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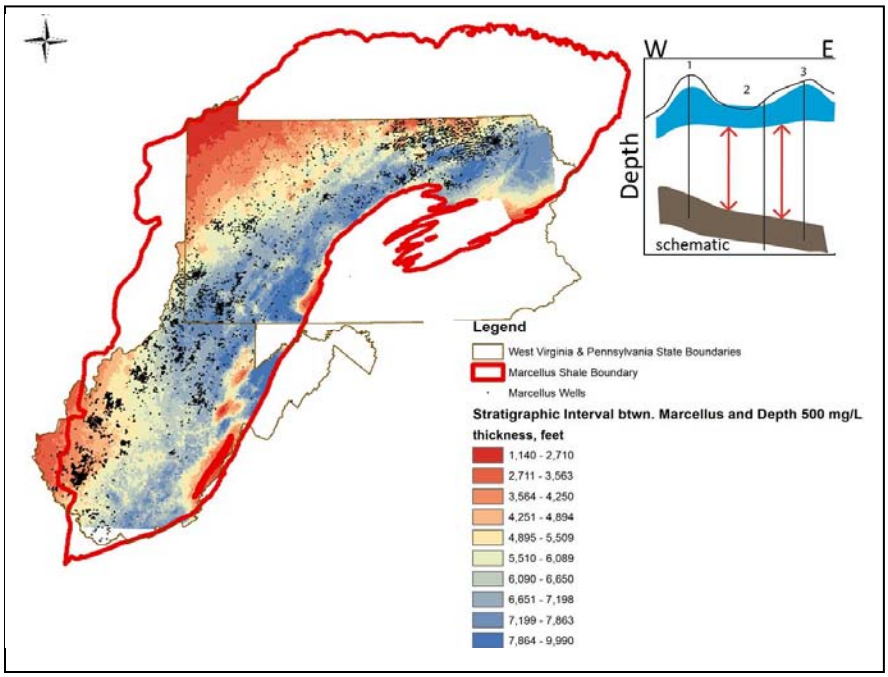

Annual Report: Unconventional Resources (UCR)

30 September 2013

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Cover Illustration: Isopach map showing the distance between the base of groundwater and top of the Marcellus Shale in West Virginia and Pennsylvania. Inset diagram is a schematic cross section from west to east across the region illustrating the general change in the distance between these two intervals.

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Annual Report: Unconventional Resources Portfolio

Office of Research and Development, National Energy Technology Laboratory

NETL-TRS-UCR-2013
30 September 2013

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Acronyms, Abbreviations, and Symbols

Acronym	Descriptive Name
BTGS	Bureau of Topographic and Geologic Survey
CCD	Completion Combustion Devices
CEC	Cation Exchange Capacity
CH_4	Methane
DCNR	Department of Conservation and Natural Resources
DOE	Department of Energy
EDF	Environmental Defense Fund
EDX	Energy Data Exchange
EPA	Environmental Protection Agency
EPAct	Energy Policy Act of 2005
eSEM	Environmental Scanning Electron Microscopy
FE	Fossil Energy
FISH	Fluorescent In-Situ Hybridization
ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared
GES	Geological and Environmental Science
GHG	Greenhouse Gas
GIS	Geographic Information System
GPS	Global Positioning System
IAM	Integrated Assessment Model
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LC-QTOF	Liquid Chromatography-Quadrupole Time of Flight
MC-ICP-MS	Multicollector Inductively Coupled Plasma Mass Spectrometry
MDE	Maryland Department of the Environment
NCB	National Center of Biotechnology
NETL	National Energy Technology Laboratory
NORM	Naturally Occurring Radioactive Materials
ORD	Office of Research and Development
PAAS	Post Archean Australian Shale
PA-DEP	Pennsylvania Department of Environmental Protection
PA IRIS	The Pennsylvania IRIS database
PASDA	Pennsylvania Spatial Data Access
Penn State or PSU	The Pennsylvania State University
PFC	Perfluorocarbon
Pitt	University of Pittsburgh

Acronym	Descriptive Name
psi	Pounds per Square Inch
PVT	Pressure-Volume-Temperature
QAPP	Quality Assurance Program Plan
REC	Reduced Emission Control
REE	Rare Earth Elements
RES	Research and Engineering Services
rRNA	Ribosomal Ribonucleic Acid
RSD	Relative Standard Deviation
RUA	Regional University Alliance
SCNGO	Strategic Center for Natural Gas and Oil
SEM	Scanning Electron Microscopy
STP	Standard Teperature and Pressure
TC	Technical Coordinator
TDS	Total Dissolved Solids
TEOM	Tapered Element Oscillating Microbalance
TIMS	Thermal Ionization Mass Spectrometry
TRS	Technical Report Series
TTC	Team Technical Coordinator
UCR	Unconventional Resources
URS	URS Corporation
USDW	Underground Sources of Drinking Water
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
VGM	Variable Grid Method
VOCs	Volatile Organic Compounds
WBS	Work Breakdown Structure
WV-DEP	West Virginia Department of Environmental Protection
WAMS	Wireless Air Monitoring System
WVU	West Virginia University
XRD	X-ray powder diffraction

1.0 Executive Summary

The objective of the UCR research portfolio was to develop research products that address safety and environmental concerns associated with shale gas development in four primary areas: (1) fugitive air emissions; (2) produced waste management; (3) subsurface migration of gas and fluids; and (4) ground motion associated with unconventional resource development. The UCR portfolio consisted of thirteen projects that leveraged a combination of field, experimental, modeling, and data mining and compilation approaches with the goal of building an understanding of how geologic and environmental systems respond to shale gas development.

Fugitive Emissions and Air Quality

Due to the uncertainty associated with greenhouse gas emissions related to unconventional shale gas development, and the importance of realistic emissions values for life cycle assessments to predict the overall greenhouse gas contribution of developing hydraulically-fractured shale resources, research focused on evaluating emissions factors used in life cycle assessments ("Greenhouse Gas Life Cycle Methane Emission Factor Assessment") and collecting air emissions data sets near active shale gas operations ("Fugitive Air Emissions Field Data").

In the project "Greenhouse Gas Life Cycle Methane Emission Factor Assessment," the team focused on reviewing the statistical approach employed by the U.S. Environmental Protection Agency (EPA) to estimate fugitive methane emissions factors for unconventional well completions. The team also developed a Bayesian statistics-based model structure as a basis for developing revised emissions factor estimates as new data become available through NETL field efforts, or field efforts from other organizations. Given a set of assumptions within the Bayesian statistical model, NETL's review of the EPA potential emission factor calculation resulted in a similar value (8,900 Mcf natural gas emitted per completion) as reported by the EPA (9,000 Mcf natural gas emitted per completion). Evaluation of new data released through a study by the Environmental Defense Fund (EDF; Allen et al., 2013) generated similar results (8,580 Mcf natural gas per completion) to both the original EPA value, and the value recalculated by NETL.

In the project "Fugitive Air Emissions Field Data," the research team used two approaches towards collecting information about methane emissions from unconventional shale gas operations: (1) through monitoring with the ambient air quality monitoring trailer, and (2) through an acetylene tracer technique for point source measurements. The air quality trailer, which was developed through prior EPAct Complementary program research efforts, includes a suite of instrumentation that measures concentrations a variety of EPA air quality parameters in addition to instruments specific for gas-phase carbon isotopes. The acetylene tracer technique, developed during this past year, involves locating leaks (or fugitive emissions) to obtain a pollutant emission rate for each leak. Results of monitoring efforts at various sites are currently being processed into a format that will be useful for calculating new emissions factors using the Bayesian statistical technique described above.

Produced Waste Management

An ability to predict and quantify flowback water quality and quantity, and means for treating produced waters and associated water treatment waste products, are important components for managing wastes associated with unconventional shale gas development.

In the project "Predicting Compositions and Volumes of Produced Water," the research team focused on a two-pronged approach to develop a means to characterize the volumes and compositions of byproduct water generated from hydraulic fracturing in the Marcellus Shale. The approach involved using numerical modeling approaches to simulate physical and chemical phenomena that control fracture network

development and recovery of fluid from the fracture network, and use of data mining approaches towards developing more computationally-efficient means of evaluating flowback composition and volume. The team completed development of a dual porosity, dual permeability, three-dimensional, fully implicit model for predicting produced water and gas volumes, and will continue with development of model components for predicting flowback fluid composition into FY14.

In the project "Baseline Environmental Signals," the research team focused on evaluating how to detect production fluid migration from on-site, lined impoundments or tanks. Application of electromagnetic (EM) methods to detect and map leaks from these types of facilities takes advantage of the high conductivity of production fluids to detect leaks into relatively non-conductive soil. Baseline EM surveys were completed at a site in Washington County, Pennsylvania, and monitoring will continue as the site is further developed for shale gas extraction.

In the project "Evaluation of the Geochemical and Microbiological Composition of Shale Gas Produced Water and Solid Wastes," the research team focused on three key areas: (1) evaluating radium in produced waters and water treatment residual solids; (2) understanding produced water microbial ecology; and (3) determining the chemical stability of produced water treatment solids. A new technique was developed for pre-processing and ICP-MS analysis of radium in produced waters, which was applied towards evaluating the solubility of radium in produced waters and its leachability from produced water treatment residuals. Findings to date suggest that barite may be reused for Ra^{2+} adsorption, and that maintaining high barite content in storage tanks may help sequester Ra^{2+} from solution. In addition, aged sludges showed less radium leaching relative to younger sludges, suggesting that it is beneficial to keep solids in the impoundment for extended periods of time to achieve permanent sequestration of radium in solid phases prior to landfill disposal.

Within the same project, investigation of the microbial community structure via multiple techniques (both pyrosequencing and use of clone libraries) showed that photosynthetic bacteria are present in open produced water storage pits, which can change carbon cycling associated with the produced waters in these types of systems. Additionally, microbes with specific metabolic functionalities were identified in produced waters from various wells, and the functionalities identified appear to correspond to the types of treatments the wells were subjected to during the course of hydraulic fracturing.

In the project, "Biogeochemical Factors that Affect Composition of Produced Waters and Utility of Geochemical Tracer Tools," the project team focused in part on sources of the dissolved solids in produced waters from Marcellus and Utica shales, and the potential leachability of Marcellus Shale drill cuttings under different environmental scenarios. Results showed that cation exchange reactions could only account for less than one percent of the calcium and sodium concentrations in the measured experimental fluids, suggesting a source other than ion exchange for elevated total dissolved solids in produced waters. Rainwater extractions of drill cuttings demonstrated that certain elements are enhanced relative to deionized water extractions, and elements for future focus include: Se, Cr, and Cd. Results from an acid-base titration extraction show that trace metal concentration trends differ between water-based and non-water-based drill cuttings, which could affect how these solids are handled during waste management.

This project also focused on characterizing chemical signatures in bulk shale samples and surrounding strata, and evaluated reactions between hydraulic fracturing fluids and shales under elevated pressure and temperature conditions. Experimental results showed that reactions between synthetic fracturing fluids and Marcellus Shale resulted in elevated concentrations of certain elements in the fluid phase, and geochemical reaction modeling of results to date indicates that major mineral reactions in the experiments with fracturing fluid are pH-driven.

In the project "Develop a Suite of Naturally Occurring Geochemical Tracer Tools that Verify the Sources of Fluids in Complex Geologic Systems," $^{87}Sr/^{86}Sr$ was applied as a tracer to identify inputs of bromide into the Allegheny Watershed, in collaboration with the Pittsburgh Water and Sewer Authority. Using multiple

geochemical signals, such as strontium and bromine, can help identify whether surface water bromide inputs are sourced from oil and gas related produced waters.

Subsurface Migration of Gas and Fluids

One concern with hydraulic fracturing of shales for gas recovery is the potential for hydraulic fracturing, and associated oil and gas operations, to create or enhance situations that would cause subsurface migration of gas and fluids. Of special interest is the potential for fluids and gas to leak into underground sources of drinking water.

Wellbores

Wellbores are considered a primary pathway for potential gas or fluid migration from target shale formations, and multiple projects within this portfolio addressed wellbore-related concerns. In the "Subsurface Gas and Fluid Migration Assessment" project, the distribution and density of legacy wells located within the areal extent of shale gas plays was investigated. As a result of this year's research, an amalgamated database was generated based off of the PA IRIS, PA SDA, and PA DEP well databases, and screened for duplicate entries. Reconstruction of historical annual drilling activity in Pennsylvania through literature reviews of drilling records revealed approximately 170,000 wells were not recorded in the PA IRIS, PA SDA, or PA DEP databases (covering the time period of 1859 – 1974). The historical records analysis also provided a source of information on the temporal distribution of well completions that can be used to assign completion years to wells from the database for which no completion year is reported.

In the project "Baseline Environmental Signals," methods for locating undocumented wells were tested in Washington County, Pennsylvania. Airborne magnetic surveys, which helped to locate undocumented wells in prior year EPAct Complementary program research efforts, were conducted during FY12, and ground-truthing and data processing progressed during FY13. The research team found that only four of the thirteen confirmed wells detected during the field magnetic survey were included in the PA IRIS database, and that the location error for the four wells was greater than 50 meters.

In the project "Gas Flow from Shallow Gas Formations," the research team focused on developing a laboratory-based experimental framework for evaluating how shallow gas affects hydration of wellbore cement integrity. The team also investigated compliance reports from the publically-available PA DEP well violations database with a focus on unconventional well drilling sites and cementing and casing/well site construction issues. Results of the analysis to date show that the greatest number of violations occurred in 2010, and that Bradford County had the highest number of violations reported.

Use of Tracers to Track Fluids and Gases

Natural geochemical tracers, and synthetic chemical tracers, can be used to track potential fluid and gas migration from hydraulically-fractured shale formations. In the project "Develop a Suite of Naturally Occurring Geochemical Tracer Tools that Verify the Sources of Fluids in Complex Geologic Systems," the research team evaluated the analytical techniques for monitoring various natural geochemical tracers, and different geologic end members that can be used to interpret field measurements. Isotope systems studied include: $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{238}U/^{235}U$, and $^{234}U/^{238}U$, and $^{7}Li/^{6}Li$, and C and H isotopes in CH_4. The potential to use rare earth elements (REEs) as tracers also was investigated. The laboratory analytical techniques developed for these different systems were applied towards field samples, and results from field monitoring in Greene County, Pennsylvania, are detailed in the project "Baseline Environmental Signals." Results from isotope monitoring at the Greene County site show that, to date and within the detection limits of the isotope systems monitored, fluids have not migrated from the hydraulically-fractured Marcellus Shale into the overlying Upper Devonian gas field (which is an intermediate geologic layer between the Marcellus Shale and underground sources of drinking water). Monitoring will continue at this site to evaluate whether tracers may be observed in the Upper Devonian monitoring wells over longer time periods.

Evaluating Groundwater Receptors across the Appalachian Basin

In order to evaluate the potential for leakage of methane and saline waters into underground sources of drinking water in the Appalachian Basin, a first step involved defining the extent and depth of groundwater aquifers across the Appalachian Basin based on existing data sets. The project "Evaluating the Distribution and Provenance of Water and Gas in Shallow Reservoirs" focused both on developing the data management framework for working with data sets from various sources through development of the Energy Data Exchange, and on developing groundwater layers to represent the depth and salinity of groundwater across the Appalachian Basin.

In the project "Hydrologic Factors Affecting Shallow Gas Migration," the project team evaluated the potential for compressed air to enter aquifers from the air-percussion drilling technique, which could cause groundwater flow surges that mobilize stray gas in shallow aquifers. The team also performed laboratory-scale flow and transport experiments to investigate the entrainment and transport of contaminants in fractured aquifers.

Fracture Propagation and Ground Motion

Hydraulic fracturing of shale formations results in changes to the geomechanical and seismic properties of the system; however, the magnitude of these changes is still being evaluated for various shale formations. The geomechanical and seismic response of the Marcellus Shale and surrounding geologic strata during hydraulic fracturing was investigated through a combination of field, laboratory, and modeling approaches.

In the project "Baseline Environmental Signals," downhole microseismic events were monitored during hydraulic fracturing of the Marcellus Shale in Greene County and Clearfield County, Pennsylvania. Although both sites are in Pennsylvania, each site displays unique features based on local geology. In the case of Greene County, certain microseismic events were detected above the Marcellus, and above the Tully Limestone upper barrier. In contrast, microseismic events monitored at the Clearfield county site were identified moving below the Marcellus and into the Oriskany formation.

A modeling scenario similar to geologic conditions encountered at the Greene County site was investigated through the project, "Geophysical and Geomechanical Factors that Affect Subsurface Fluid and Gas Migration." Results from the modeling study indicate that the Tully Limestone is a good barrier to dampen energy propagated during hydraulic fracturing of the Marcellus, however, only if the Tully is intact. Vertical fracture growth above the Tully was simulated under conditions where the Tully is fractured and results were similar to the observed field microseismic events.

Additional field data collected as part of the "Baseline Environmental Signals" project indicated that surface seismometers were able to detect ground motion events associated with hydraulic fracturing at two different sites in western Pennsylvania; however, the magnitude of the events was three orders of magnitude below what could be sensed by most humans, and five orders of magnitude below what is needed to damage structures on the surface.

Induced seismic events also have been associated with wastewater injection events. The project "Application of Field Measurements and Observations towards Predicting Subsurface Phenomena" was focused on evaluating the potential for fracture propagation in subsurface formations due to long-term fluid injection into the Marcellus Shale. Based on the simulation results, the lateral extent of formation damage due to fluid injection in the reservoir was limited to the region around the injection well.

2.0 Technology Highlights and Key Results

Greenhouse Gas Life Cycle Methane Emission Factor Assessment

The objective of this effort is to review the statistical approach employed by the U.S. EPA to estimate the fugitive methane emissions factor resulting from hydraulic fracturing emissions in unconventional formations, and to create a model structure to facilitate efforts of the NETL to develop a revised emissions factor estimate as additional primary data become available from field measurements.

There is significant uncertainty associated with assessed greenhouse gas (GHG) emissions for unconventional natural gas resulting from uncertainties in emissions factors for key unit processes associated with drilling, completion (hydraulic fracturing activities), production, and natural gas transport. Uncertainties in emissions from these unit operations propagate through life cycle analysis and contribute to uncertainty in overall estimates of life cycle GHG performance of unconventional natural gas; large uncertainties can complicate the discussion of the overall environmental performance of those resources. As more and better field data on fugitive emissions becomes available from completions, workovers, and other unit operations associated with unconventional gas production it will be valuable to have a strong understanding of statistical approaches to employ those new data to reduce uncertainty and improve confidence in fugitive methane emissions factors, and assessments of overall life cycle GHG performance.

In the process of developing new horizontal wells with multi-stage hydraulic fractures, some natural gas can escape to the atmosphere. Our team reviewed the data and statistical analysis approach used by the U.S. EPA (U.S. EPA, 2012b) to characterize potential emissions of natural gas per unconventional well completion in a three step approach:

1. Review of published data and Bayesian interval analysis.
2. Application of EPA's prescribed potential emission factor and distributions developed to assess GHG emissions per completion, given different completion emissions control technologies - deterministic or stochastic (Monte Carlo) modeling.
3. Provide example estimates of national average GHG emissions per new completion based on national well count and completion practices under different regulatory settings.

