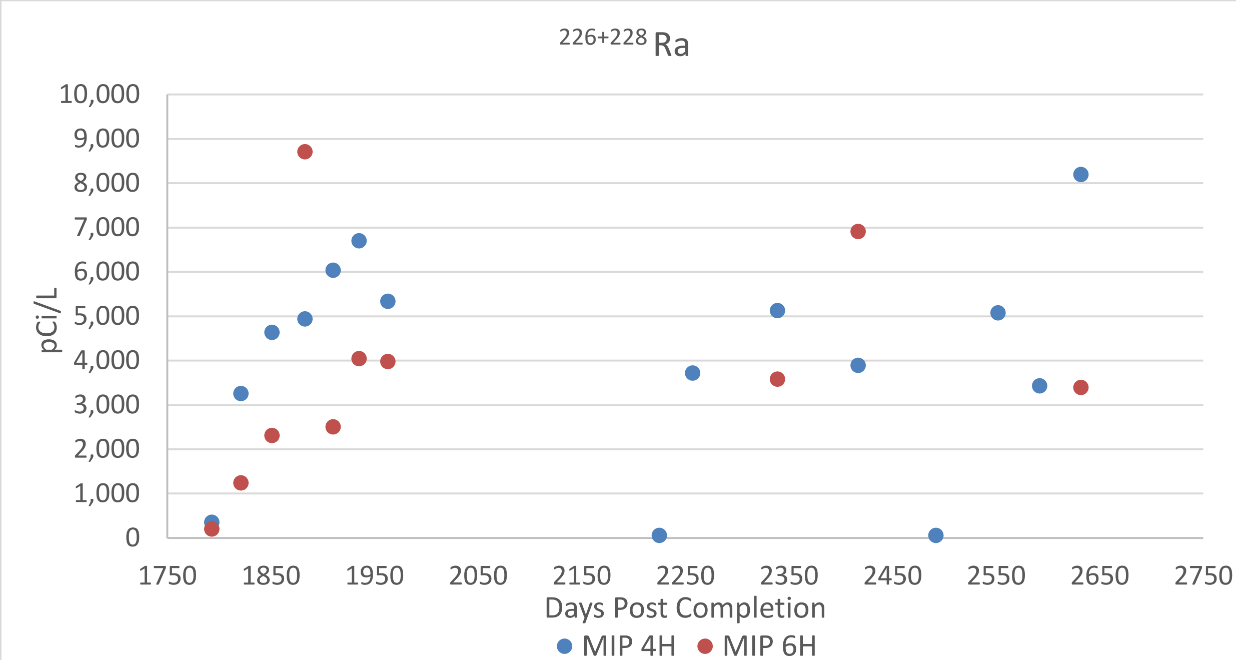


Figure 4.7: The radium isotopes are plotted against days post well completion. Well 4H and 6H were choked at day 1963. At day 2225, 4H was reopened showing a value of 58 pCi/L and reopened again at day 2492 showing a value of 57 pCi/L.

Figure 4.8 and Figure 4.9 show the relationship between gross alpha and ^{226}Ra at 3H and 5H.

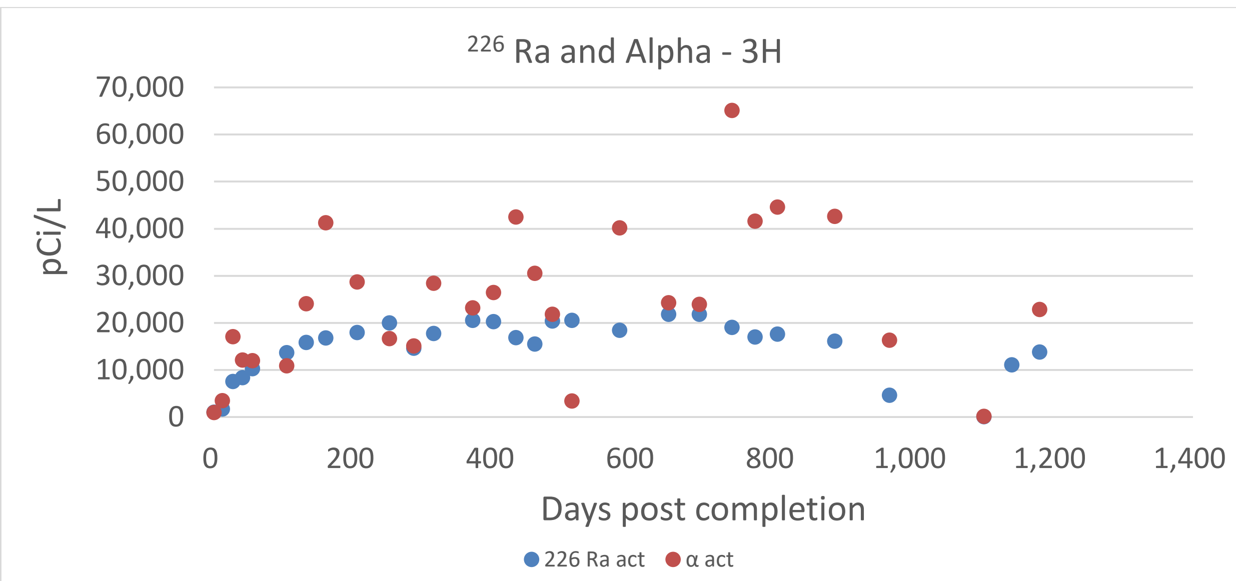


Figure 4.8: The relationship between gross alpha and ^{226}Ra as a function of time post completion at 3H.