Some minor discrepancies were noted in the interpretation of data used in the EPA analysis, but those discrepancies did not impact the final results. The assumption that the prior dataset were total natural gas emissions, when they were originally referenced as methane emissions, more significantly affected the calculations. Analysis shows that this difference could result in a mean potential natural gas emission factor that is almost 20 percent higher than the EPA's assessed value. However, assuming a non-informative prior in the NETL calculation, the posterior distribution is only based on new data collected, resulting in a mean of 8,900 thousand cubic feet (Mcf) natural gas emitted per completion. This value is comparable to the EPA prescribed potential emission factor (9,000 Mcf natural gas emitted per completion).

Following review of the EPA's Bayesian analysis, NETL researchers performed a second analysis to understand the impact of new data on unconventional well completion recently reported in the peer-reviewed literature (Allen et al., 2013). Of the 27 new well completion emissions collected, 24 were considered to be of sufficient quality in assessing potential emissions. This represents a relatively large set of new, high-quality data in comparison to previous analysis by the EPA, which used only four new data points to develop their revised emission factor. The 24 new samples from the Allen et al., (2013) study had a mean of 6,500 Mcf of methane potentially emitted per unconventional well completion and a standard deviation of 2,520 Mcf. Applying the Bayesian interval analysis approach, a revised posterior

normal distribution for unconventional well completion potential emissions was found to have a mean of 7,142 Mcf and a standard deviation of 2,157 Mcf of methane per unconventional well completion.

Assuming the natural gas volumetric methane composition of 0.8324 (EPA, 2012b), potential methane emission factor corresponds to a whole natural gas emission factor with a mean of 8,580 Mcf natural gas per completion, a standard deviation of 2,591 Mscf natural gas per completion, and a corresponding lower and upper 95 percent confidence bounds of 3,501 and 13,659 Mcf of natural gas per unconventional completion. Therefore, even considering these new data from the Allen et al., (2013) study, the potential emission factor of 9,000 Mcf natural gas per completion used by the EPA in emissions inventories of unconventional natural gas extraction is still justified.

The well completion potential emission factor represents the amount of natural gas that comes out of the ground during an unconventional natural gas well completion, not the amount of natural gas emitted to the atmosphere. Those potential emissions can be significantly reduced through engineered controls including application of reduced emission control (REC) approaches (green completion) and completion combustion devices (CCD, or flaring). New rules have been promulgated under the New Source Performance Standard that require application of these control technologies (U.S. EPA, 2012a). An uncontrolled well with potential natural gas emissions of 9,000 Mscf/completion would vent approximately 3,500 tonnes CO_2 equivalent per unconventional completion; a more representative scenario with flaring of those potential emissions would reduce CO_2 equivalent emissions by more than 80 percent, applying RECs without flaring of uncaptured gas would reduce CO_2 equivalent emissions by 90 percent, and applying with CCD will destroy nearly 95 percent of potential CO_2 equivalent emissions. On average, real emissions of natural gas from unconventional natural gas well completions are, therefore, much lower than the potential emissions; as the NSPS Final Rule moves to full implementation the average real emission per unconventional natural gas well completion likely will be further reduced.

Data and methodology review for potential emission factor, consideration of real emissions after application of engineering controls, and discussion of implications of NSPS subpart OOOO implementation on GHG emissions are detailed in a NETL Technical Report Series document undergoing review at the time of this report.

Predicting Compositions and Volumes of Produced Water

The objective of this effort is to develop improved characterization of the factors that impact the volumes and compositions of byproduct water generated from hydraulic fracturing in unconventional formations. These improved characterizations will provide information on the development of regional- or industry-scale strategies for management of aqueous byproduct streams. Research efforts in FY13 were focused on the following:

- Defining appropriate flowback water modeling approach(es).
- Identifying, exploring, and incorporating key datasets and model elements.
- Developing models to begin to predict volumes and salinity of water produced through flowback period.

Flowback Water Modeling Approach

A model integrating flowback system attributes has been developed to predict the volume and compositions of water produced from hydraulic fracturing of gas shales. System variables affecting the volume of water that returns to the surface after hydraulic fracturing include: geologic properties formation, well/lateral configuration, and stimulation properties. The model also considers water compositional changes as they vary through the flowback period, generally becoming more concentrated with total dissolved solids (TDS) over time. The composition of flowback water varies as a function of other factors in the model, including: composition and volume of injected water, connate water composition and initial saturation, composition of shale matrix, and stimulated reservoir volume/fracture surface area. The resulting model will have the capability to characterize uncertainties associated with the performance of this complex system. To address this problem, researchers have adopted a two-pronged approach to: (1) use numerical modeling approaches to simulate important physical and chemical phenomena of the system by describing fracture network development and cleanup of fracture fluid from that fracture network (a "bottom-up" approach) and (2) use reduced-physics and/or data mining approaches to develop more computationally-efficient characterizations of flowback performance in support of rapid, screening-level analysis.

Identify and Incorporate Key Datasets and Model Element Characterizations

Researchers worked to build a database of information from a representative set of horizontal, hydraulically-fractured wells, and interpreted those data to support model development. Statistical approaches were used to explore relationships among parameters. Prior to statistical analysis, some engineering analyses were performed to determine mean, standard deviation, and maximum and minimum values for each parameter in the database for horizontal wells.

To better understand the distribution of key engineering parameters associated with well completion, histograms of total fracture fluid, total proppant, vertical depth, lateral length, number of stages, treatment rate, initial production (gas and oil), and one-year cumulative production (gas, oil, and water) were developed. Results based on the 16 distributions considered include:

- Fracture fluid volume ranges from 3 to 7.5 million gallons, with a mean of 4.99 million gallons.
- Proppant mass applied ranges from 3 to 6.5 million pound mass (lbm), with a mean of 4.46 million lbm. The vertical depth ranges from 6,500 to 7,500 feet, with a mean of 7,081 feet.
- Lateral length ranges from 3,000 to 6,500 feet, with a mean 4,690 feet.
- Number of stages ranges from 8 to 16, with a mean of 11.58, and the treatment rate ranges from 77.5 to 100 barrels per minute (bpm), with a mean of 87.38 bpm.

- Initial volumetric gas production rate ranges from 1,000 to 4,000 million cubic feet per day (mcf/d), with a mean of 2,735 mcf/d, and the initial volumetric oil production rate ranges from 0 to 20 barrels per day (bbl/d), with a mean of 6.24 bbl/d.
- One year cumulative gas production ranges from 40 to 1,000 mmcf, with a mean of 172.58 mmcf.
- One year cumulative water production ranges from 0 to 15 million bbl, with a mean of 8,972 million bbl.
- One year cumulative oil production ranges from 0 to 3,000 bbl, with a mean of 1,053 bbl.

Preliminary analysis of these data showed that there is poor correlation between cumulative gas production and total volume of hydraulic fracturing fluid applied. Similarly, weak or no correlation between one-year cumulative water production and total fracture fluid volume was observed. Advancing beyond this preliminary assessment, information on the geologic setting in the Marcellus was used to classify the wells into different groups, taking into account formation thickness, depth to formation, vitrinite reflectance (Ro – a proxy for shale thermal maturity), and pressure maps of Marcellus in West Virginia. Figure 1 below shows that three primary groups were identified through that analysis, with wells corresponding to each group falling into distinct spatial subdomain. Statistics and engineering analysis were conducted to identify different correlations within each category.

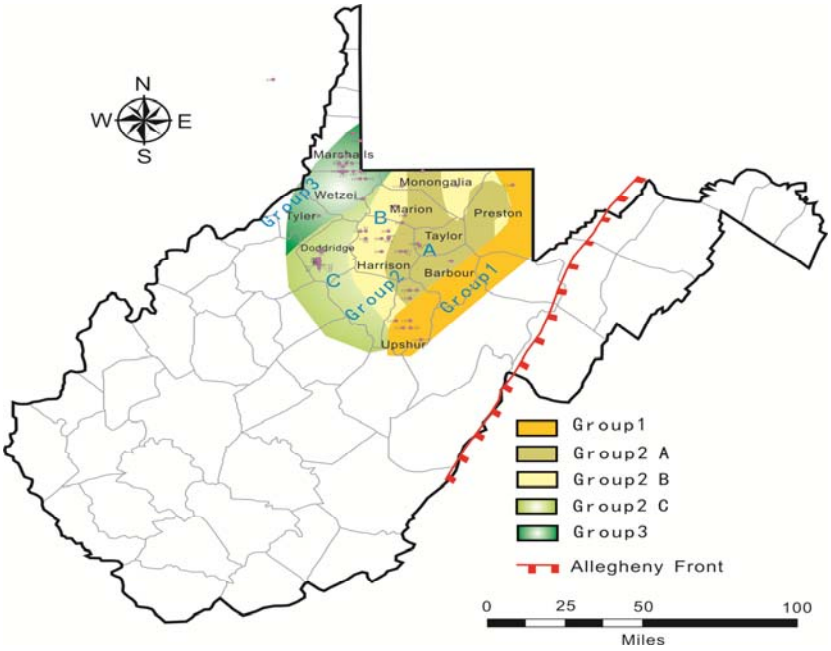


Figure 1: Groups of Marcellus in West Virginia (NETL, 2010).

In general, lateral length and number of fractured stages were found to have much stronger correlation factors than other parameters. It was found that, for Group 1 and Group 3, gas production increases as lateral length or number of stage increases. Water production decreases as the lateral length or number of fractured stages decreases. However, for Group 2, both gas and water production increase as the lateral length or number of fractured stages increase. Reasons for these differences are the focus of continued investigation. One area of further consideration will be the wettability characteristics of formation rock, for example, in Group 1 and Group 3 sub-regions, the pore surface may be water wet, such that, as the lateral length or number of stages increase, water may be more absorbed on the pore surface, so the water production might decrease in relative terms.

Develop Model of Volumes and Salinity of Flowback Water

Numerical model development efforts focused on model validation and debugging processes. The validation of the hydraulic fracture propagation model was performed by matching fracture treatment pressure. A dual porosity, dual permeability, two-phase, three-dimensional, fully implicit model for predicting the volume of produced water and gas from highly fractured reservoirs was developed.

Hydraulic Fracture Propagation Model

The fracture propagation model was validated by matching data collected from field hydraulic fracturing activity (at standard temperature and pressure) with stimulated hydraulic fracturing fluid pressure (P_{frac}). Good correlation was obtained. In addition to Standard Temperature and Pressure (STP), the numerical simulation also requires information on formation rock geomechanical properties and stress field characteristics. Critical values such as principle stresses and fracture toughness are often not available for every well; in this case, this matching technique could be applied to estimate these parameters.

While validating this fracture propagation model, the two-phase propagation model was validated. The proppant transportation module was also developed and validated. As shown in Figure 2, the simulated result and calculated fracturing pressure showed quite a meaningful match.

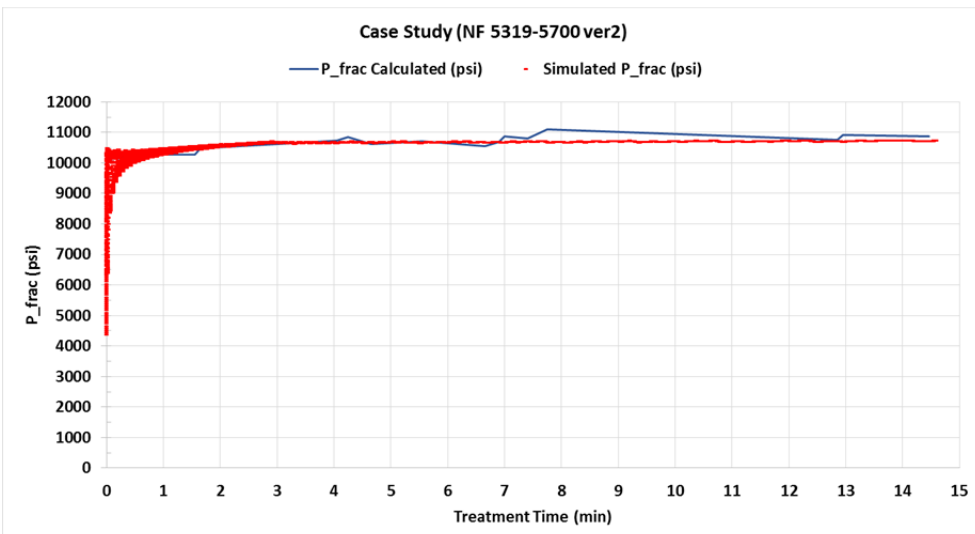


Figure 2: Validation result.

Flowback Water Characterization/Cleanup Model

The flow chart used to develop the cleanup model is shown in Figure 3. “Cleanup” refers to the recovery of injected fluids from the fractured reservoir. The scenarios where flow rates are specified are working well; the model predicts values for the sandface pressure correctly using the fully implicit approach. Work continues for the reciprocal scenario, when pressure is specified and flow is calculated.

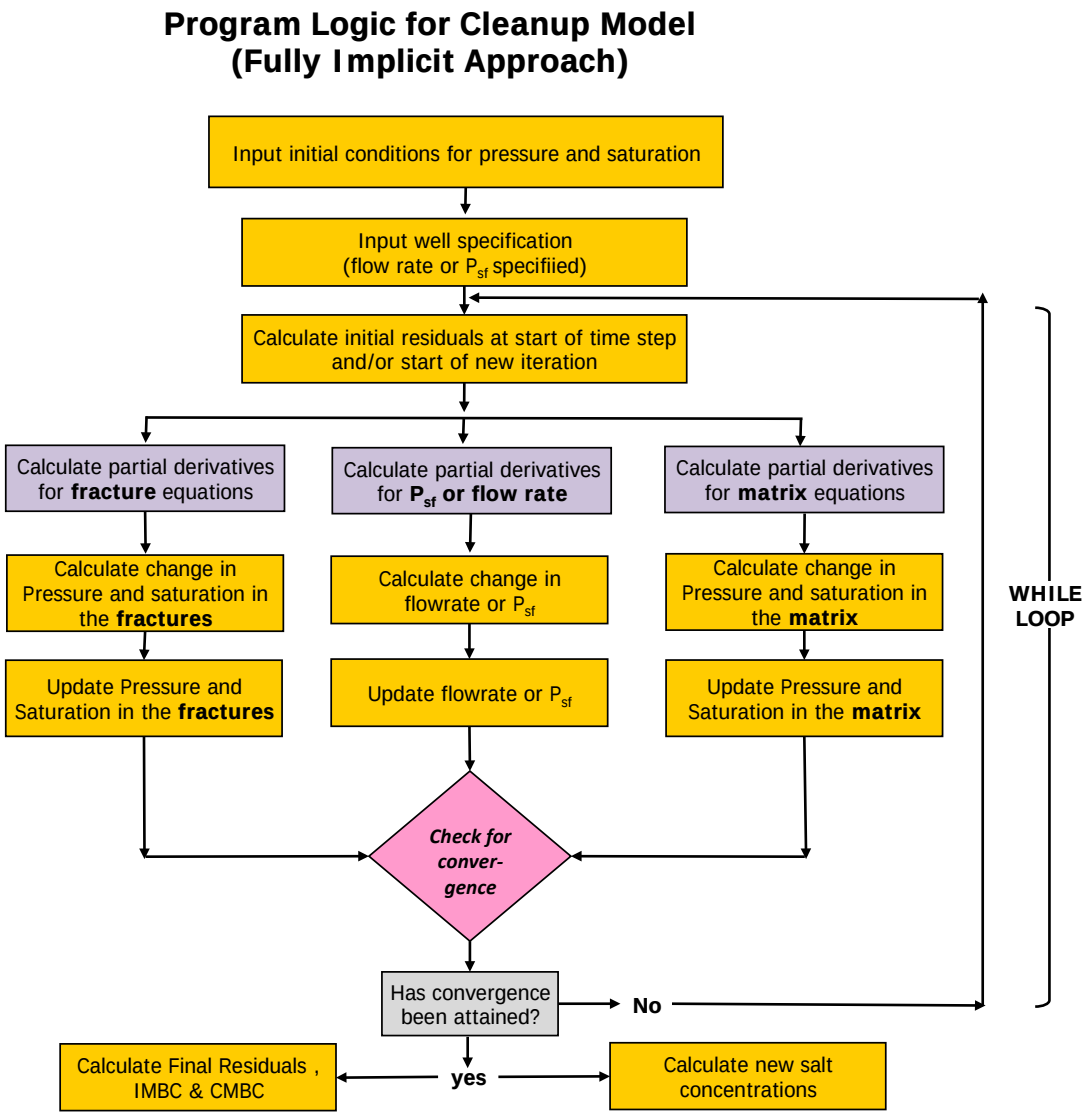


Figure 3: Programming logic for cleanup model.

Development of a dual porosity, dual permeability, two-phase, three-dimensional, fully implicit model for predicting the volume of produced water and gas from highly fractured reservoirs is complete, and continued effort is focused on application of that model to simulate cleanup of hydraulic fracturing fluids from the formation, and incorporation of fluid mixing and salt dissolution from reservoir rock matrix. Figure 4 shows the current status.

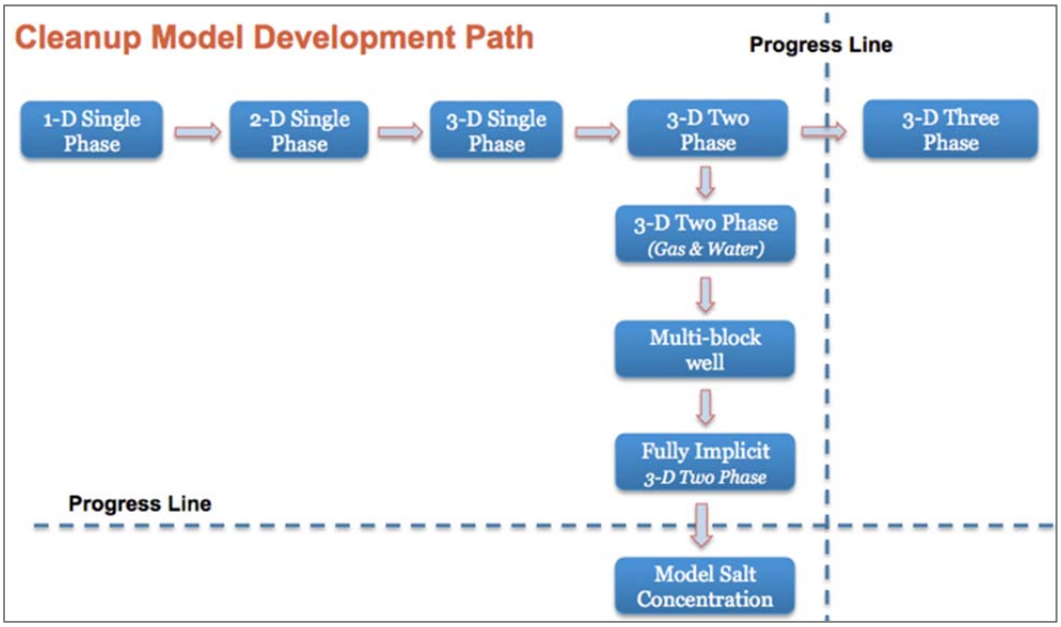


Figure 4: Cleanup model status.