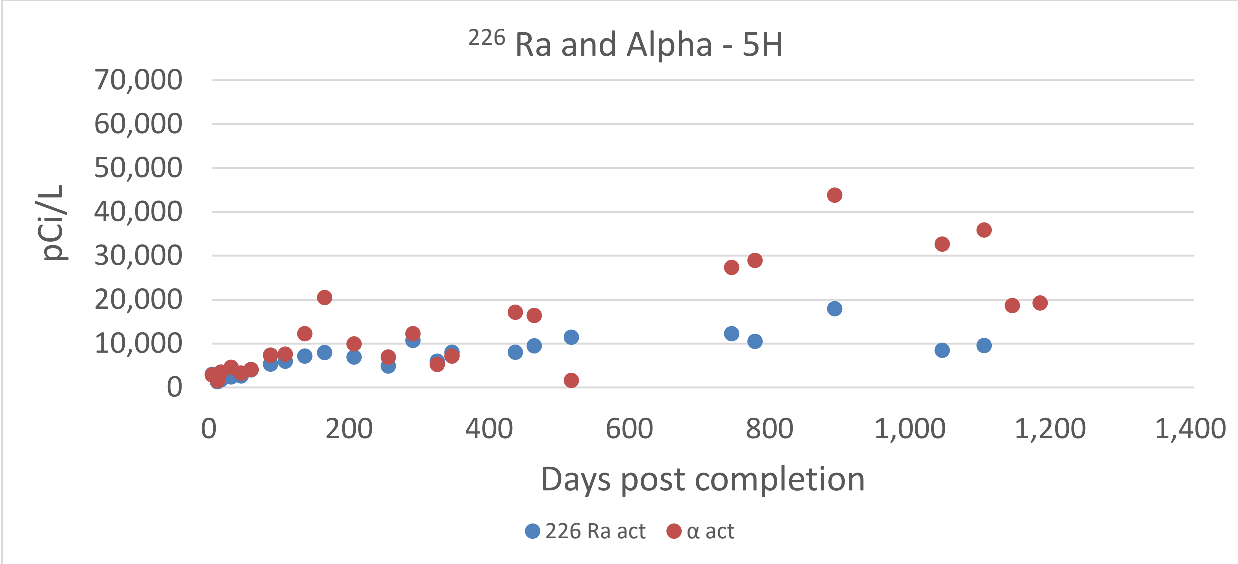


Figure 4.9: The relationship between gross alpha and ^{226}Ra as a function of time post completion at 5H.

The highest values reported in the older wells at 4H and 6H were 17,550 pCi/L gross alpha and 8,197 pCi/L ^{226}Ra. The relationship between gross alpha and ^{226}Ra for wells 4H and 6H are shown in Figure 4.10 and Figure 4.11.

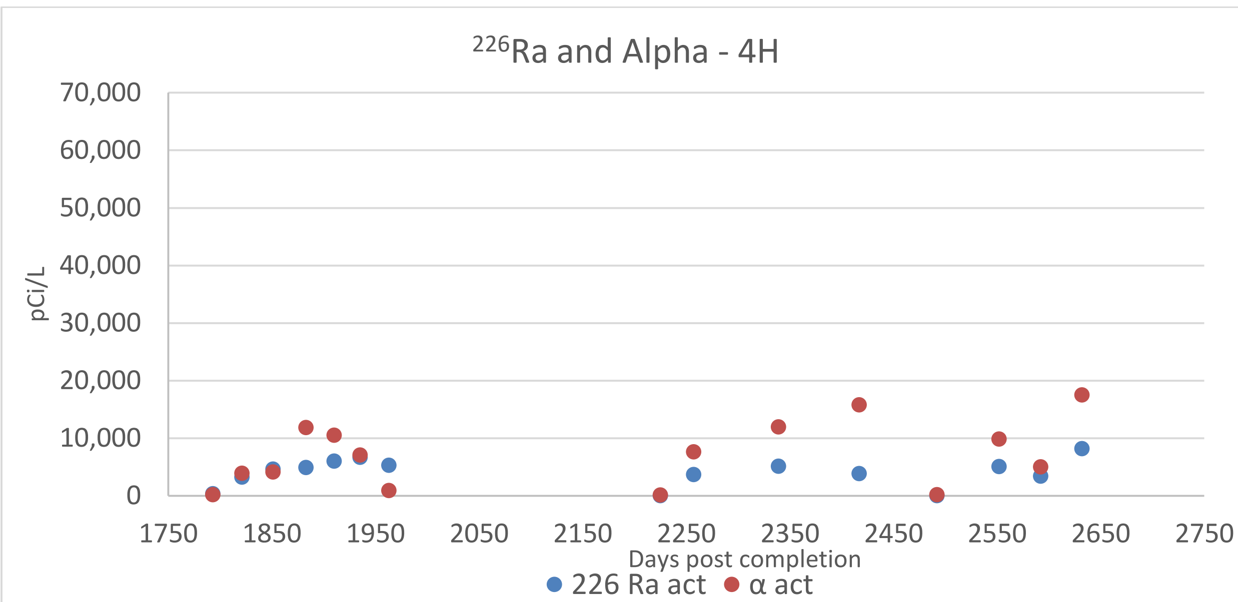


Figure 4.10: The relationship between gross alpha and ^{226}Ra as a function of time post completion at 4H.

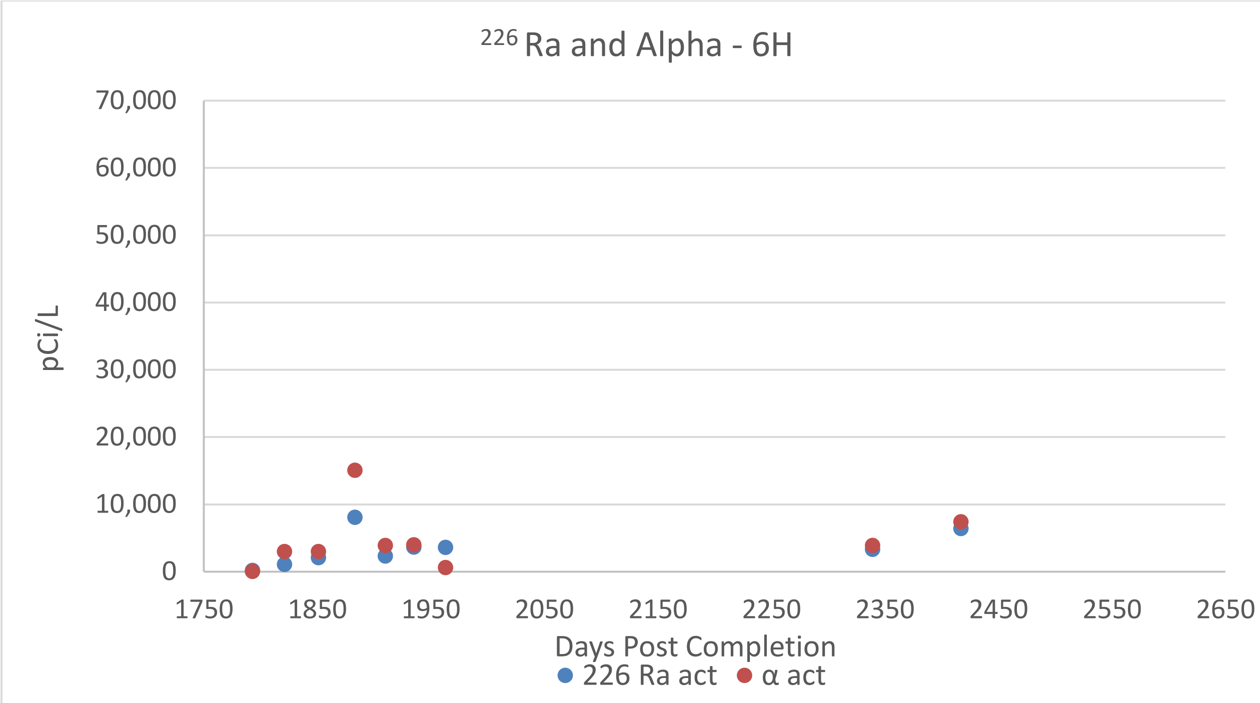


Figure 4.11: The relationship between gross alpha and ^{226}Ra as a function of time post completion at 6H.

Products

None for this quarter.

Plan for Next Quarter

We will continue monthly sampling and analyze flowback/produced water (FPW) from MIP 3H, 4H, 5H and 6H if they are online.

We will begin sampling at Boggess Pad control wells 9H and 17H. Plans include collection of hydraulic fracturing fluid, flowback, produced water, drilling muds and drill cuttings. Following the same protocols used at MIP wells, we will characterize their inorganic, organic and radio chemistries.

Topic 5 – Environmental Monitoring: Air & Vehicular

Approach

During this quarter the CAFEE team completed their 8th and 9th audit of the MSEEL site. The 10th audit will occur on April 17th and correspond with a visit from students from Argentina with Dr. Eduardo Sosa's Chevron program. The indirect system has now been deployed for data collection during audits and at other times to trouble shoot the data collection system and to further refine data processing methodologies. In addition, the complete stationary tower system has been finalized. Whereas the vehicle mounted system will examine OTM 33A and other dispersion methods, the station tower will be deployed for extended periods to assess baseline eddy covariance methods.

Figure 5.1 shows the complete station tower system as mounted on a mobile trailer. Based on solar data for industrial park region, the solar powered system was designed to operate for up to 2-4 days without any sun. The analyzers are mounted at a height of approximately 4 m with respect to the ground and will likely be transferred to the old electric pole at MSEEL 1.0 for long term deployments. The DAQ system has been finalized to run unmanned. Data files are recorded at 1 hr intervals and stored on an SD card. The system is controlled with a BeagleBone which uses WVU developed software for data collection. A 3G/4G cellular modem has been incorporated using the Hologram network. The system will send text messages and emails to alert researchers of any software issues. Prior to deployment at MSEEL 1.0 the system (both as vehicle and stationary versions) will be exposed to controlled releases at WVU Reedsville Farms to collect baseline dispersion data.

Figure 5.1: Completed eddy-covariance system for extended deployments.

In addition to progress on the physical data collection systems. The team has also improved the data analysis software. Figure 5.2 shows a mapping program that is capable of loading mobile geospatial data with respect to the MSEEL 1.0 site geometry. Key natural gas components are included, and audit data are uploading base on general locations. This will be used in understating the micrometeorological limitations for onsite mobile measurements for comparison with directly quantified emissions rates.