Reduced Complexity or Neural Network Modeling

The computationally-expensive nature of numerical reservoir models means that they cannot be easily used as a tool to inform high-level decision making about resource management and related policy. In an effort to make insights from this research effort more accessible for stakeholders, an effort was initiated to consider how reduced complexity models and/or data driven (e.g., neural network) models can be used to develop a reliable tool for screening level analysis of formation performance with respect to water recovery and composition. Pending results of the quarter one review, these efforts will continue in FY14 and any predictive tool generated through this effort will be validated with numerical simulations and, to the extent practicable, field data.

Subsurface Gas and Fluid Migration Assessment

The objective of this effort is to improve characterizations of density and distribution of legacy wells that are located within the areal extent of shale gas plays for application in integrated assessment of risks associated with subsurface fluid and gas migration induced by resource development.

Legacy wells can serve as conduits through which fluids (stray natural gas, fracturing fluid) associated with unconventional hydrocarbon-bearing formations (shales, mudstones, tight sandstones) could migrate to overlying receptors and cause unwanted impacts (USDW impairment, atmospheric GHG emissions, etc.). It is, therefore, important to understand where these legacy wells are in relation to new unconventional wells that are stimulated through hydraulic fracturing, and the attributes of those legacy wells. This research is focused on mining, processing, and interpreting data related to legacy wells that are geospatially co-located with unconventional fossil resource, and synthesizing these data to create a model structure to characterize salient attributes of the population of undocumented wells.

Developing Unified Database of Documented Oil and Gas Wells

The project objective was to characterize documented wells and their attributes. Several published datasets contain location and attribute information for documented wells. However, gaps in data coverage and inconsistencies in quality between those datasets complicate compilation of the data. Data were collected, processed, and interpreted to produce a more comprehensive statewide inventory of documented wells for Pennsylvania. Steps taken in developing a unified database of documented oil and gas wells in Pennsylvania include: (1) identification of relevant accessible datasets, (2) processing and interpretation of original data sources, (3) proximity analysis to confirm well uniqueness, (4) error checking of well attributes, and (5) generation of the unified well database. Well attribute data from three primary data sources were used in this effort: (1) The Pennsylvania IRIS database (PA IRIS) (Pennsylvania Department of Conservation and Environmental Resources 2013), (2) The Pennsylvania Department of Environmental Protection Bureau of Mines data accessed from Pennsylvania Spatial Data Access (PASDA) (PASDA 2013), and (3) Pennsylvania Department of Environmental Protection (PA-DEP) Abandoned and Orphaned Well program data (Pennsylvania Department of Environmental Protection 2012).

The PA IRIS database is a paid subscription service maintained by the Pennsylvania Department of Conservation and Natural Resources (DCNR), descended from records maintained by the Bureau of Topographic and Geologic Survey (BTGS). Oil and gas drillers, land title companies and other partners in the private sector continue to contribute data to the PA IRIS database. The PASDA database provides point locations and attributes of oil and gas wells originally from PA-DEP Bureau of Mines field data, BTGS, and well completion maps. The PA-DEP abandoned and orphan well dataset is PA-DEP's official record of abandoned and orphan wells in the State. The wells in this dataset are predominantly legacy wells which PA-DEP characterizes as either "abandoned" or "orphaned." An orphan well has no identifiable owner or operator, and the PA-DEP is responsible for plugging orphan wells (2011 revisions to PA Oil and Gas Act); abandoned wells, in contrast, have private parties responsible for plugging.

As a result of processing and interpretation, 194,188 unique wells and available attributes were compiled into the unified well database. Of those wells, 99,371 are recorded in more than one of the relevant databases.

Based on proximity analysis, 290 PA IRIS, and 226 PASDA wells were identified as being redundant for an overall error rate of ~0.1 percent in each of these databases. No PA-DEP wells redundant with wells in other databases were identified. At the completion of the duplicate removal process, the PA IRIS database contained 54,632 unique wells, PASDA contained 39,842 unique wells, and PA-DEP contained 343 unique wells (Table 1). At the completion of attribute checking, 18 of the 143,509 originally reported PASDA wells were incorrectly identified as undrilled wells (a 0.012 percent error rate), and none of the

PA IRIS wells were incorrectly identified as undrilled. Comparison of abandonment state (plug status) attributes reported in PA IRIS and PASDA databases shows that 1,616 wells were identified as plugged in the PASDA database but were not identified as plugged in the PA IRIS database (one percent error), and that all wells identified as plugged in the PA IRIS database were also identified as plugged in PASDA.

Table 1: Number of records contained in each original database, and number of records contained in each database at each step in the record redundancy removal process

Database	PA IRIS	PASDA	PA-DEP
Total number of records	153,793	143,509	8,267
Total non-duplicate records	153,793	138,931	8,267
Total unique records by API	54,922	40,069	343
Total unique records by proximity analysis	54,632	39,842	343

The amalgamated database was explored to identify important spatial and temporal trends. Figures below provide illustration of some of those trends. Figure 5, Figure 6, and Figure 7 show wells completed per year, scatter plot of completion depth as a function of completion year, and the number of wells per one square kilometer grid cell, respectively. Average well density and depth of documented wells per one square km grid cell are plotted below in Figure 8 and Figure 9.

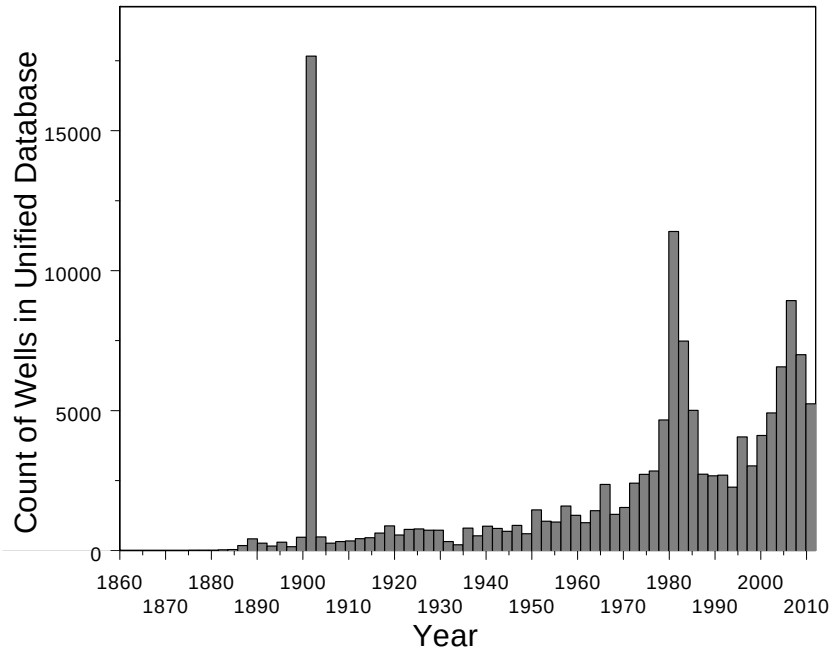


Figure 5: Histogram of wells in the database plotted by completion year. Anomaly at 1901 results from tagging of wells with unknown completion year using that year.

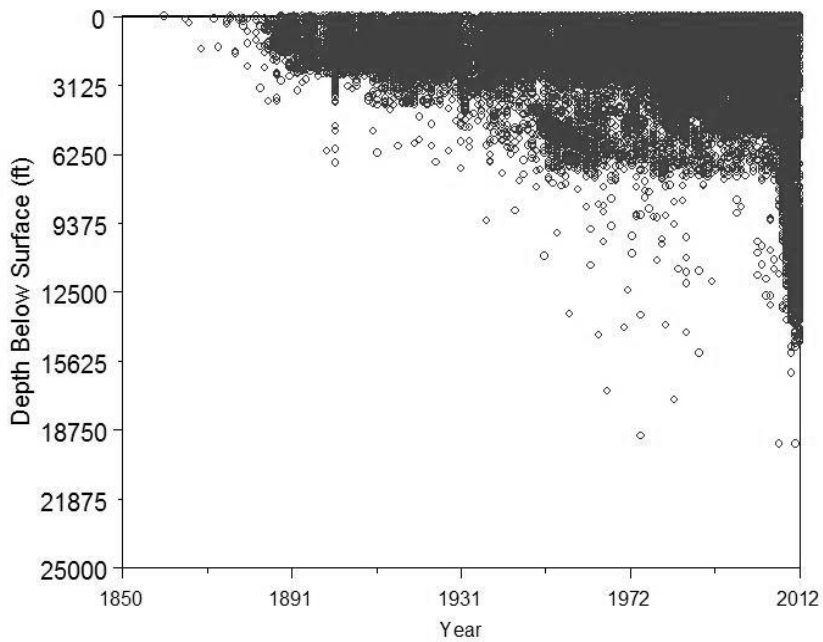


Figure 6: Scatter plot of penetration depth for individual well records reported in the unified well database showing trend of increased well depth over time. Penetration depth is plotted relative to local ground surface.

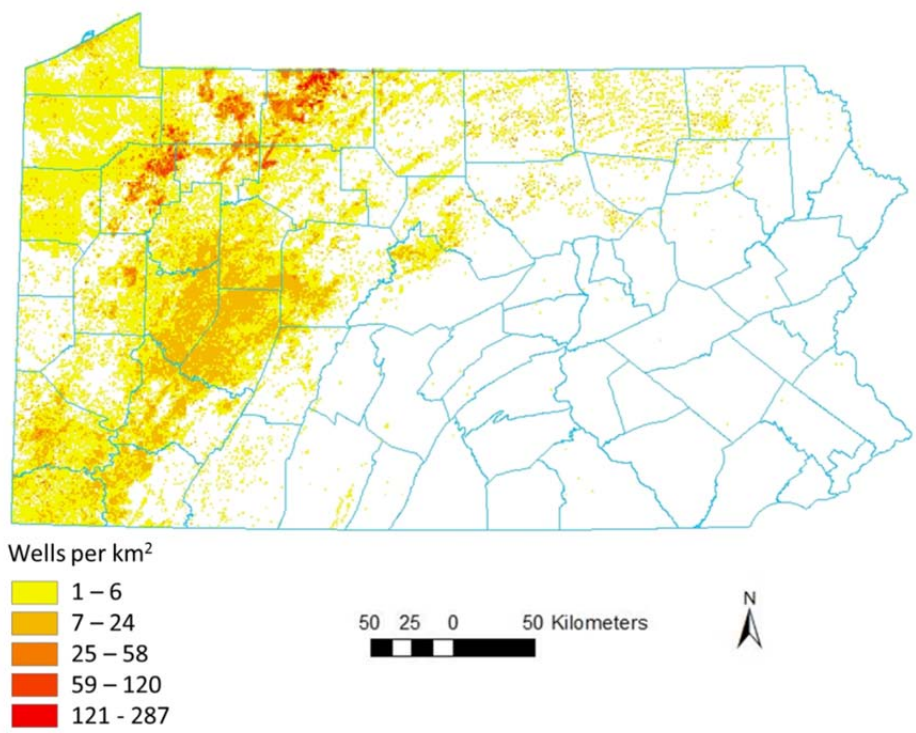


Figure 7: Number of wells per one square kilometer grid cell

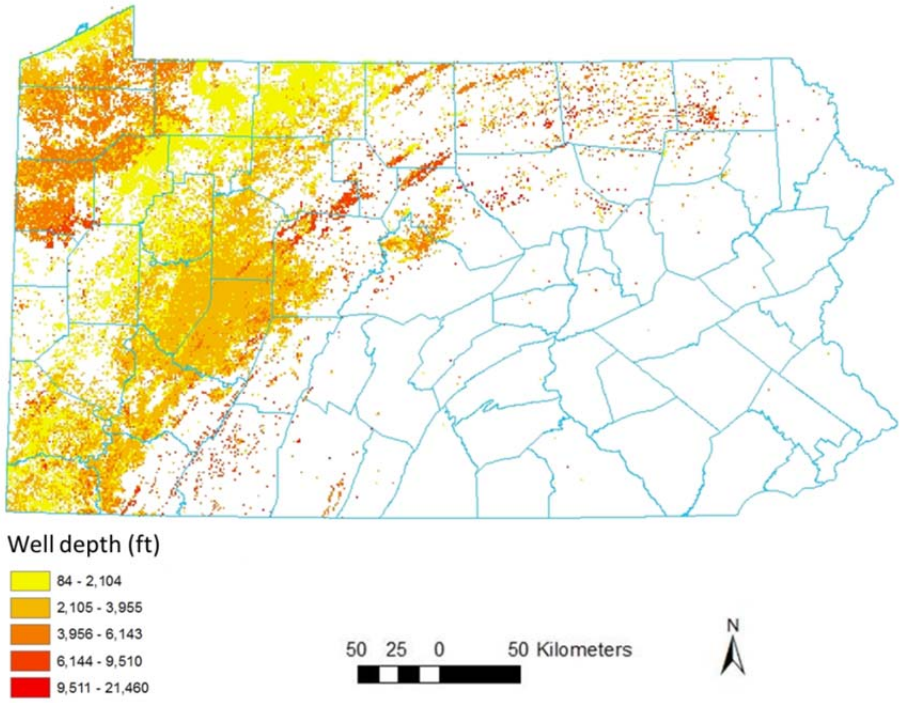


Figure 8: Average depth (feet) of wells per one square kilometer grid cell. Depth is reported relative to local ground surface.

To address these information gaps and arrive at a characterization of all wells, including those not documented in these databases, additional sources of information were sought, and imputation approaches were applied to replace missing data with substituted values.

Reconstructing Historical Annual Drilling Activity in Pennsylvania

An additional source of information to inform characterization of the occurrence and status of historical oil and gas wells in Pennsylvania was used to improve understanding of the historical activity and, in particular, to assign representative completion dates and ages to the population of historical wells. Analog copies of historical records on number of oil and gas well completions were collected, and that information was used as the basis to reconstruct an annual record of well completions in Pennsylvania.

For the years 1859 through 1929, data compiled by Arnold and Kemnitzer (1931) was utilized. One of the challenges in examining Pennsylvania drilling activity is the tendency to lump activity in New York and Pennsylvania together (Crew and Ashburner, 1887; Boyle, 1898; Arnold and Kemnitzer, 1931, Minerals Yearbook series). Fortunately, Arnold and Kemnitzer (1931) partition the accumulated wells completed between 1859 and 1928 to those in New York (20240) and those in Pennsylvania (168190). Therefore to estimate the wells in the Arnold and Kemnitzer (1931) record in Pennsylvania, we used a simple proportion (~0.89) and rounded the resulting product. Following 1929, records were collected from three primary sources: (1) Oil Weekly Annual activity reports, (2) Minerals Yearbooks (Bureau of Mines), and (3) PA Division of Oil and Gas Annual Reports. When there were multiple records indicated for a year, the largest value was used. The plot below shows this synthetic record for the years between 1859 and 1974.

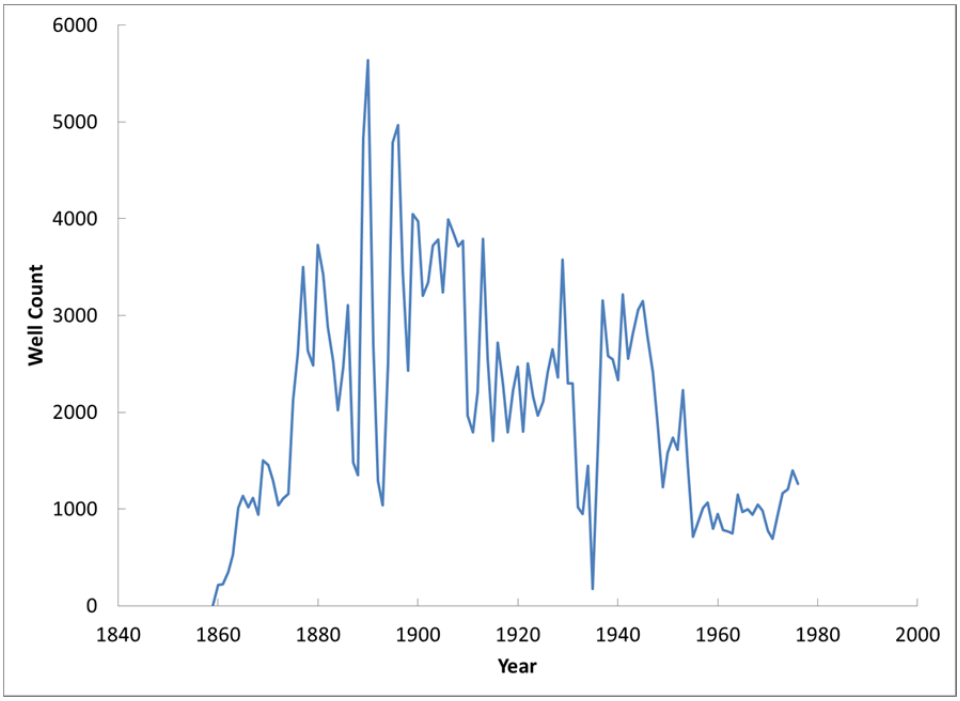


Figure 9: Plot well completions (oil and gas) in Pennsylvania between 1859 and 1974 as reported in historical publications. There are approximately 174,000 more wells in this data set than in the PASDA/PA IRIS/DEP database for this period.

This new information provides a source of information on well counts before well permitting became a requirement (1956), but also a source of information on the temporal distribution of well completions that can be used to assign completion years to wells from the database for which no completion year is reported.

Given the data and information sources available, gap analysis was performed to identify those key aspects of the system for which there is inadequate representation, or for which there is no representation at all. Based on that evaluation, the following key parameters were identified as having insufficient characterization: the total number of oil and gas wells emplaced in Pennsylvania, the completion year for the set of all wells, the operational lifetime of oil and gas wells, the geospatial location of all oil and gas wells, and the state of abandonment of all wells. Figure 10 provides a simplified schematic outlining manipulations being performed to arrive at a revised characterization of legacy wells in the Commonwealth of Pennsylvania.

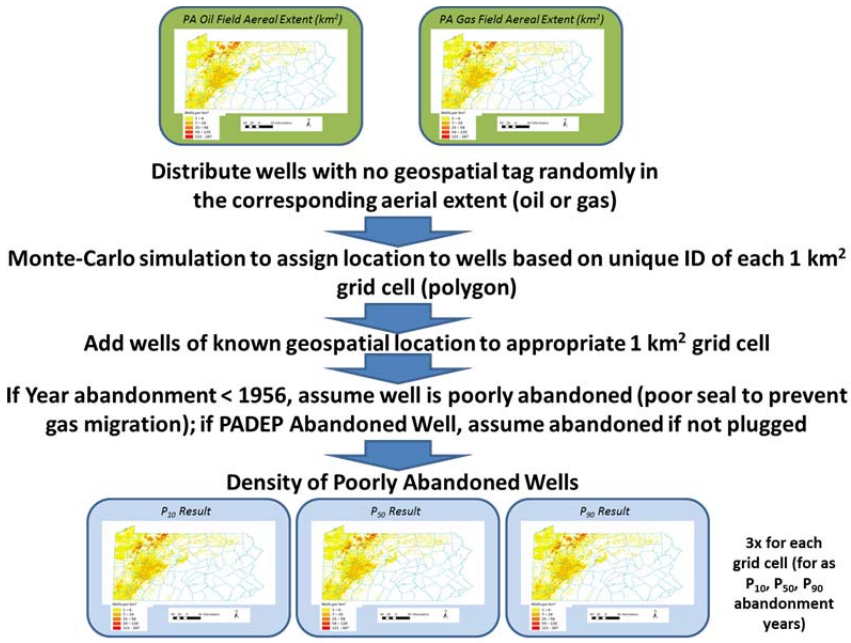


Figure 10: Simplified schematic outlining workflow to describe the spatial distribution and year of abandonment for the set of documented and undocumented wells in the Commonwealth of Pennsylvania.

Application of Field Measurements and Observations Towards Predicting Subsurface Phenomena

The objective of this effort is to develop knowledge of the science base behind geophysical and geomechanical events detected using field-based microseismic tools, as they occur due to wastewater disposal particularly that associated with unconventional gas activities. Geophysical and geomechanical information for sites where field data are being collected will be used to test predictive capabilities, with an ultimate goal of developing better geomechanical understanding of subsurface phenomena and modeling capabilities that decision-makers can use to help determine how to account for induced seismicity risk in site selection, site operation, and monitoring for early detection.

Laboratory experiments were performed to measure the stress states in core samples during a fracture propagation and slip event. Over 300 acoustic emissions events were recorded for samples from the Mt. Airy Granite, which was used as a calibration sample for the measurements. Only a few events were measured in the Marcellus shale sample, due to its low strength. Initial work was started on FLAC3D and RS3 models to simulate those laboratory tests.

To complete tomographic analysis of field microseismic data, a data set of full waveforms (approximately 145 GB of data) from a hydraulic fracturing site was transmitted and analyzed. Arrival times have been requested and discussions were held with the site operator regarding the availability of arrival times. The initial event locations were based on the difference between P- and S-wave arrival times, and no unique arrival times were recorded.

A large scale finite element model of failure events was also developed to predict fracture propagation due to long-term fluid injection. Input parameters such as geometric details and material properties were identified for simulation of long-term fluid injection into a geologic formation. The overburden layers were replaced by surface loading on the caprock layer to simulate geostatic stress conditions. The model geometry consists of an overburden layer, a tight caprock, a reservoir layer, and an underburden. Figure 11 shows the finite element mesh used for the model. A constant Elastic Modulus of 5,802,146 pounds per Square Inch (psi) (4e+07 kilopascals [kPa]) and a Poisson's ratio of 0.25 were used for all rock layers. The reservoir permeability was assumed to be 100 millidarcy (mD). Geostatic analysis was performed to define initial conditions. Figure 12 shows the initial vertical effective stress and Figure 13 shows the pore pressure distribution prior to injection.

Finite element modeling was then initiated. A high permeability zone around the injection well was considered in the Marcellus Shale layer to simulate a fractured zone. A (revised) constant Elastic Modulus of 3,451,898 psi (2.38e+07 kPa) and (same) Poisson's ratio of 0.25 were used for all rock layers. The Mohr-Coulomb failure criterion was used to investigate the extent of damage zone in the reservoir and the overburden layers due to fluid injection. Geostatic analysis was performed to define initial stress conditions.

An axisymmetric finite element model was constructed based on an idealized geologic column which was generated from published literature. The Mohr-Coulomb failure criteria was set at $c=0$ and $\varphi = 20°$. Geostatic analysis was performed to define initial stress conditions. Fluid was injected at a differential pressure of 2,000 psi (13,788 kPa) for 10 years. Figure 14 shows the equivalent plastic strains developed in the reservoir after 10 years of injection. The plastic strains indicate that the reservoir rock has reached failure state according to the Mohr-Coulomb criterion. The lateral extent of the damage due to fluid injection in the reservoir was limited to the region around the injection well.

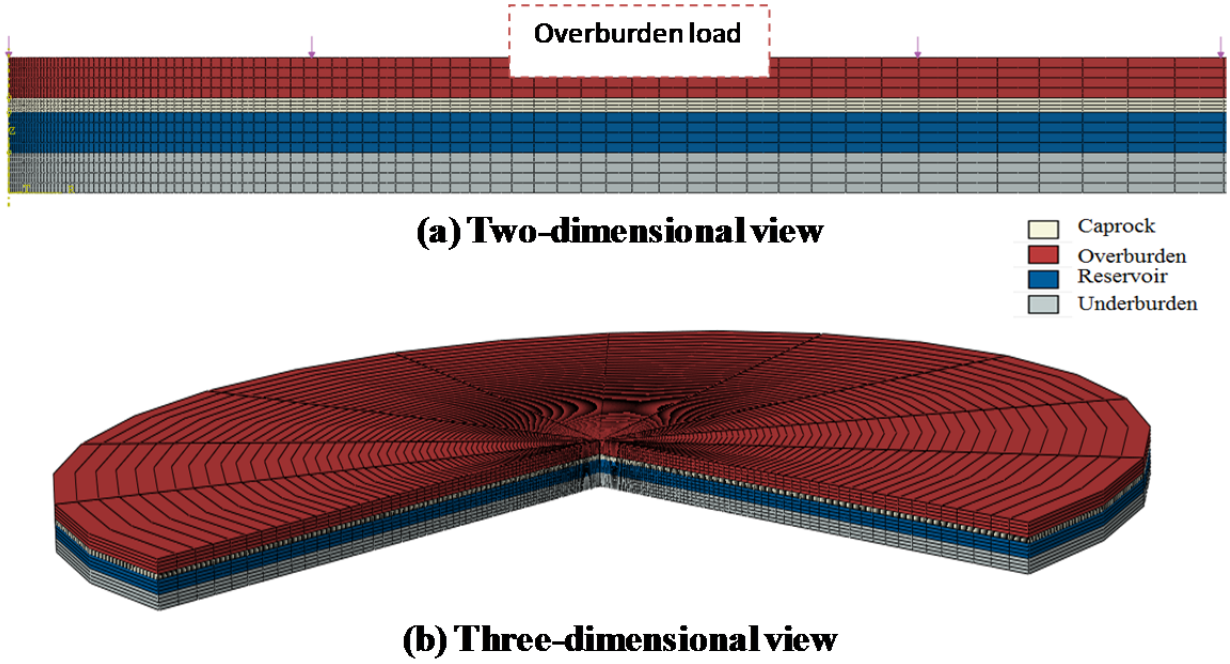


Figure 11: Finite element mesh (not to scale).

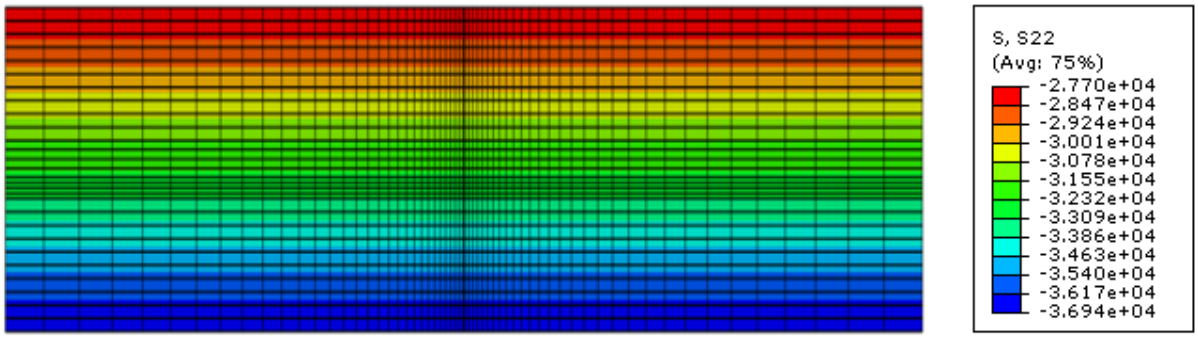


Figure 12: Initial vertical effective stress (kPa) (not to scale).

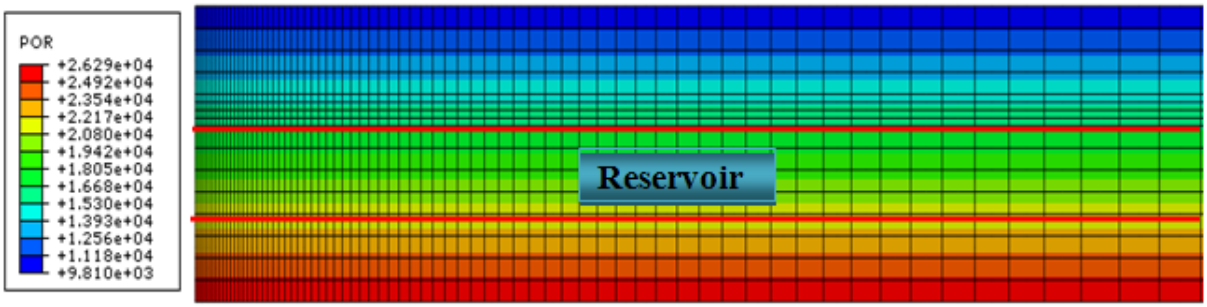


Figure 13: Initial pore pressure distribution (kPa) (not to scale).

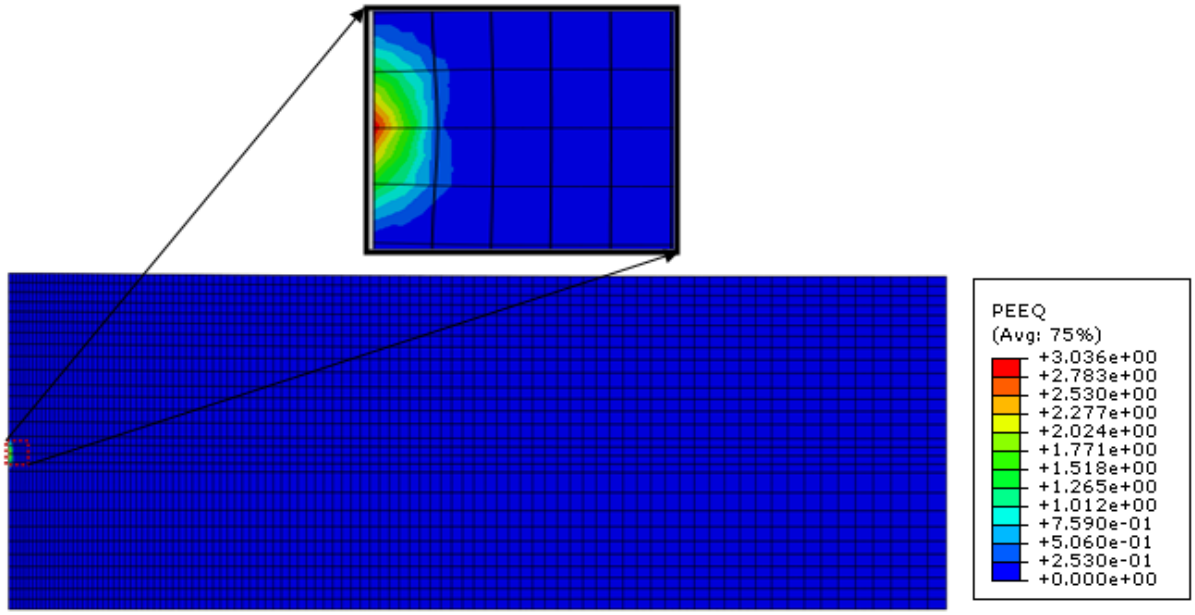


Figure 14: Equivalent plastic strains after 10 years of fluid injection.

Baseline Environmental Signals

NETL has ongoing studies at four Marcellus Shale gas locations in Pennsylvania to document environmental changes that accompany shale gas development. The research at these sites was designed to provide real world answers to questions that the public has asked about shale gas development including:

- How high do created fractures extend above hydraulically fractured wells?
- Do fluids and gas migrate upward from the hydraulically fractured formation to underground sources of drinking water?
- Does hydraulic fracturing induce seismicity that can cause damage to surface structures overlying shale gas operations?
- What is the effect of shale gas operations on indigenous wildlife?

In addition, access to these locations has allowed NETL to field test tools that may help interested stakeholders (e.g., gas industry, regulators) find undocumented, legacy wells and detect leaks from produced water impoundments.

How High do Created Fractures Extend Above Hydraulically Fractured Wells?

NETL has monitored fracture height growth during hydraulic fracturing at six horizontal Marcellus Shale gas wells in southwestern Pennsylvania (Greene County) and at one horizontal Marcellus Shale gas well in central Pennsylvania (Clearfield County). Although the wells at both locations were completed in the same formation, the structural setting and the direction and magnitude of fracture height growth at the two areas are different. In Greene County, the predominant structures that impact hydraulic fracturing are Middle Devonian age reverse faults. Microseismic monitoring showed that these faults provided a pathway for the upward growth of fractures through the Tully Limestone, which is believed to be a frac barrier when intact. At the Greene County site, microseismic monitoring showed that the effect of hydraulic fracturing extended about 1,900 feet above the treatment well and more than 1,600 feet above the Tully Limestone (Figure 15). However, at the Clearfield County Site, induced fractures remained below the Tully Limestone. Instead, the fractures at the Clearfield County well grew downward more than those at Greene County, and ultimately connected the Marcellus Shale well with the wet Oriskany Formation about 50 feet below the treatment well (Figure 16). Connection with the Oriskany Formation has been proposed as the reason why Marcellus wells in Clearfield County produce more water than typical Marcellus Shale wells. This field study provides evidence in support of that hypothesis.

Fracture height growth during hydraulic fracturing at the Greene County Site was monitored using a single, eight-tool, vertical geophone array that was deployed in available vertical Marcellus Shale wells (microseismic observation wells). However, in Clearfield County, two 12-tool geophone arrays were placed in two vertical Oriskany wells (located on opposite sides of the horizontal Marcellus Shale treatment well) to monitor fracture height growth. Simultaneous monitoring of microseismic events from two arrays provided more precise locations for the events and allowed the detection of a larger number of events. Further, the two Oriskany monitoring wells provided the opportunity to collect cross-well seismic tomograms prior to and after hydraulic fracturing. The resolution of cross-well seismic is five-times better than that of surface seismic and, thereby, shows structural and stratigraphic features unresolved by surface seismic. A difference tomogram obtained by subtracting the pre-frac tomogram from the post-frac tomogram revealed an area where p-waves were slowed and a separate area where s-waves were slowed in the post-frac tomogram. The area of p-wave slowing corresponded with an area of intense microseismic activity while the area of s-wave slowing was an area with no microseismic activity. These observations may be key to understanding the hydraulic fracturing process and answering questions about

why certain areas are intensely fractured while adjacent areas do not respond to treatment. This is the first time that cross-well seismic tomography has been used in the Marcellus Shale play.

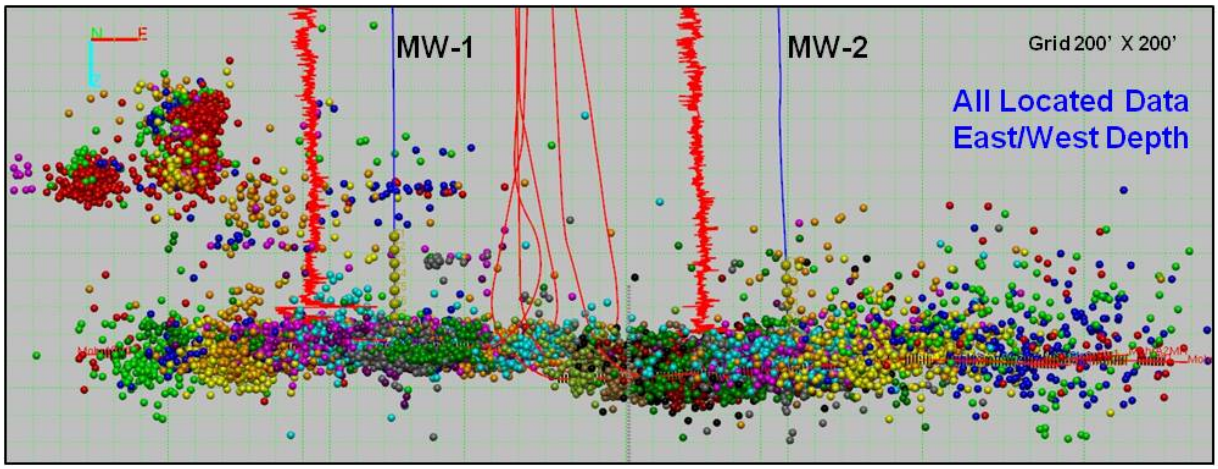


Figure 15: East-west depth section looking north that shows the vertical distribution of microseismic events located during the hydraulic fracturing of six horizontal Marcellus Shale gas wells at the Greene County Site in southwestern Pennsylvania.

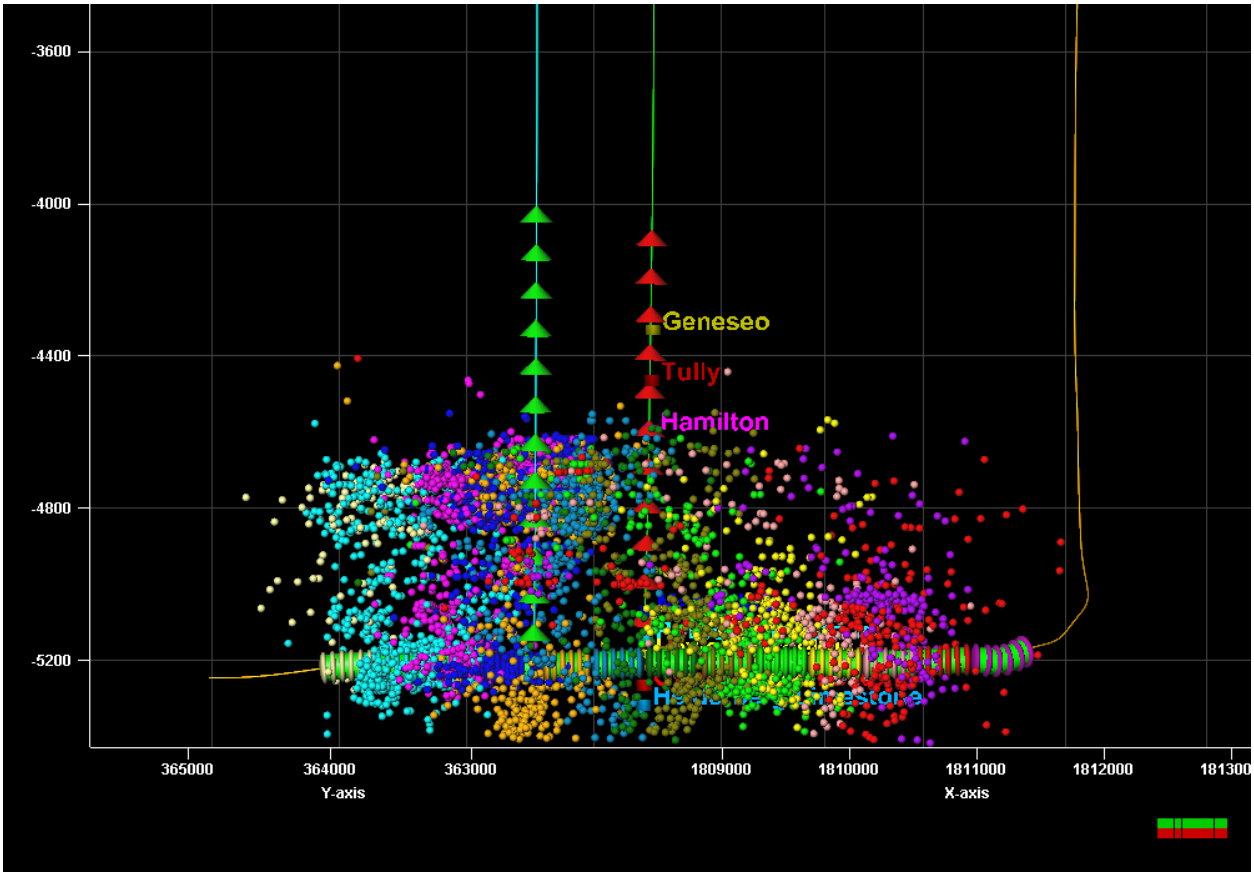


Figure 16: Northwest-southeast depth section looking northeast that shows the vertical distribution of microseismic events located during the hydraulic fracturing of a horizontal Marcellus Shale gas well at the Clearfield County Site in central Pennsylvania.