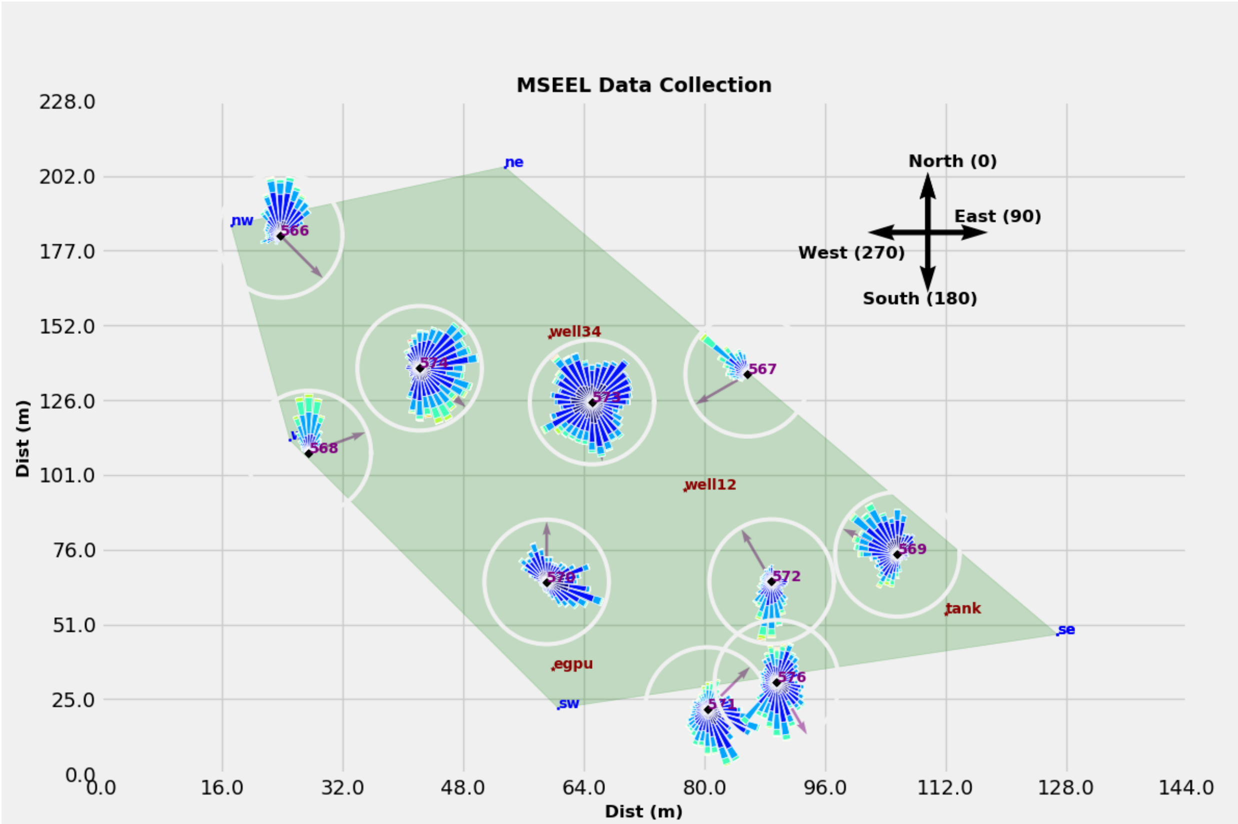


Figure 5.2: Geospatial mapping system that includes mobile measurement results on a point basis with respect to physical component locations and emission rates.

Results & Discussion

Figure 5.3 shows an updated bar chart summarizing the results from the first nine audits. Note that Audit 7 is well beyond the scale at 43.4 kg/hr. Since our sample size is low, this possible outlier or fat-tail significantly increased our average emissions rate up to 6.6 kg/hr. However, we have included the geometric means in addition to our average (arithmetic means). Our geometric mean still lies between the geometric and arithmetic means of the Rella et al. studies. We previously discussed that the main contributor to site emissions was the produced water tank which is vented to the atmosphere. It was also the main contributor to the excessive emissions during Audit 7 (43.3 kg/hr). We note that emissions were higher than normal since an EPGU was just replaced and wells brought back online. We previously discussed the possibility of a stuck dump valve on this new unit. We see in subsequent Audits 8 and 9 that the tank emissions returned to the values previously seen in similar audits.

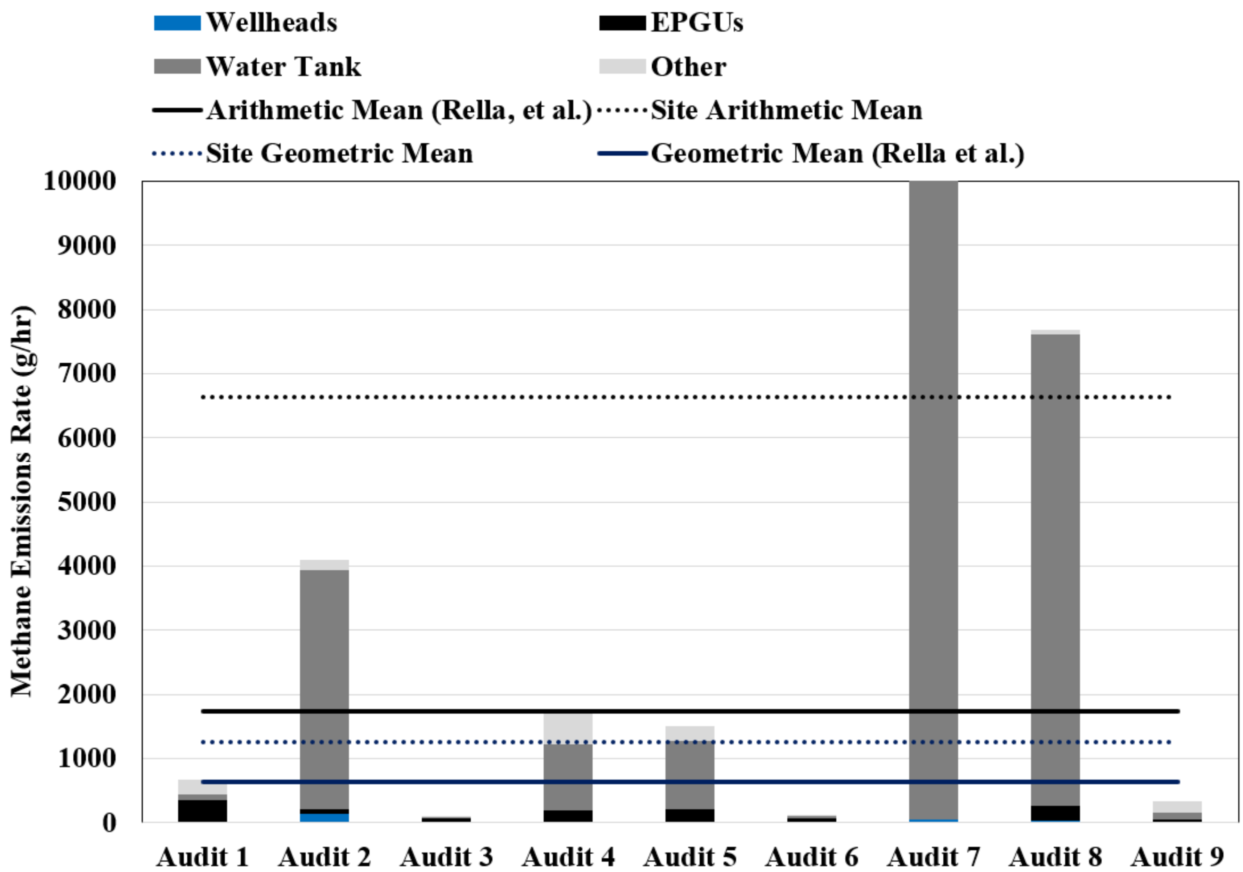


Figure 5.3: Methane emissions from Audits 1-9.

Products

- Johnson, D., Heltzel, R., and Oliver, D., "Temporal Variations in Methane Emissions from an Unconventional Well Site," *ACS Omega*, 2019. DOI: 10.1021/acsomega.8b03246.