Do Fluids and Gas Migrate Upward from the Hydraulically Fractured Formation to Underground Sources of Drinking Water?

At the Greene County Site, gas and water produced from a conventional Upper Devonian/Lower Mississippian gas field that is about 4,000 feet above hydraulically fractured horizontal wells in the Marcellus Shale were monitored for evidence of gas and fluid migration from the Marcellus Shale. The monitored zone was approximately mid-depth between the hydraulically fractured formation at 8,300 feet and the deepest freshwater aquifer at about 800 feet. The evidence consisted of: (1) pressure and production histories, (2) gas isotopes, (3) produced water isotopes, and (4) tracers injected into a horizontal Marcellus Shale well with the hydraulic fracturing fluids.

Pressure and Production Histories

Pressure and production histories from three Upper Devonian/Lower Mississippian gas wells that directly overlie hydraulically fractured, horizontal Marcellus Shale gas wells were reviewed for the period starting three years before hydraulic fracturing, during hydraulic fracturing, and for one year after hydraulic fracturing. The expectation was that any significant migration of gas from the over-pressured Marcellus Shale to the under-pressured Upper Devonian/Lower Mississippian gas field would be accompanied by a detectable increase in gas pressure and production from the overlying wells. A review of the pressure and production history before and after hydraulic fracturing showed only fluctuations consistent with the routine operation of low pressure gas wells (periodic soaping or swabbing). There was no evidence of

significant migration of gas into the Upper Devonian/Lower Mississippian gas wells from a formation of greater pressure.

Natural Gas Isotopes

Natural gas samples were collected from seven Upper Devonian/Lower Mississippian gas wells that overlie hydraulically fractured, horizontal Marcellus Shale gas wells and analyzed for $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ (Figure 17). Previous sampling had shown that $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ can detect the intermixing of Marcellus Shale gas with the gas produced from Upper Devonian sand reservoirs. A minimum of 10 percent Marcellus Shale gas in the gas from the Upper Devonian/Lower Mississippian reservoirs would be needed for positive detection. The $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values for gas samples from the seven Upper Devonian/Lower Mississippian gas wells showed no evidence of the intermixing of shale gas during the 10 month monitoring period after hydraulic fracturing.

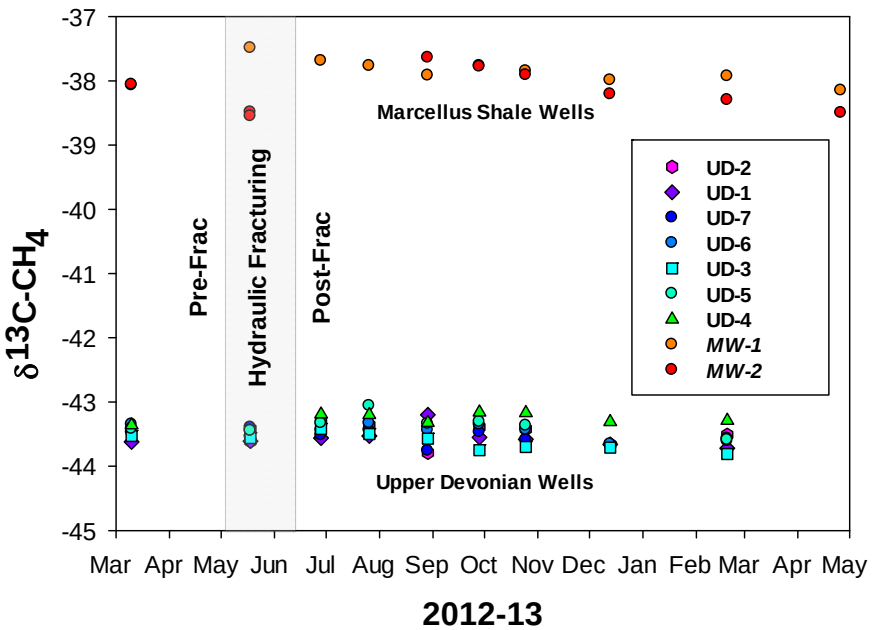


Figure 17: $\delta^{13}C_{CH4}$ values for gas from Upper Devonian/Lower Mississippian gas wells and Marcellus Shale gas wells at the Greene County Site before and after hydraulic fracturing.

Produced Water Isotopes

Produced water samples from five Upper Devonian/Lower Mississippian gas wells that overlie hydraulically fractured, horizontal Marcellus Shale gas wells were analyzed for strontium isotopes (Figure 18). Like natural gas isotopes, strontium isotopes are good indicators of whether produced water is from the Middle Devonian age Marcellus Shale or the Upper Devonian/Lower Mississippian sandstone reservoirs. Strontium isotope results for produced water samples collected monthly for five months after hydraulic fracturing show no evidence of the intermixing of brine from the Marcellus Shale. A minimum of five percent Marcellus Shale brine in the Upper Devonian/Lower Mississippian produced water would be needed for positive detection.

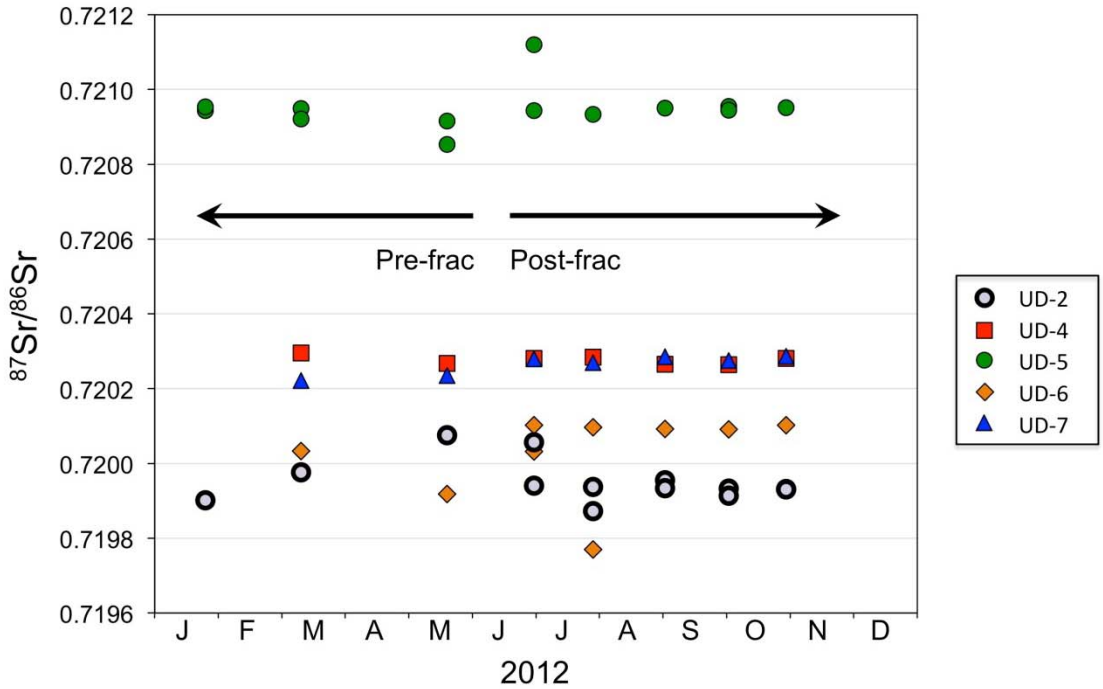


Figure 18: Strontium isotope ratios for produced water from Upper Devonian/Lower Mississippian gas wells showing no significant isotopic change after hydraulic fracturing in the Marcellus Shale, approximately 4,000 feet below.

Perfluorocarbon Tracers

Four perfluorocarbon (PFC) tracers were injected with the hydraulic fracturing fluid into 10 stages of a 14-stage horizontal Marcellus Shale well during hydraulic fracturing. Gas samples were collected from: (1) the well where PFC tracers were injected, (2) a parallel horizontal Marcellus Shale well offset 750 feet, (3) two Upper Devonian/Lower Mississippian gas wells that directly overlie the PFC injection well, and (4) the annulus gas from a vertical Marcellus Shale gas well that was about 200 feet away from the tracer injection well. PFC analysis of the gas found all four tracers in gas produced from the injection well indicating that PFC tracers were not entirely absorbed by the formation. Gas produced from the offset well contained the two PFC tracers that would be expected to migrate to the monitored well, based on perforation position and fracture azimuth. No tracers were detected in the gas produced from two overlying Upper Devonian/Lower Mississippian wells but monitoring was only for a two-month period. Two PFC tracers were detected in the annulus gas from the vertical Marcellus Shale gas well that was approximately 200 feet from the injection well, as shown in Figure 19. Because the gas produced from the vertical Marcellus Shale was expected to contain PFC tracer, the finding of PFC tracer in the annulus gas may indicate gas seepage through joints in the production tubing or gas migration up through the cement at the bottom of the well.

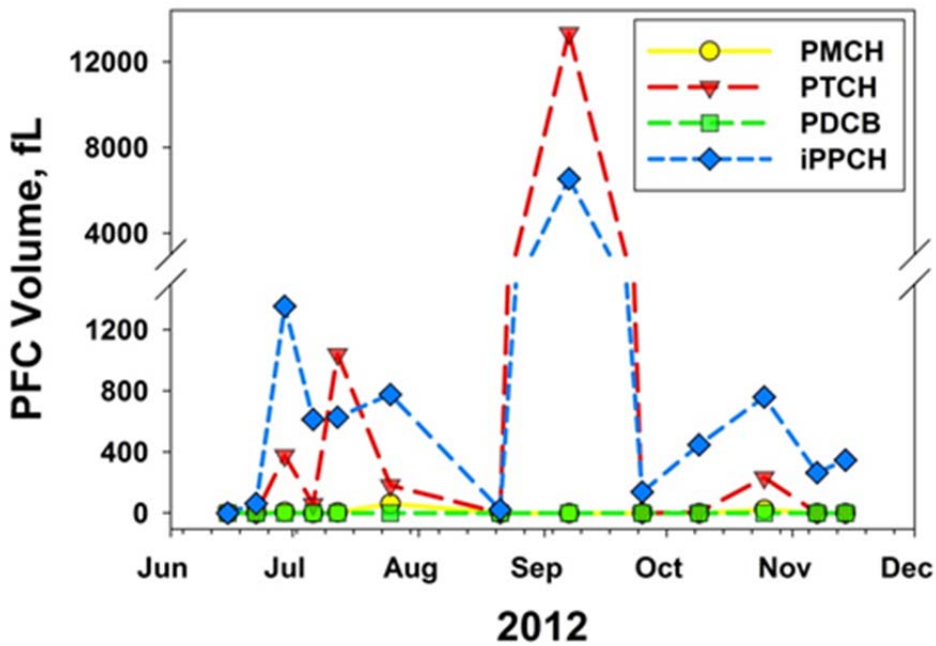


Figure 19: PFC tracers detected in annulus gas from vertical Marcellus Shale gas well located approximately 200 feet from horizontal Marcellus Shale gas well where PFC tracers were injected during hydraulic fracturing.

Conclusion

Four independent lines of evidence indicate that the hydraulic fracturing of six horizontal Marcellus Shale gas wells at the Greene County Site did not result in significant migration of gas and fluids from the hydraulically fractured formation to a monitored zone about 4,000 feet above. Rapid gas and fluid migration through such pathways as unplugged, uncased boreholes and open fractures would have been detected. Monitoring will continue into FY14 to look for evidence of gas seepage from the hydraulically fractured formation.

Does Hydraulic Fracturing Induce Seismicity That Can Cause Damage to Surface Structures Overlying Shale Gas Operations?

Broadband seismometers were placed at or near the surface to monitor earth motion attributable to nearby hydraulic fracturing activities. The seismometers were deployed at two sites: (1) the Greene County Site where one instrument was located above three horizontal Marcellus Shale gas wells during hydraulic fracturing and (2) the Butler County site where three instruments were placed at positions around the perimeter of an underground document repository. While the timing and location of hydraulic fracturing activities at the Greene County Site were known to us, the timing and location of hydraulic fracturing activities at the Butler County Site were not revealed by the industry partner. The withholding of this information was meant to see if seismic activity from hydraulic fracturing could be distinguished from ambient seismicity without the benefit of *a priori* knowledge.

Research at these field sites determined that:

- The seismic signature of hydraulic fracturing events can be distinguished from natural seismicity and other forms of anthropogenic seismicity.
- Ground movement (particle acceleration) measured at the Greene County Site and at the Butler County Site was observed to be three orders of magnitude below what could be sensed by most humans and five orders of magnitude below what is needed to damage structures on the surface.

What is the Effect of Shale Gas Operations on Indigenous Wildlife?

Prior to 2012, NETL-Regional University Alliance (RUA) studied the effect of shale gas development on migratory songbird species at a wildlife management area in West Virginia. The focal species for these initial studies were the Cerulean Warbler and the Louisiana Waterthrush, songbirds whose populations had been in decline since 1960 for unknown reasons. These studies found that emerging shale gas development in the area had a slightly negative impact on the Louisiana Waterthrush and a positive impact on the Cerulean Warbler. In 2012, NETL-RUA completed a baseline (predevelopment) study of shrubland birds at a proposed Marcellus Shale drill site in Washington County, Pennsylvania. However, avian studies at this site were suspended at the request of the landowner before shale gas development commenced. In 2013, the interrupted shrubland bird studies were completed on state-owned lands in western Pennsylvania and northern West Virginia, areas with Marcellus Shale development and similar avian habitat to the Range Resources Site.

Blue-winged Warblers, Field Sparrows, and Eastern Towhees (Figure 20) were the focal species selected for the shrubland bird study.

Figure 20: Photo of an Eastern Towhee.

The shrubland bird study consisted of:

- Nest searching for three focal species.
- Recording the relative abundance and percent occurrence of all species.
- Documenting nest success and productivity for each species.
- Collecting vegetation data for nests of focal species.

- Monitoring of acoustic and light levels.

Accomplishments:

- All three rounds of point counts were completed on the three study areas. At the 24 point count locations, 65 avian species were detected for a total of 1,642 detections.
- Nest searching and monitoring was completed for 96 nests of the three focal species: Blue-winged Warblers (6), Field Sparrows (78), and Eastern Towhees (12).
- Recording of light and sound levels was completed at the three study areas for nest sites and point count locations.
- Vegetation sampling plots were completed at 95 nests, 24 point count locations, 199 random points, and 6 Blue-winged Warbler territories.
- Preliminary data summaries were completed for the 2012 and 2013 field seasons.
- Preliminary summaries were completed for the sound data files with the "Soundscapes" software; 1,602 hours of sound recordings were gathered in 2012 and 10,743 hours in 2013.

Methods for Locating Undocumented Wells

The PA-DEP may be requiring gas producers to locate all existing wells within a 1,000-foot radius of new vertical wells and within a 1,000-foot buffer around the footprint of new horizontal wells. It will be difficult for industry to comply with this potential requirement in hilly, heavily vegetated areas where legacy wells are difficult to locate. Since 2005, NETL has been developing a toolbox of airborne and ground-based methods for locating existing wells. In March 2012, NETL conducted a helicopter magnetic survey of an area in Washington County, Pennsylvania to locate existing wells before impending Marcellus Shale development. The helicopter survey located 144 magnetic targets that were evaluated by ground reconnaissance in 2013.

A field reconnaissance was conducted to investigate each well-type magnetic target identified by the helicopter magnetic survey of March 2012 (Figure 21). Twenty well-type magnetic targets were down-selected from the 144 magnetic anomalies identified in the helicopter survey. Part of the down selection process was to review recent aerial photography to exclude well-type magnetic anomalies that are likely to be domestic water supply wells. The twenty targets were then placed in a more detailed Geographic Information System (GIS) database to facilitate the field reconnaissance that was conducted from May to October 2013.

In FY13, 17 of the 20 well-type magnetic targets were investigated with ground reconnaissance. Of the 17 targets, 13 were confirmed to be wells; 2 wells are still in production. However, four well-type magnetic anomalies were not wells but were two trash dumps, a fence corner, and a power pole. Only four of 13 confirmed wells were listed in the PA IRIS data base; the location error for the four wells in the PA IRIS database was found to be more than 50 meters. Two additional wells that did not have well-type magnetic anomalies were identified using a combination of LiDAR (topographic footprint showing a pad or access road), and historic 1930's aerial photography (showing derrick and pump house). Of 15 confirmed well locations, a well-type signature could be seen in the LiDAR data at seven sites and a derrick and pumphouse could be seen on historic geo-referenced aerial photographs at six locations. At four confirmed well locations there was no visible evidence of well infrastructure and a field magnetometer was needed to locate the well casing under heavy brush and thin soil cover. A resistivity survey and a detailed ground magnetic survey was completed at the site of a broad, weak magnetic anomaly to confirm a well site where well casing was likely removed.

Field data collected to date have been organized into a GIS project that includes the Global Positioning System (GPS) location, field picture, site description, magnetic response from airborne survey, and data sources used to confirm the well site.