Plan for Next Quarter

- Complete 10th and possibly 11th audit depending on scheduling
- Complete baseline controlled releases for indirect methane system baselines as part of additional NSF program (both mobile vehicle and stationary tower)
- Integrate methane/ethane analyzer into data acquisition system (NSF and other funding)
- Deploy stationary system at MSEEL 1.0
- Review data acquisition system requirements for energy audits as part of MSEEL 2.0 and hire new graduate student for energy audit focus
- As part of the NSF program at MSEEL 1.0 – PhD students Robert Heltzel and Mohammed Tamim will attend a LiCor training session in Lincoln, Nebraska.

Topic 6 – Water Treatment

Approach

As part of this subtask, the Dr. Morrissey is characterizing the chemical and biological factors that influence radium accumulation in sludge from produced water. This research could lead to the development of low cost treatments for produced water that prevent the accumulation or radioactive sludge. This work is in service of Milestone 33: *Results of techniques for low cost treatment of flowback waters*. To accomplish this milestone, the team is performing a series of laboratory microcosm experiments. Produced water is incubated for 21 days in the laboratory with or without additions of sulfate (2000mg/L) and nutrients (carbon, nitrogen and phosphorus). The addition of nutrients is intended to stimulate the activity of microorganisms to immobilize sulfate and prevent it from precipitating with radium. Tests have utilized produced water from the 3H.

Milestones for project year March 2018-2019

Milestone 1: Characterize chemical transformations during produced water storage from well 3H. We will complete characterization of changes in produced water chemistry (specifically Fe, Sr, Ba, Ra 226, Ra 228) and biological activity (CO_2 and CH_4 production) that occur during short term storage (20 days). Measure Ra activity (Ra 226 and Ra 228) of solid precipitate formed during short term storage of produced water. We expect to complete this analysis on a minimum of 5 independently collected produced water samples collected between December 2017 and January 2019.

Results for Milestone 1

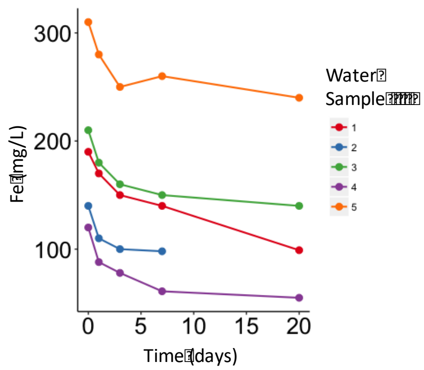


Figure 6.1: Iron concentration over time during storage of five independently collected produced water samples from well 3H.

Analysis of five independently collected water samples gathered between December 2017 and August 2018 revealed high variation in water chemistry. The concentrations of important scale forming cations (e.g. Ba and Sr) as well as Ra did not change over time (Table 1). Similarly, concentrations of Na, Ca, and Cl were stable over time. Sulfate concentrations were always below detection. The only ion that changed over the 20-day incubation was Fe, which decreased ~70 mg/L on average. A relatively small amount of Ra precipitated over the 20-day incubation, 31.4 pg ^{226}Ra/L on average (range 8.8 -76.6 pg ^{226}Ra/L). Biological activity, as estimated by CO_2 and CH_4 production, also varied among samples (Figure 2). Rates of methane production were highest immediately after sampling and declined over the 20-day incubation. In general CO_2 production rates were ten fold higher than CH_4 production rates.

Table 6.2: Concentration of select cations in produced water from well 3H.

	Sr (mg/L)	Ba (mg/L)	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)
Mean	1918	4204	13839	800.7
Min	522	1160	3691	181.3
Max	3140	7020	20903	1244.5

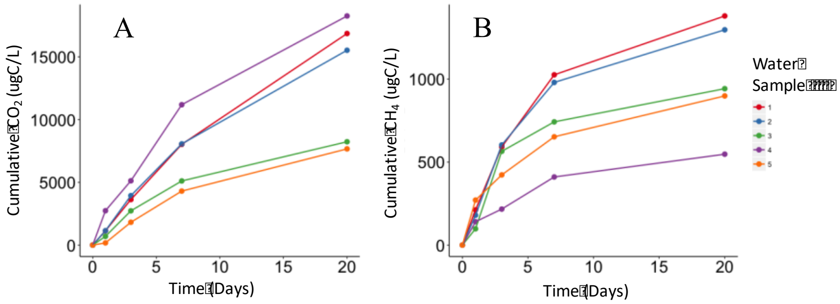


Figure 6.3: Cumulative production of CO_2 (A) and CH_4 (B) from five independently collected produced water samples.

Milestone 2. Document effects of sulfate and nutrient additions on chemical transformations during produced water storage from well 3H. We will characterize the effect of sulfate and nutrient additions on changes in produced water chemistry (specifically Fe, Sr, Ba, Ra 226, Ra 228) and biological activity (CO_2 and CH_4 production) during short term storage (20 days). Effects on Ra activity (Ra 226 and Ra 228) of solid precipitate formed will also be measured. We expect to complete these analyses on a minimum of 3 independently collected produced water samples collected between December 2017 and January 2019.

Results for Milestone 2

Sulfate and nutrient additions were added to three independently collected water samples gathered between January and August 2018. Nutrient additions had no detectable impact on water chemistry dynamics but did increase CO_2 production rates. The amount of 226Ra in solid precipitate slight increased with nutrient additions averaging 331 pg/L (range 263-425 pg/L). Sulfate addition caused a near immediate drop in the concentration of Ba (Fig 3A). The chemistry suggests that one mole of sulfate precipitates ~0.8 moles of Ba. When Ba precipitates Ra concentrations decrease proportionally (Fig 3). Consequently, SO_4 caused Ra to accumulate

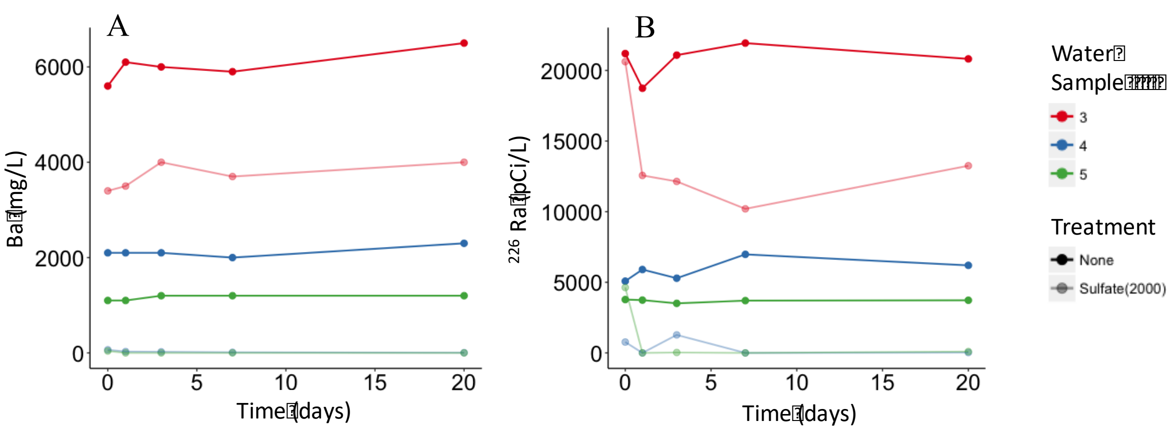


Figure 6.4: Changes in Ba (A) and 226 Ra (B) due to the addition of SO_4. Data is shown for three independently collected water samples indicated by color, samples amended with SO_4 are shown in a lighter shade.

in the solid precipitate in proportion to it's original concentration in the produced water sample (Fig 4). Our data suggests Ra can be removed by SO_4 addition via co-precipitation with Ba.

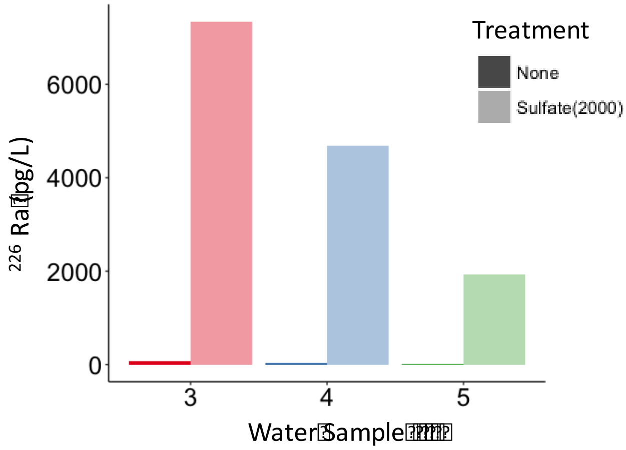


Figure 6.5: Mass of ^{226}Ra in solid precipitate per liter of produced water in three untreated (dark shade) and sulfate amended (light shade) water samples from well 3H (indicated by color).

Topic 7 – Database Development

Approach

All MSEEL data is online and available to researchers (Figure 7.1 and 7.2). The website has been updated with the latest production beyond the end of the quarter (Figure 7.3). Work continues and we are adding data from MSEEL 3 Boggess Pad.

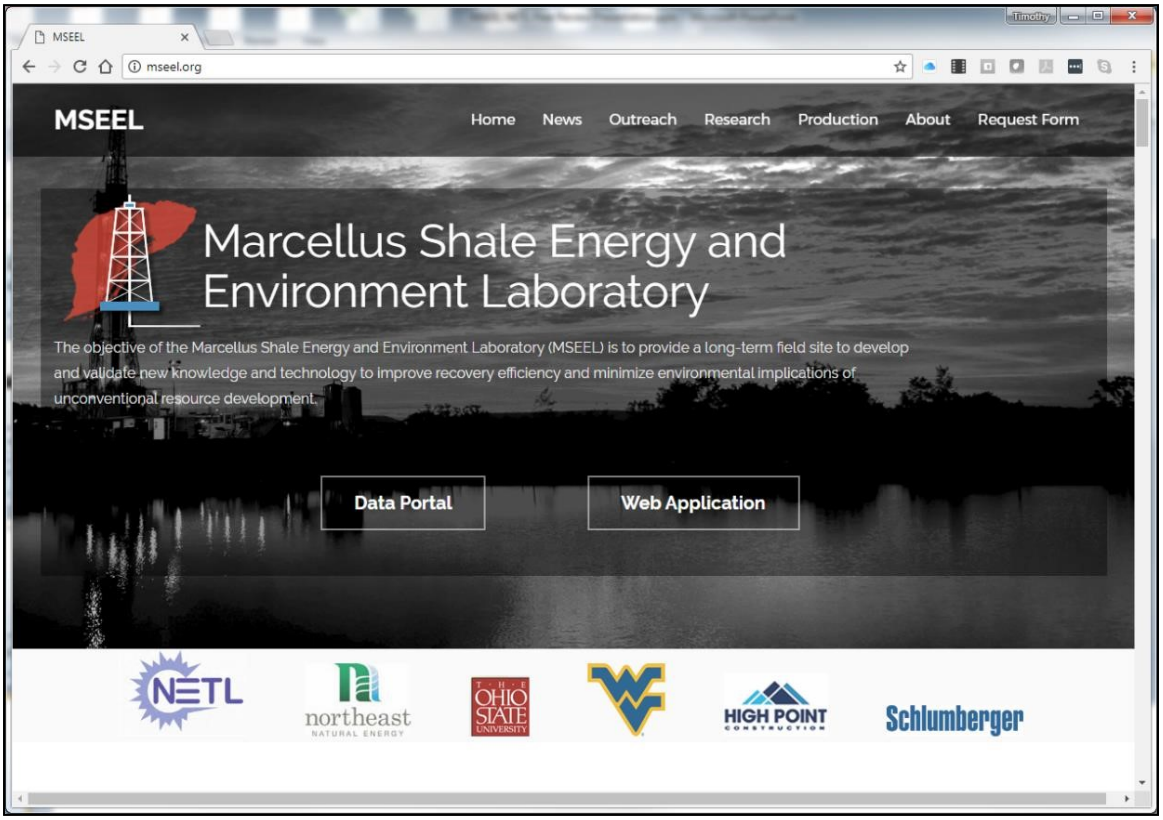


Figure 7.1: MSEEL website at http://mseel.org/.