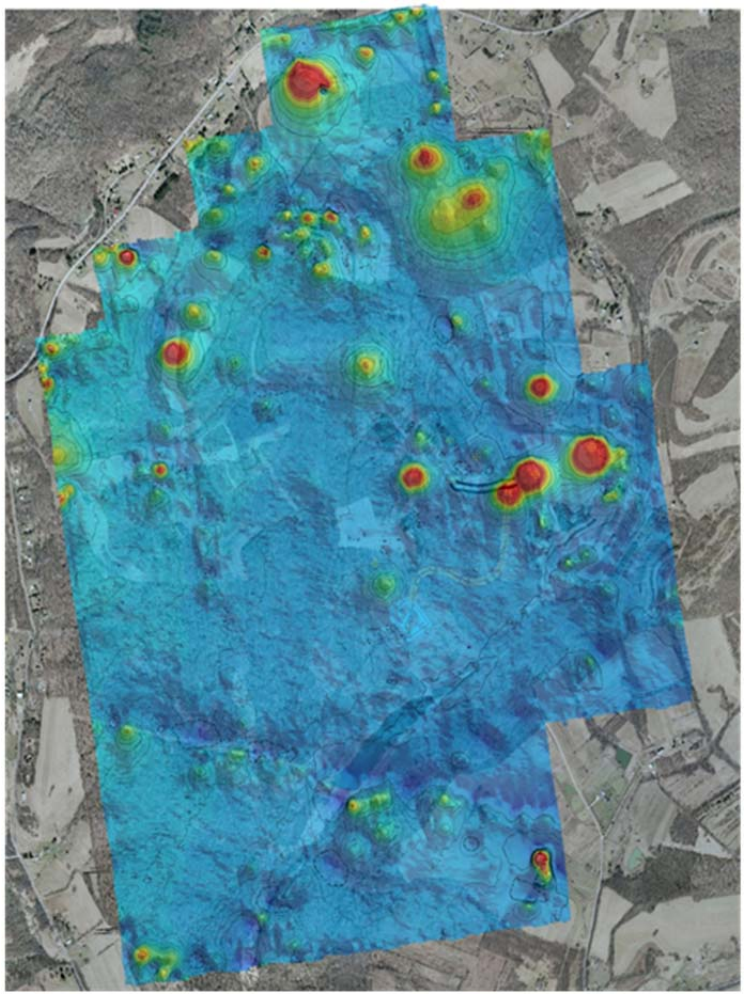


Figure 21: Helicopter magnetic map of emerging Marcellus Shale gas development area showing well-type magnetic anomalies.

Methods for Detecting Production Fluid Migration

Fluids associated with the drilling and completion of unconventional oil and gas wells are often stored in on-site, lined impoundments or tanks prior to reuse or disposal. NETL is evaluating electromagnetic (EM) methods to detect and map leaks from these facilities, should they occur. EM takes advantage of the high conductivity of production fluids to detect leaks into relatively nonconductive soil. In FY13, NETL conducted EM surveys of a Marcellus Shale gas site undergoing development. The first EM survey was conducted prior to any development and showed differences in ground conductivity consistent with underlying geology. Next, EM surveys of the pad area and surroundings were conducted to determine the distribution of conductivity after the pad was constructed. Results of the pre-construction survey (Figure 22) were compared with that of the post-construction survey (Figure 23) to determine changes in the conductivity distribution that can be attributed to construction activities. Some minor changes were noted and attributed to the excavation of pyritic material and relocation to fill areas. The overall ground conductivity of the constructed pad area and surroundings is low with maximum conductivities of about

40 mS/m. The low conductivity will provide an optimum background to detect undesired migrations of highly conductive production fluids.

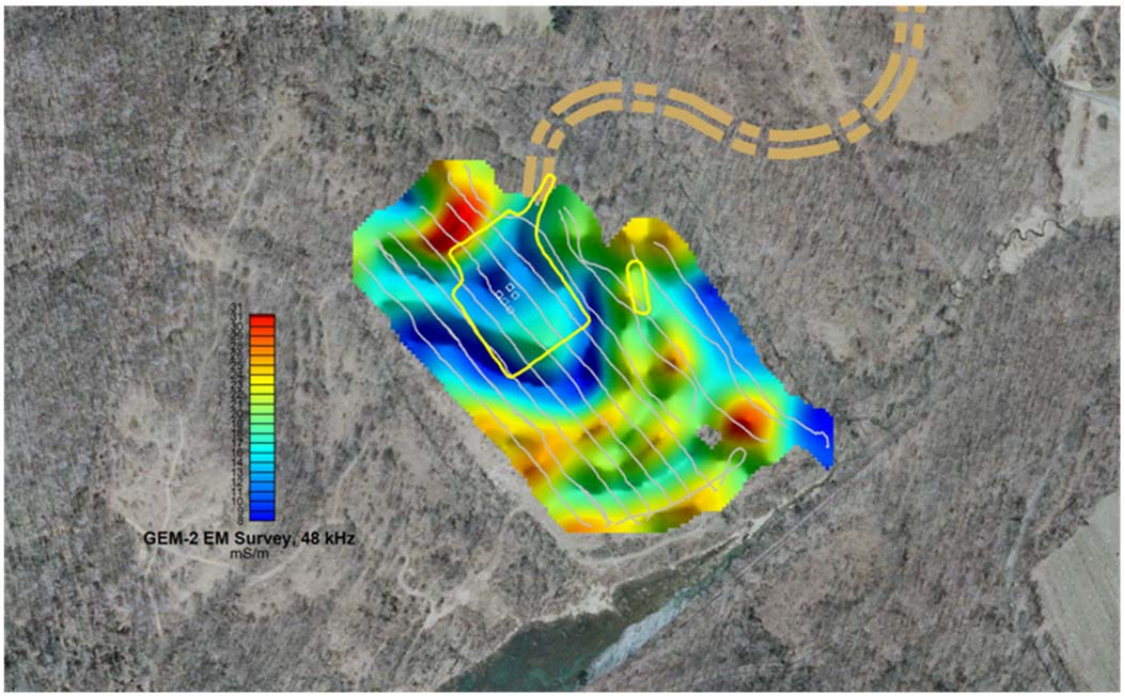


Figure 22: Pre-construction ground conductivity at the Washington County Site. Yellow line denotes pad boundary.

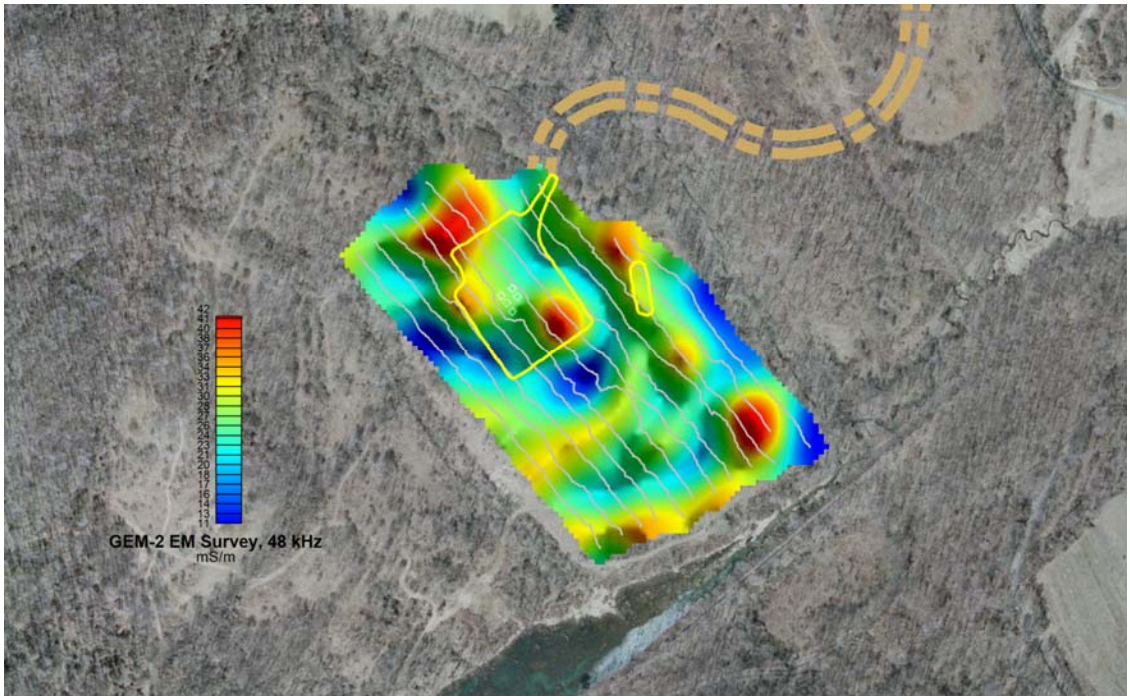


Figure 23: Post-construction ground conductivity at the Washington County site and surroundings. Yellow line denotes pad boundary.

Fugitive Air Emissions Field Data

The objective of this effort is to determine if the assumptions made in greenhouse gas life cycle assessments for shale gas can be improved with collection of fugitive methane emissions measurements specific to Marcellus Shale natural gas exploration and production activities. Field emissions measurements will be converted to a format appropriate for input to the current life cycle analysis to improve life cycle assessments that serve to inform decision makers and assess emissions performance of alternative operational scenarios.

Measurement of Pollutant Concentrations During Hydraulic Fracturing/Well Completions Using the Ambient Air Monitoring Laboratory

The laboratory consists of an 18-foot trailer housing several air pollution monitoring devices with samples of ambient air being drawn from inlets on the trailer roof. The laboratory was designed to operate unattended with continuous, automatic collection of data. A satellite link provides the capability to remotely download data and control some instruments. Instrumentation includes: Perkin Elmer Ozone Precursor Analyzer System; a GC-FID with thermal desorption for measurement of 52 volatile organic compounds (VOCs); Teledyne API ozone analyzer; Teledyne API NO_x analyzer; Teledyne API SO_2 analyzer; Thermo Fisher Tapered Element Oscillating Microbalance (TEOM) for measurement of PM10 and PM2.5; Sunset Laboratory Organic and Elemental Carbon in Aerosols field analyzer; Picarro ammonia analyzer; Picarro methane/CO_2 and methane/CO_2 isotopes analyzer; Pylon radon analyzer; and a Davis Instruments meteorological station for measurement of temperature, relative humidity, wind speed and direction, rainfall, barometric pressure, and solar intensity. The laboratory can be situated downwind of a pollution source for measurement of ambient concentrations of pollutants. Source contribution to ambient pollutant concentrations can be determined by comparing periods when wind direction is consistent with transport from the source to periods when wind comes from other directions. Several criteria for site selection when using the mobile air monitoring laboratory include: (1) a source of electric power, (2) a location that is typically downwind of the source, (3) no other significant sources nearby, (4) exposure to southern skies for satellite transmission of data, and (5) easy, but secure, accessibility for maintenance.

The mobile air monitoring laboratory is committed to collecting data while there is activity at the Marcellus test site in Washington County, with a focus on documenting air quality during different stages of site development. However, as the schedule permits, the mobile air monitoring laboratory can be deployed to additional sites during hydraulic fracturing/well completion for short-term (approximately one month) campaigns.

The mobile air monitoring laboratory was used to evaluate off-well pad air quality at six Marcellus shale drilling sites from July – November 2012. The six sites were in various stages of operation, including vertical drilling, horizontal drilling, hydraulic fracturing, and flaring. The Wireless Air Monitoring System (WAMS) was located at each site to collect additional data for particulate matter and bulk volatile organic compounds. The resulting data was compiled into a data report that was submitted to the West Virginia Department of Environmental Protection in December 2012 and published online in July 2013 (McCawley 2013). The data report will be available as a Technical Report Series (TRS) document (Pekney and Reeder et al., 2013). NETL-RUA researchers continue to work to further analyze the data such that a peer-reviewed publication (anticipated publication date of June 2014) will result. The American Industrial Hygiene Association's Annual Conference and Exhibition in Montreal, Canada on May 23 allowed the results of this research project to be presented in a two-part presentation that focused on the project design and execution, and conclusions about appropriateness of setting a setback distance (Pekney and McCawley, 2013). Setback distance refers to the minimum distance that a well pad can be from an occupied dwelling.

NETL staff met with a shale gas operator to request access to an additional Marcellus shale well pad for air monitoring using NETL's mobile air monitoring laboratory. The operator agreed to grant access to a new Marcellus shale well pad in Greene County, Pennsylvania. The mobile air monitoring laboratory was moved to the site to conduct monitoring for one month, June 11-July 11, 2013, during hydraulic fracturing and flowback of the wells. Data is currently being analyzed. A publication summarizing the measurements collected at this and other shale gas well pads is expected in FY14-Q4. The publication will describe calculation of the average methane emission rate during well completion from six sites.

NETL continues work on a manuscript that summarizes the measurements collected March-June 2012 at an additional Greene County Marcellus shale well pad (different than that described above) using the mobile air monitoring laboratory. Submission to a peer-reviewed journal is planned for December 2013. The American Association for Petroleum Geologists Annual Conference and Exhibition was attended in Pittsburgh, Pennsylvania, on May 20, 2013, to present the results of this research (Pekney and Veloski et al., 2013). Also, results of this air monitoring campaign were presented at Engineering Conference International's "Overcoming the Environmental and Community Challenges of Hydraulic Fracturing for Shale Gas" conference in Boulder, Colorado (Reeder and Pekney, 2013).

The Mobile Air Monitoring Laboratory was moved to a shale gas development site in Washington County, Pennsylvania, in order to collect data during the drilling phase of development. NETL previously collected baseline data at the same location for approximately eight months in 2011-2012. The operator completed vertical drilling of the wells at the site. Horizontal drilling is expected to begin in FY14-Q1, and well completion is expected to begin in FY14-Q2. The laboratory will continue to collect data at this site until the wells are in production.

NETL was contacted by the Maryland Department of the Environment (MDE) with a request to conduct baseline air monitoring in northwestern Maryland with the NETL mobile air monitoring laboratory. Maryland currently has a moratorium on Marcellus shale development. The MDE would like to collect pre-development ambient air quality measurements in anticipation of the moratorium being lifted and development occurring. NETL has agreed to conduct month-long monitoring campaigns during each of the four seasons over the next two years while the moratorium is in place, with the intention to return for more monitoring if/when development should occur for a during- or post-development comparison. NETL signed an MOU with the MDE to conduct baseline monitoring in Garret or Allegany County in Maryland. Currently, researchers are discussing potential monitoring locations. The MDE is preparing a list of sites, and NETL plans to conduct site visits to make a selection during FY14-Q1. Work on this aspect of the project will be scheduled according to research priorities and logistics.

NETL's manuscript describing the use of the Mobile Air Monitoring Laboratory to conduct an air monitoring campaign in 2011 in the Allegheny National Forest was submitted to the Journal of the Air and Waste Management Association, and is currently being revised after peer review (Pekney et al., under review).

Point Source Emissions Measurements

Although ambient air monitoring at or very near Marcellus shale well pads yields useful information about the overall impact of the operations on air quality, a clear breakdown of emissions by individual source that result in the ambient concentrations measured at the mobile air monitoring laboratory location is not always achievable. To obtain source-specific pollutant emission rates, a point source sampling approach was developed. This approach involves locating leaks, or fugitive emissions, from all process components at many sites and then measuring pollutant concentration and flow rate to obtain a pollutant emission rate for each leak. The resulting emission rates can be averaged for each process component to develop estimates for fugitive emissions that can be directly compared to the estimates currently used in NETL's life cycle assessment.

The research team concluded that a Picarro methane/acetylene analyzer would be effective for monitoring methane emissions measurements during shale gas well completions. The approach involves using a tracer, acetylene, to estimate emissions of methane from the well pad during well completion. A continuously releasing source (gas cylinder) of acetylene is placed on or near the well pad while the Picarro analyzer simultaneously measures methane and acetylene concentration some distance downwind of the well pad. Given the known acetylene emission rate at the well pad and the known concentrations measured downwind, the methane emission rate at the well pad can be estimated using a simple ratio calculation. The analyzer has an integrated GPS, such that surveys of methane/acetylene concentration can be conducted while the analyzer, located in the back of a vehicle, is being driven around the well pad. Concurrently, infrared cameras will be used to scan the well pad to detect fugitive emissions of VOCs associated with natural gas so that when high methane emissions are observed, the source(s) can be identified.

Prior to using FLIR GF 320 infrared cameras for identifying locations of fugitive emissions of VOCs that cannot be detected by the naked eye, NETL staff received training from a FLIR technician on their operation and maintenance. The methane-acetylene analyzer was received along with other supplies and materials (gas cylinder regulators, gas cylinders, analyzer case and air conditioner, batteries, etc.).

During flowback at one of the Greene County sites, the research team performed methane/acetylene surveys on public roads surrounding the well pad, in addition to the well pad access road. The goals were to determine if measurable amounts of acetylene could be detected downwind, and if there were coincident peaks in methane concentration that indicated the detection of a plume of well pad methane emissions. Unfortunately, the weather during this time was very hot with calm winds or stagnant conditions, which is not ideal for the tracer measurement approach (moderate winds are optimal). The NETL staff was able to detect low concentrations of acetylene, less than 10ppb, downwind of the well pad during some of the surveys, but there were no coincident methane peaks. This indicates either little to no methane was emitted during the time of the surveys, or a problem exists with the instrument or technique. NETL will examine the ambient methane concentration data collected at the mobile air monitoring laboratory during the surveys to determine if there were in fact peaks in methane concentration. It is possible that during flowback, emissions were episodic in nature and were missed at the times the surveys were conducted.

NETL prepared to participate in the Environmental Defense Fund's (EDF) Barnett Air Monitoring Campaign, October 16-30, 2013. NETL anticipated using the acetylene tracer/methane survey approach to estimate methane emissions from approximately eight compressor stations in the Dallas/Fort Worth area. Researchers participated in planning conference calls with EDF and worked on fixing problems that the methane/acetylene analyzer was experiencing. Unfortunately, due to the government shutdown in October 2013, NETL's participation in the EDF campaign was cancelled. NETL will maintain contact with the EDF project organizer for information about possible future campaigns.

Statistical Modeling of Air Quality Impacts

The research team focused on developing statistical methods to represent the air quality impact from Marcellus Shale drilling and fracking activities based on the field data collected. The modeling effort involves two components: (1) statistical methods to differentiate between background air pollutant concentrations and contributions from sources and (2) application of an atmospheric chemistry and transport model.

Initial statistical analysis began on an existing ambient air field data set from shale operations monitoring, to characterize variations in pollutant concentrations as a function of wind direction for both background sites and those located near shale gas drilling wells. Methods were implemented for fitting spline curves to concentration as a function of wind direction and determining whether the relationship is statistically different from a null hypothesis where concentration is independent of wind direction. Nonparametric

confidence intervals were characterized for data assumed to represent background (not near a drilling site or other point source of the measured compounds).

Analysis at a background site indicated a small, though statistically significant difference in the ambient NO_2 concentration when the wind blows from different directions. Evaluation of a site near well fields suggested a much larger directional variation, including high values when the wind came from the well fields. Work also began on data collection at the test sites.

Evaluation of the Geochemical and Microbiological Composition of Shale Gas Produced Water and Solid Wastes

The objective of this effort is to characterize the chemical and microbiological transformations that occur during the lifecycle of waters associated with unconventional gas development. Specifically, this research is directed at:

- Radium (a radioactive component of produced water) including the development of more rapid analytical techniques to determine radium activity in produced water; understanding the nature of radium occurrence in produced water; developing treatment methods to remove radium from produced water; determining the radium content of water treatment residuals, and determining worker exposure to radon gas (a radium daughter) emanating from produced water and produced water treatment residuals.
- Understanding the microbial ecology of produced water in the well environment and during temporary storage in surface impoundments.
- Determining the chemical stability of produced water treatment solids when disposed in landfills or buried at the well site.

Radium in Produced Water

Development of Rapid Analytical Method for Radium in Produced Water

NETL-RUA researchers are developing and testing a rapid method to quantify radium concentrations in produced water. The radium (Ra) limit for drinking water is 5 pC/L; an activity that is too low for measurement by ICP-OES or ICP-MS. Radium concentrations are currently measured using a radiometric technique that requires 21 days to complete. The new technique employs two Ra pre-concentration steps using ion exchange followed by detection with ICP-MS and reduces analysis time from 21 days to less than one day. EPA has expressed interest in testing the new technique for possible EPA certification.