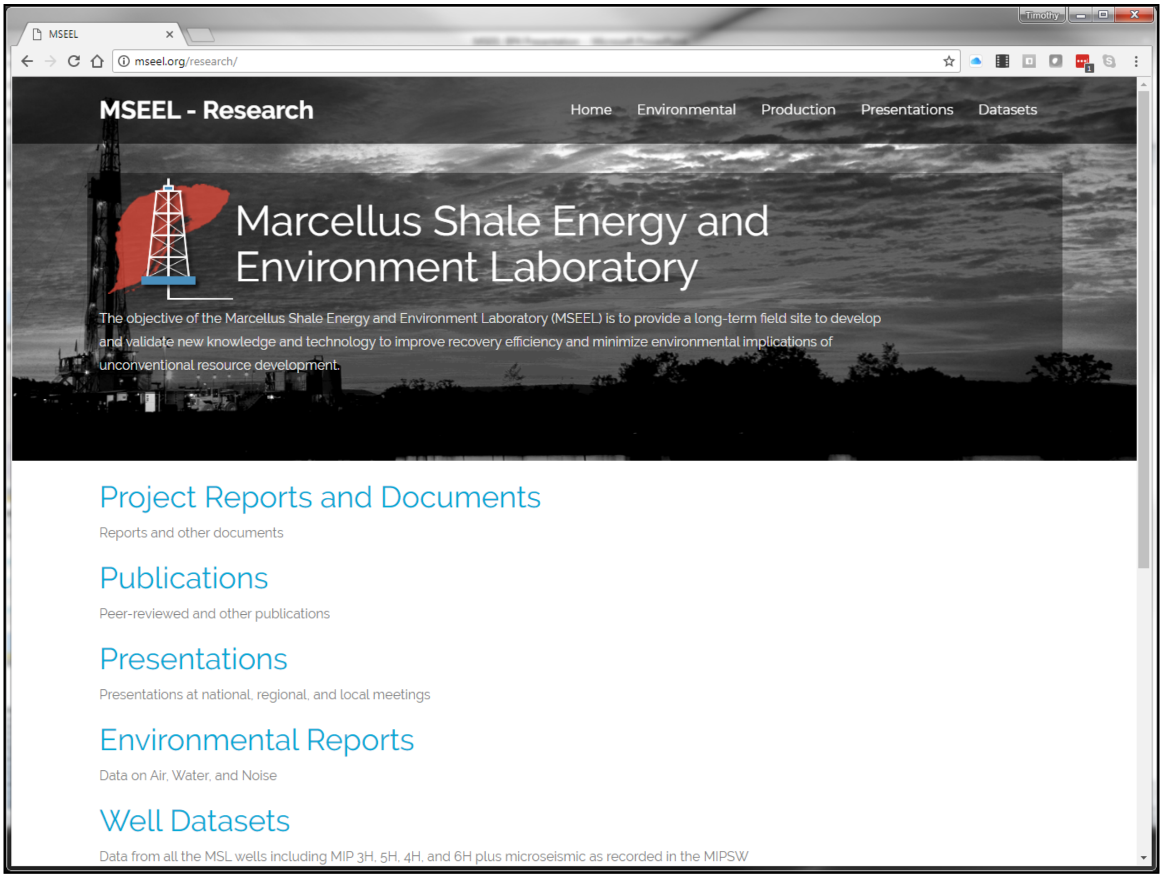
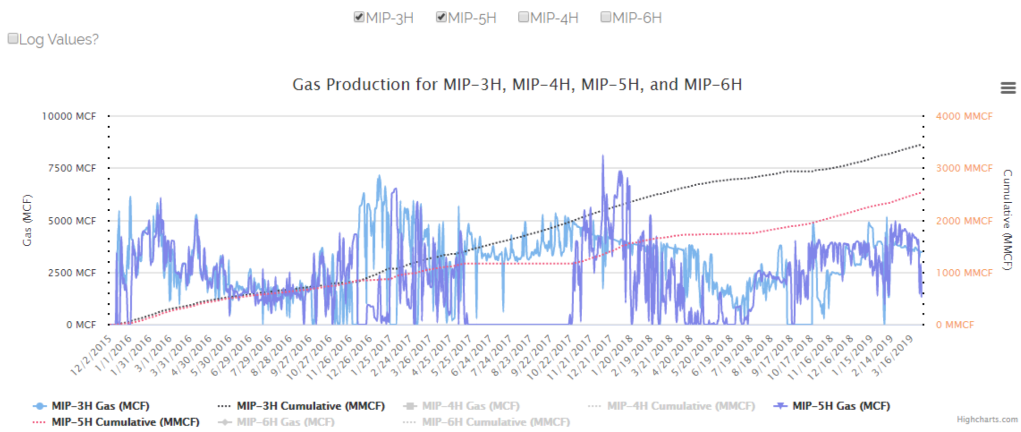


Figure 7.2: All data generated by the MSEEL project is available for download at http://mseel.org/.