In FY13, the development of the Ra analysis ICP-MS technique continued with investigation of previously observed low Ra recovery from the preconcentration step, and refinement of the technique to improve recovery. The resulting extraction procedure allowed for the successful separation of Ra/Ba/Sr from other cations while keeping Ra recovery above 90 percent. A series of 15 samples required approximately 12 hours to process and analyze—a significant time savings compared to the required 20 day equilibration time and 24 hour counting time per sample for traditional gamma spectrometry.

The use of 50W resin to separate Ba/Sr/Ra from other cations in flowback water prior to analysis by ICP-MS is relatively expensive and labor intensive. Therefore, co-precipitation was evaluated as a possible separation step to simplify the separation protocol. Ba/Sr/Ra is co-precipitated with sulfate by adding excess sulfate to the produced water sample. The solids were filtered and transferred into a saturated sodium carbonate solution at 80°C to convert the co-precipitate into a carbonate form that is easily dissolvable in weak acid. The resulting solution contains only Ba, Sr, and Ra that can be further processed by liquid-liquid extraction (Sr*Spec resin) to extract only Ra for analysis by ICP-MS. Total Ra recovery achieved in the initial trial was 84.5 percent.

Ra recovery using the new ICP-MS method decreases from 97.72 percent for low salinity solution (TDS=17,785 ppm) to 81.18 percent for high salinity solution (TDS=137,000 ppm). Ra recovery becomes unacceptable (<80 percent) for higher salinity solutions; the lowest recovery of 51.3 percent was observed for the highest TDS that might be observed in the produced water (TDS=300,000 ppm) (Figure 24).

During the ICP-MS measurement, each sample is analyzed 60 times and the relative standard deviation (RSD) of the measurement was determined for each sample. The RSD was found to increase as the

salinity increases and as the percent recovery decreases (Figure 24). Even though the mechanism of correlation between the RSD and Ra recovery is unclear, RSD can serve as an indicator to control the reliability of Ra measurement. In general, to guarantee decent Ra recovery for ICP-MS measurement, TDS of the produced water sample should not exceed 150,000 ppm and samples with higher TDS would have to be diluted to avoid the loss of Ra. RSD should be below 6 percent to accept the analysis by this method.

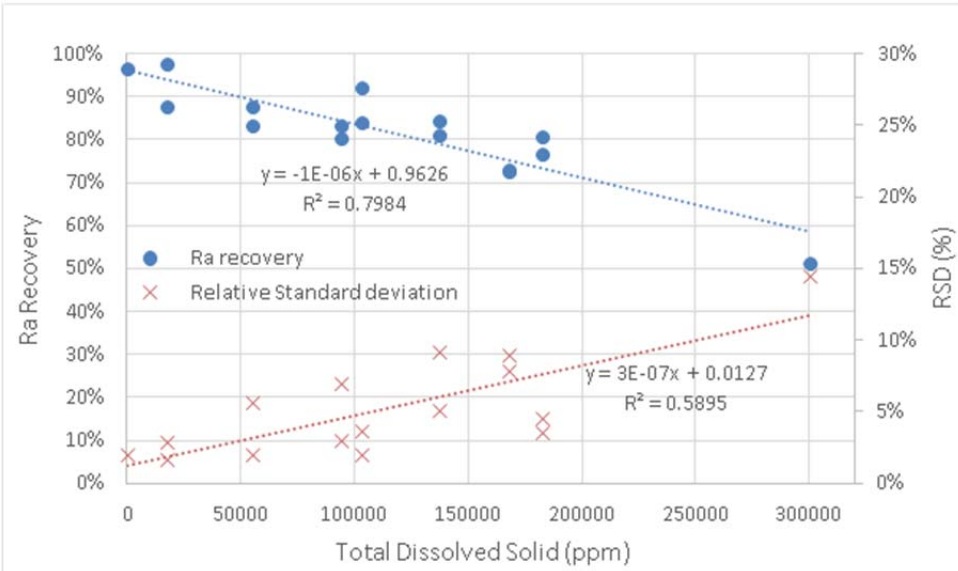


Figure 24: Radium recovery and RSD measured by ICP-MS in relation to TDS.

Occurrence of Radium in Produced Water

The radium-226 content in flowback water from a typical Marcellus Shale gas well in southwestern Pennsylvania was analyzed by gamma-spectrometry (Table 2). Radium content increased with flowback time but the Ra^{226}/Ba ratio decreased from very high levels in the first 4 days to relatively stable values after 15 days. Previous studies analyzing Ra^{228}/Pb^{212} ratios in the flowback water revealed that this ratio is consistently close to 1.0, suggesting Ra^{228} must have been present in the liquid phase for at least 5.1 years to achieve this secular equilibrium. This finding indicates that radium in flowback water originates from the formation brine rather than from soluble cation content in shale.

Table 2: Ra and Ba Concentrations in flowback and produced water

	Flowback Water					**Produced Water**
Days after hydraulic fracturing	Day 2	Day 4	Day 12	Day 15	Day 29	**~2 years**
Ra^{226} (pCi/L)	875	1470	2925	3325	3565	**6925**
Ba (ppm)	70	179	2193	2687	2987	**3924**
Ra^{226}:Ba (arbitrary unit)	12.48	8.22	1.33	1.24	1.19	**1.76**

Removal of Radium from Produced Water

Radium removal via co-precipitation with $BaSO_4$ was found to be enhanced in electrolyte solutions of greater ionic strength (ionic strength (IS) =1, 2, and 3M, Figure 25). This behavior can be explained by the enhanced zeta potential due to the compression of the double layer, which attracts more cations (including Ra) to the surface of the $BaSO_4$ crystal and increases the possibility for lattice replacement reaction. In Ra-Ba-Sr-SO_4 mixture system, where Ba:Sr=1, Ra in solution is controlled by co-precipitation of Ra-Ba-SO_4 due to much faster kinetic of $BaSO_4$ nucleation compared to $SrSO_4$. Hence, the correlation between Ra and Ba removal is very similar as in the case with just Ra-Ba-SO_4 system.

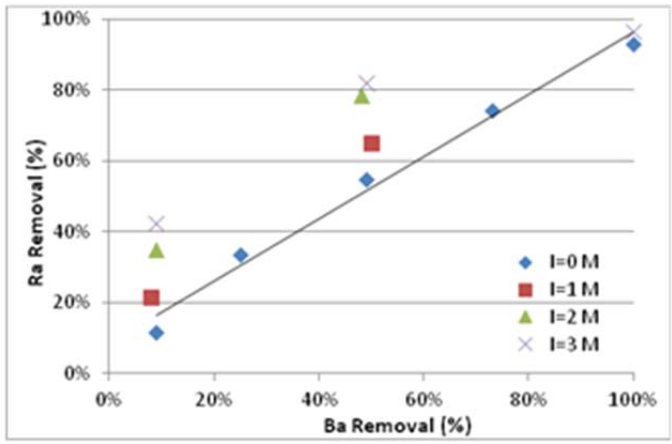


Figure 25: Cross plot of Ra removal vs. Ba removal for electrolytes of increasing ionic strength.

The study of Ra-Ba-SO_4 system then focused on better understanding of lattice replacement reactions in an effort to develop an effective sorbent for Ra removal. In the case of co-precipitation reactions, Ra precipitates together with the formation and growth of the carrier ($BaSO_4$) so that inclusion (lattice replacement); occlusion (adsorbed Ra get physically trapped inside the crystal); and adsorption on surface of the crystal are possible mechanisms for Ra uptake. In the case of lattice replacement reactions where preformed carrier precipitate is added to the solution, the inclusion mechanism is not feasible. Ra removal by preformed barite is strongly depressed when 0.5 mM of Ba^{2+} is added to the solution. Addition of Sr^{2+} to the solution had very limited impact on Ra uptake because the competition between Ra^{2+} with Ba^{2+} is much more intensive due to similarities in the ion properties. The impact of Ba^{2+} presence on Ra^{2+} removal could be balanced by increasing the concentration of $BaSO_4$ solids in solution. Desorption of Ra^{2+} at pH 0.5 was studied to understand the potential of Ra release under most severe environmental conditions. These studies showed that Ra was strongly bonded in the barite lattice and that about 20 percent of Ra could leach out under these conditions. In addition, when the Ra enriched barite was again exposed to Ra^{2+} in solution, Ra^{2+} removal was the same as for the freshly prepared barite. Hence, it is possible to reuse barite for Ra^{2+} adsorption and maintain high barite content in the storage tanks; impoundments would help sequester Ra^{2+} from the solution.

Fate of Radium in Produced Water Impoundments

Most drilling sites store produced water in local impoundments before it is treated on site (oxidant addition plus filtration) and mixed with makeup water for hydraulic fracturing. The fate of Ra during temporary produced water storage in surface impoundments and storage tanks was investigated to determine if the radium concentration increases in the water or sludge during recycling operations. Samples were collected from two on-site produced water storage impoundments in early 2011 and again in May 2013. Ra concentrations in liquid and solid samples were measured by gamma spectrometry.

Radium concentrations in the liquid samples after multiple cycles of water reuse in one impoundment increased from 1,410 pCi/L in early 2011 to 2,510 pCi/L in May 2013. The second impoundment had no radium in the liquid samples taken in early 2011 because the water had been treated using sulfate precipitation before storage. However, samples taken in May 2013 revealed an average radium concentration of 1,470 pCi/L. The increase in Ra^{226} activity in these two impoundments over a two-year period was not significant for two reasons: 1) the mixing of produced water with makeup water serves to dilute the radium concentration and 2) rock-water interactions are governed by the exchange equilibrium. In addition, adsorption of Ra^{226} onto the solids that precipitate at the bottom of these impoundments was quite significant. For example, radium concentration in dry solids collected from the first and second impoundment were 859 pCi/g and 121 pCi/g, respectively.

Monitoring of produced water impoundments in southwestern Pennsylvania showed that Ra^{226} concentrations in both the liquid phase and in bottom sludge increases with each wastewater reuse for hydraulic fracturing. TCLP was conducted with these sludge samples to investigate the leaching behavior of radium in landfill scenario. Radium is weakly bound to sludge created in the early phases of impoundment operation (sludge samples were collected in 2010) resulting in considerable radium leaching (86 percent) in a TCLP test. During normal fill and draw operations of the impoundment as part of the water reuse program, radium is enriched in the aged sludge collected in 2013. However, due to the changing composition of the solids in the bottom sludge, Ra^{226} becomes firmly incorporated in these solids and no Ra^{226} leaching was observed in TCLP tests with aged sludge. This finding suggests that it is beneficial to keep the solids in the impoundment to achieve permanent sequestration of Ra^{226} and minimize its potential impact in solid waste landfills.

Possible Radiation Exposure to Workers

Ra^{226} is an alpha emitter-even a piece of paper or the dead outer layer of human skin will stop alpha particles. Hence, there is no radiation exposure impact from Ra^{226}unless it is ingested into the body. However, $Radon^{222}$, a progeny of Ra^{226}, which can emanate from produced water and its solid residuals may be inhaled, thereby leading to significant radiation exposure. Inhalation of radon is the main pathway of radiation exposure from Marcellus Shale flowback produced water.

The radon emanation fraction is defined as the percent of radon released into the air. With moderate shaking, radon can emanate from water resulting in an emanation fraction close to 100 percent. However, radon emanation from Ra-bearing solids is depressed due to the physical properties of the material, such as distribution of Ra within the material and porosity and moisture of the material. Relevant research shows that mean radon emanation fraction from petroleum pipe scale (mainly barite) is 9 percent, compared with a 21 percent emanation fraction from soil at the same site. It may, therefore, be desirable to lock the radon precursor (i.e., Ra^{226}) into a solid phase (i.e., co-precipitation with barite) to reduce occupational radiation exposure.

Microbial Ecology of Produced Water

Microbial Ecology of Produced Water in Surface Impoundments

In order to understand the microbial ecology and nutrient cycling that occurs in impoundments during the temporary storage of produced water, which could affect the chemistry of produced water over time, bar-coded pyrosequencing was performed on DNA isolates from Marcellus Shale produced water (Figure 26). Pyrosequencing enables the recovery of more than 10 times the number of sequences and, therefore, provides a more comprehensive overview of microbial diversity than utilizing clone libraries. However, pyrosequencing is currently limited to 200-300 base pairs of DNA and limits population analyses to family and class level analyses, which is much less specific than clone libraries. The techniques are complimentary when used together - pyrosequencing will better assess microbial diversity while clone libraries will provide the critical detail of species-level information.

The upper cartoon in Figure 26 shows the broad groups of organisms that were detected in produced water using fluorescent in-situ hybridization (FISH) and clone library techniques as a comparison to results from the pyrosequencing (lower cartoon). Characterizing the taxonomy of microorganisms in produced water storage impoundments is improved relative to the FISH technique as it allows for characterization at the genus level. One group identified by both FISH and clone libraries (*Methanolobus*) was found to have insignificant biological function that could affect water chemistry.

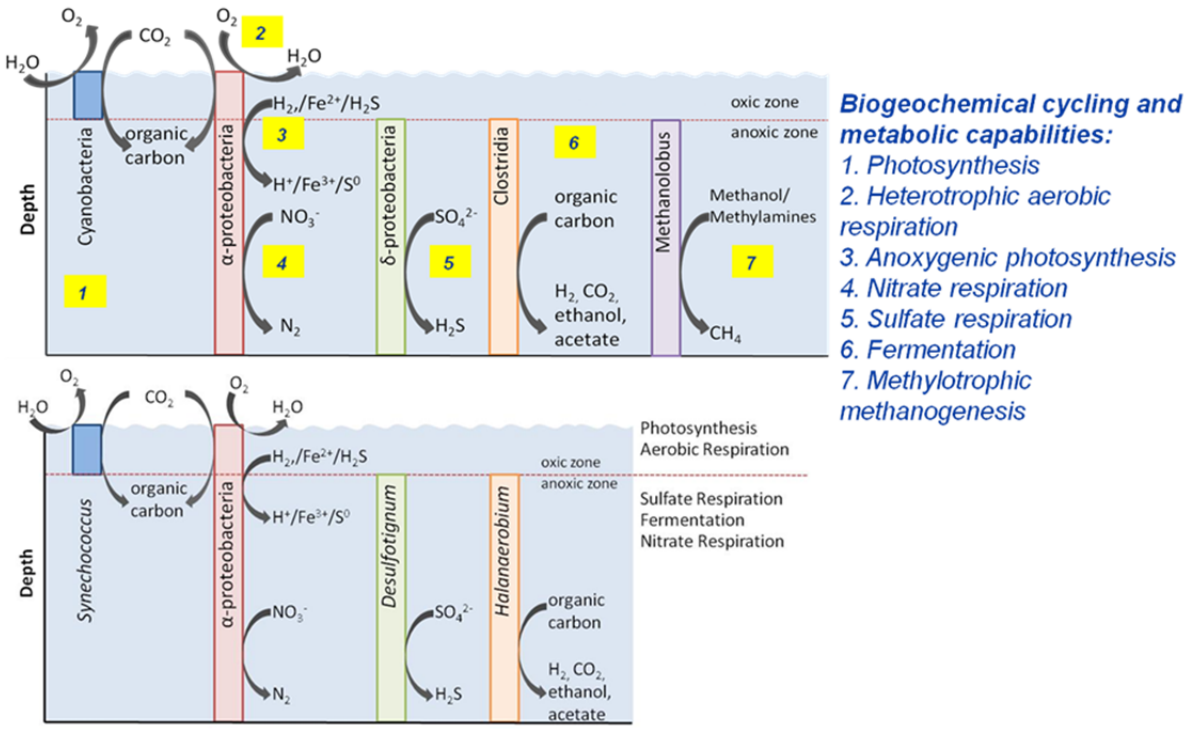


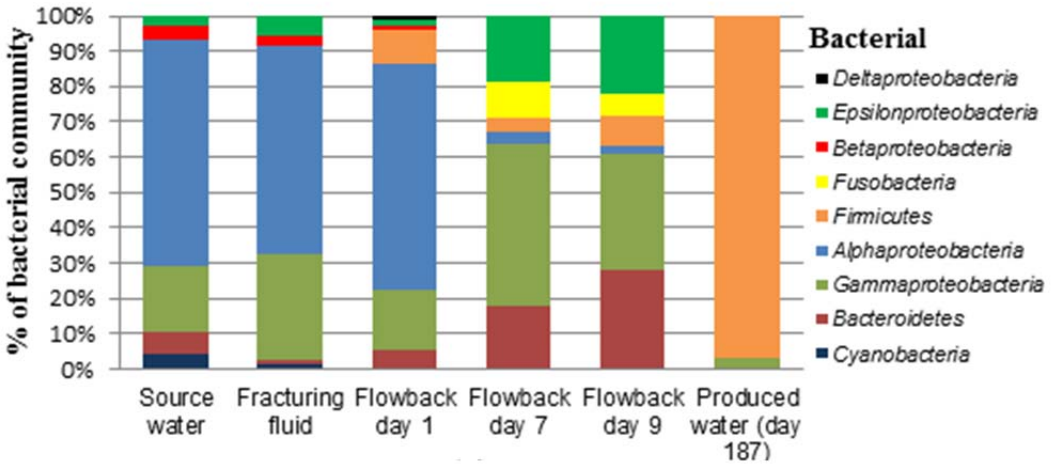
Figure 26: Biogeochemical Cycling and Metabolic Capabilities.