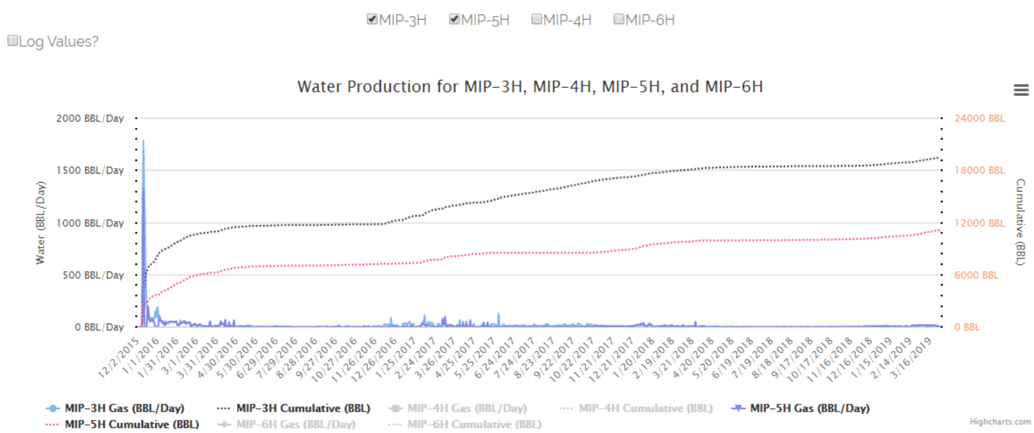


Figure 7.3: Gas and water production have been updated through the end of the quarter and are available at **http://mseel.org/**.

Results & Discussion

Data and publications are now available at http://mseel.org/.

Products

Web site enhanced and updated.

Plan for Next Quarter

Working to add data from the new Boggess Pad

Topic 8 – Economic and Societal

<u>This task is complete and will not be updated in future reports.</u>

Cost Status

Year 1

Start: 10/01/2014 End:
09/30/2019

Baseline Reporting Quarter

	Q1 (12/31/14)	Q2 (3/30/15)	Q3 (6/30/15)	Q4 (9/30/15)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share	$549,000		$3,549,000	
Non-Federal Share	$0.00		$0.00	
Total Planned (Federal and Non-Federal)	$549,000		$3,549,000	
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$0.00	$14,760.39	$237,451.36	$300,925.66
Non-Federal Share	$0.00	$0.00	$0.00	$0.00
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$0.00	$14,760.39	$237,451.36	$300,925.66
Cumulative Incurred Costs	$0.00	$14,760.39	$252,211.75	$553,137.41
Uncosted				
Federal Share	$549,000	$534,239.61	$3,296,788.25	$2,995,862.59
Non-Federal Share	$0.00	$0.00	$2,814,930.00	$2,814,930.00
Total Uncosted - Quarterly (Federal and Non-Federal)	$549,000	$534,239.61	$6,111,718.25	$5,810,792.59

Start: 10/01/2014 End:
09/30/2019

Baseline Reporting Quarter

	Q5 (12/31/15)	Q6 (3/30/16)	Q7 (6/30/16)	Q8 (9/30/16)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share	$6,247,367		$7,297,926	
Non-Federal Share	2,814,930		$4,342,480	
Total Planned (Federal and Non-Federal)	$9,062,297	$9,062,297.00	$11,640,406	
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$577,065.91	$4,480,939.42	$845,967.23	$556,511.68
Non-Federal Share	$0.00	$2,189,863.30	$2,154,120.23	$0.00
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$577,065.91	$6,670,802.72	$3,000,087.46	$556,551.68
Cumulative Incurred Costs	$1,130,203.32	$7,801,006.04	$10,637,732.23	$11,194,243.91
Uncosted				
Federal Share	$5,117,163.68	$636,224.26	$1,004,177.30	$447,665.62
Non-Federal Share	$2,814,930.00	$625,066.70	($1,503.53)	($1,503.53)
Total Uncosted - Quarterly (Federal and Non-Federal)	$2,418,796.68	$1,261,290.96	$1,002,673.77	$446,162.09

Start: 10/01/2014 End: 09/30/2019

Baseline Reporting Quarter

	Q9 (12/31/16)	Q10 (3/30/17)	Q11 (6/30/17)	Q12 (9/30/17)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share				$9,128,731
Non-Federal Share				$4,520,922
Total Planned (Federal and Non-Federal)				$13,649,653
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$113,223.71	$196,266.36	$120,801.19	$1,147,988.73
Non-Federal Share	$0.00	$0.00	$0.00	$0.00
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$113,223.71	$196,266.36	$120,801.19	$1,147,988.73
Cumulative Incurred Costs	$11,307,467.62	$11,503,733.98	$11,624535.17	$12,772,523.90
Uncosted				
Federal Share	$334,441.91	$138,175.55	$17,374.36	$700,190.63
Non-Federal Share	($1,503.53)	($1,503.53)	($1,503.53)	$176,938.47
Total Uncosted - Quarterly (Federal and Non-Federal)	$332,938.38	$136,672.02	$15,870.83	$877,129.10

Start: 10/01/2014 End: 09/30/2019

Baseline Reporting Quarter

	Q13 (12/31/17)	Q14 (3/30/18)	Q15 (6/30/18)	Q15 (9/30/18)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share				$11,794,054
Non-Federal Share				$5,222,242
Total Planned (Federal and Non-Federal)				$17,016,296.00
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$112,075.89	$349,908.08	$182,207.84	$120,550.20
Non-Federal Share	$0.00	$31,500.23	$10,262.40	$4,338.00
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$112,075.89	$381,408.31	$192,470.24	$124,888.20
Cumulative Incurred Costs	$12,884,599.79	$13,266,008.10	$13,458,478.34	$13,583,366.54
Uncosted				
Federal Share	$588,114.74	$238,206.66	$55,998.82	$2,600,771.62
Non-Federal Share	$176,938.47	$145,438.24	$135,175.84	$832,157.84
Total Uncosted - Quarterly (Federal and Non-Federal)	$765,053.21	$383,644.90	$191,174.66	$3,432,929.46

Start: 10/01/2014 End: 03/31/2019

Baseline Reporting Quarter	Q17 (12/31/18)	Q18 (3/30/19)	Q19 (6/30/19)	Q20 (9/30/19)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share				
Non-Federal Share				
Total Planned (Federal and Non-Federal)				
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$80,800.03	$133,776.98		
Non-Federal Share	$4,805.05	$130,449.21		
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$85,605.08	$264,226.19		
Cumulative Incurred Costs	$13,668,971.62	$13,933,197.81		
Uncosted				
Federal Share	$2,519,971.59	$2,386,194.61		
Non-Federal Share	$827,352.79	$696,903.58		
Total Uncosted - Quarterly (Federal and Non-Federal)	$3,347,324.38	$3,083,098.19		

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