Microbial Ecology in the Well Environment

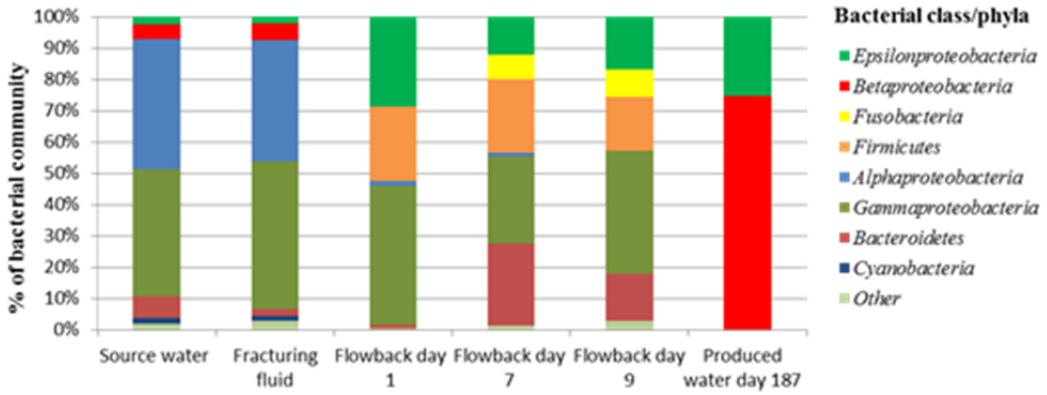
Taxonomic Results from Clone Libraries and Bar-Coded Pyrosequencing

Microbial communities in make-up water, hydraulic fracturing fluid, flowback water (three different sampling times), and produced water (187 days post-stimulation) were examined using

clone libraries and pyrosequencing. A comparison of results (

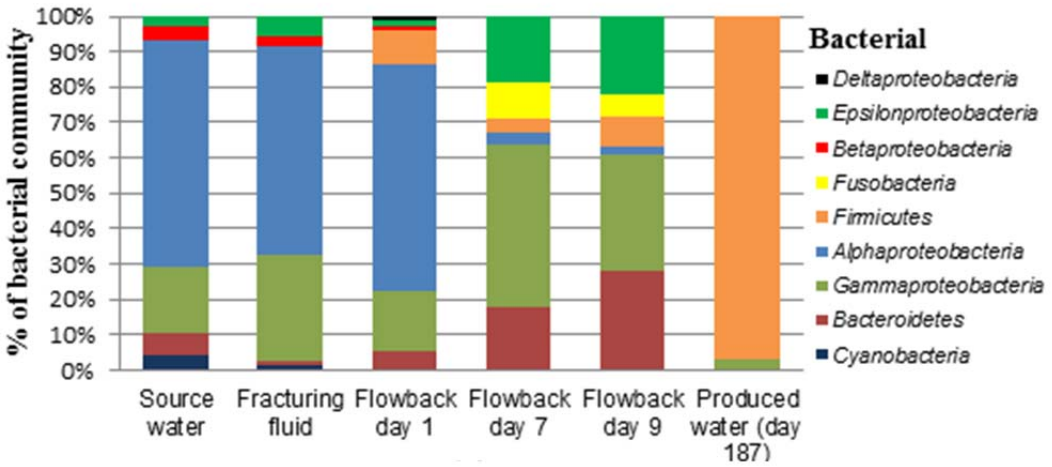


(a) 16S rRNA gene based clone libraries

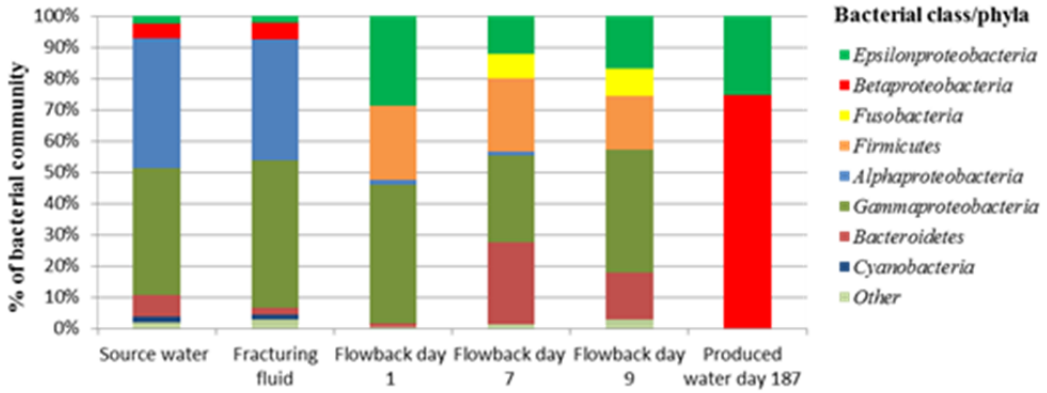


(b) Pyrosequencing

Figure 27) revealed that the two methods provided similar results for most of the samples analyzed; however, distinct differences between the clone libraries and pyrosequencing were revealed for the Day 1 flowback water and produced water.



(a) 16S rRNA gene based clone libraries



(b) Pyrosequencing

Figure 27 (a)(b): Microbial community characterization at the class/phyla specificity using (a) 16S rRNA gene based clone libraries (b) Pyrosequencing.

The unexpected disparity between the findings from the two methods was found to be caused by the inappropriate handling and storage of samples used for pryrosequencing of DNA extracts. When samples were re-prepared and submitted for pyrosequencing, results from clone libraries and pyrosequencing were comparable (Figure 28).

Diversity and species richness estimates (based on ≥ 97 percent sequence identity) from the two techniques are shown in Table 3 and

Table 4. Although the pyrosequencing libraries were an order of magnitude larger than the corresponding clone libraries, the trends for diversity and richness between the two techniques were similar with diversity decreasing towards the later day flowback and produced water samples. Further, coverage estimates showed that pyrosequencing was able to capture a greater fraction of the microbial community than clone libraries. The genetic sequences recovered from this study were submitted to the National Center for Biotechnology (NCB) Genbank database. A heat map (Table 5) depicts the relative abundance of bacterial orders in the different samples from pyrosequencing.

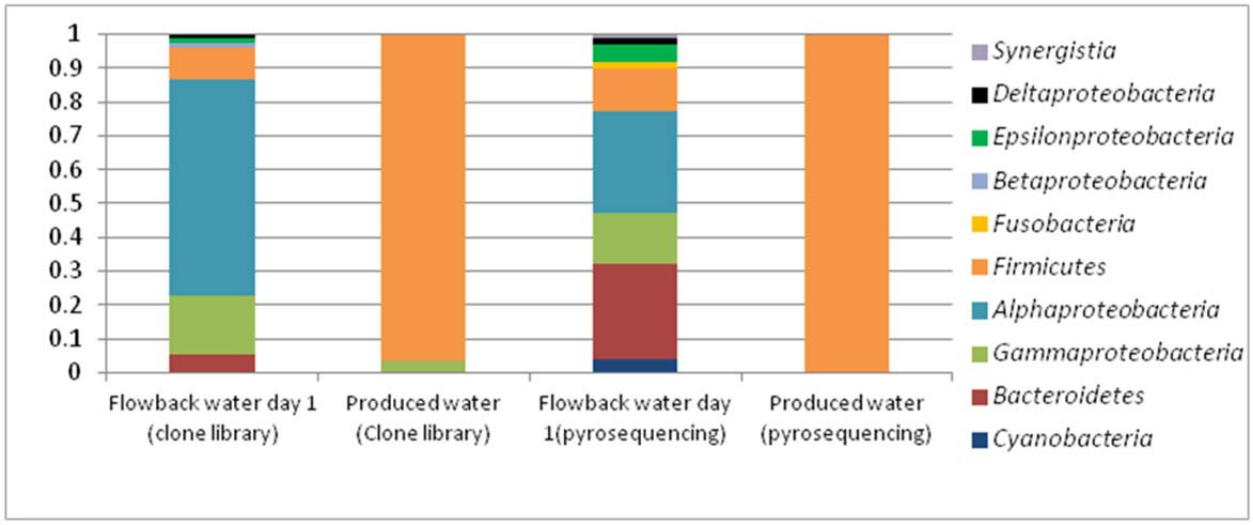


Figure 28: Microbial community characterization at the class/phyla specificity for Day 1 Flowback samples and Produced Water samples using clone library and pyrosequencing techniques.

Table 3: Diversity Richness and Coverage Estimates[1] of Bacterial 16S rRNA Genes in Source Water, Fracturing Fluid, Flowback Water (Days[2] 1,7,9) and Produced Water (Day 187) from Pyrosequencing

Sample name	No. of sequences	$OTUs_{0.03}$	Chao Diversity Index	Abundance-based Coverage Estimation Diversity Index	Shannon-Weaver	% Coverage
Source water	2941	168	285	387	3.5	98
Fracturing fluid	4014	237	435	562	3.5	97
FB 1	7738	566	1373	3165	4.3	94
FB 7	4692	161	393	577	3.3	98
FB 9	2092	85	124	146	2.9	99
Produced water (day 187)	21283	176	489	902	0.5	99

Table 4: Diversity and Richness Estimates[1], Coverage and Abundance of Bacterial 16S rRNA genes in Source Water, Fracturing Fluid, Flowback Water (Days[2] 1, 7, 9) and Produced Water (Day 187) from Clone Libraries

Sample Name	No. Of Sequences	$Otus_{0.03}$	Chao Diversity Index	Abundance-Based Coverage Estimation Diversity Index	Shannon-Weaver	% Coverage
Source water	75	33	57	64	2.9	75
Fracturing fluid	71	33	79	115	3.0	72
FB 1	75	30	49	53	2.9	79
FB 7	83	27	44	56	2.6	82
FB 9	82	24	160	141	2.4	78
Produced water (day 187)	90	3	3	4	0.2	99

Table 5: Relative Abundance of Major Bacterial Orders (>3 percent of the community in at least one of the samples) in Fracturing Source Water (SW), Fracturing Fluid (FF), Flowback Water (FB1, FB7, and FB9) and Produced Water (PW) from Pyrosequencing Results.

Order (Class)	Sample name					
	SW	FF	FB1	FB7	FB9	PW
Rhodobacterales (Alphaproteobacteria)						
Sphingomonadales (Alphaproteobacteria)						
Caulobacterales (Alphaproteobacteria)						
Rhodospirillales (Alphaproteobacteria)						
Pseudomonadales (Gammaproteobacteria)						
Vibrionales (Gammaproteobacteria)						
Alteromonadales (Gammaproteobacteria)						
Chromatiales (Gammaproteobacteria)						
Campylobacterales (Epsilonproteobacteria)						
Burkholderiales (Betaproteobacteria)						
Thermoanaerobacterales (Clostridia)						
Halanaerobiales (Clostridia)						
Clostridiales (Clostridia)						
Bacteroidales (Bacteroidetes)						
Flavobacteriales (Flavobacteria)						
Fusobacteriales (Fusobacteria)						
Bacillales (Bacilli)						
Lactobacillales (Bacilli)						

Legend (% of bacterial community)

0%	
>0 - 5%	
>5-10%	
>10-20%	
>20-30%	
>30-50%	
>99%	

Metagenomic Sequencing of Produced Water Microbial Communities

Produced water microbial communities can be characterized as having low diversity relative to injected waters and early stage flowback produced waters. Samples of produced water from multiple wells of differing age have shown the consistent presence of halophilic, fermentative bacterial species that dominate these low diversity populations. Metagenomics involves the sequencing of total community DNA and provides a snapshot of the metabolic potential that can then be correlated with physicochemical conditions in the environment. This work is intended to provide information on the potential biogeochemical cycling taking place in fractured natural gas wells.

Samples of fracturing source water and flowback (Day 1 and Day 9) from a Marcellus Shale gas well in southwestern Pennsylvania were submitted for metagenomic sequencing, which provided a thorough taxonomic characterization of DNA present in these samples and a functional annotation of genes. This is the first metagenomic study of produced water from any oil or gas reservoir. Figure 29 and Figure 30 present a high level overview of taxonomic data and functional abundance from the metagenomic analysis.

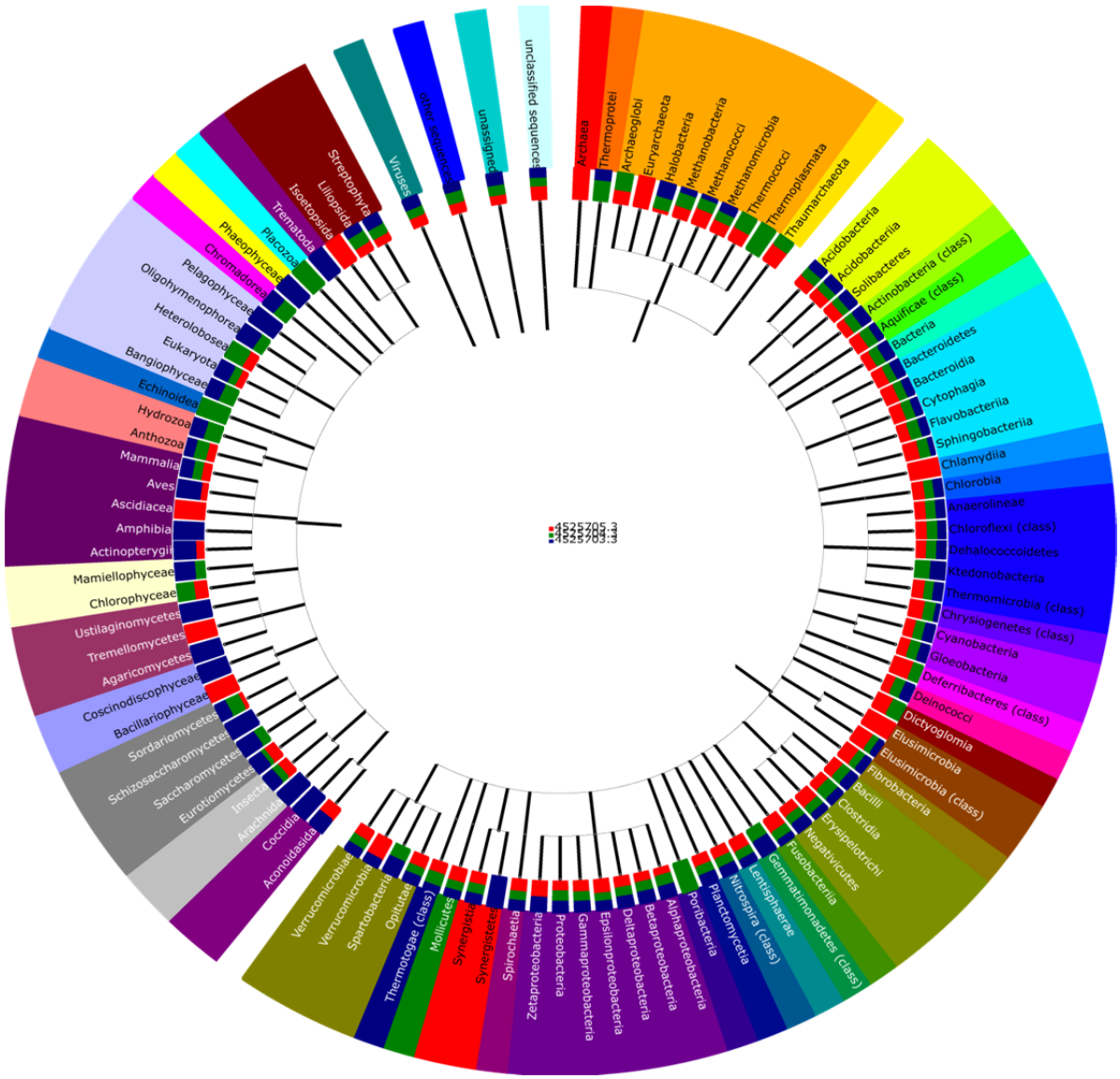


Figure 29: Relative abundance of prokaryotic and eukaryotic classes in fracturing source water (red), produced water day one (green), and produced water day nine (blue). Red, green and blue designations are showin in the inner portion of the circle. Colors on the outer portion of the circle indicate common phyla of the microbes.

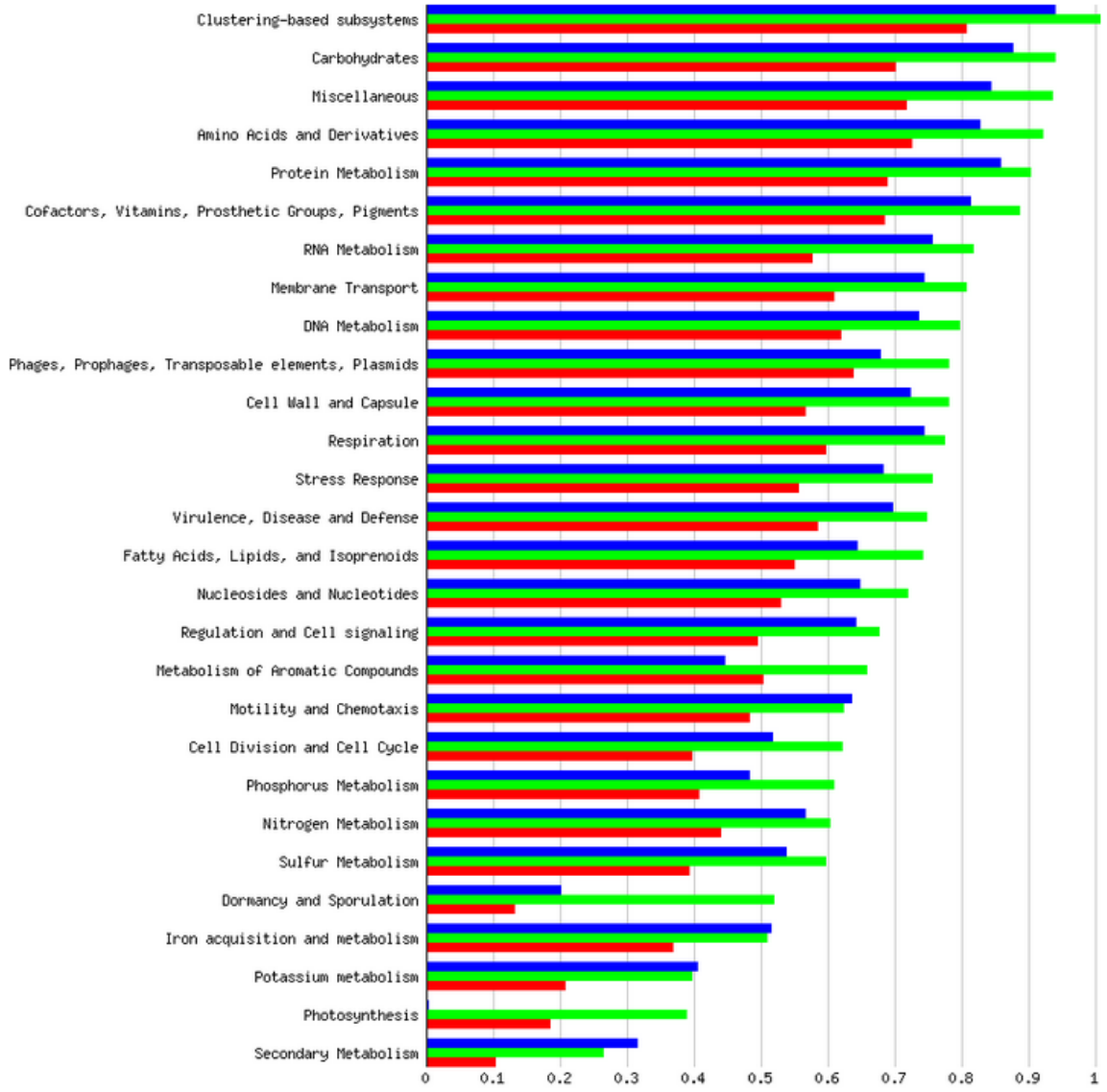


Figure 30: Relative comparison of functional abundance in fracturing source water (red), produced water day one (green), and produced water day 9 (blue). The functional annotations to genes were provided based on comparison to the subsystems database.

MG-RAST (the Metagenomics RAST) server is an automated analysis platform for metagenomes providing quantitative insights into microbial populations based on sequence data, and this was used to provide insights into the functional genes provided in the sequence data above. Level 1information indicates the broadest set of functional categories to which sequences are assigned. Level 2 refers to more specific functional assignments within the broad Level 1 category. The metabolic potential (based on Level 1 and Level 2 functional categories) between samples of fracturing water and flowback water (Day 1 and Day 9) was compared in a normalized manner to account for differences in community structure, size of the library, and gene content between samples; and to effectively compare low categories that are in low abundance (Figure 31and Figure 32).

The five most abundant Level 1 functional categories in all three samples were found to be clustering-based subsystems (e.g.: genes where functional coupling is evident but function is unknown;~14 percent),

carbohydrate metabolism (7-9 percent), amino acids and derivatives (e.g.: genes associated with amino acid metabolism, ammonia assimilation, and urea cycle; 7-8 percent), miscellaneous (e.g.: genes associated with iron sulfur cluster assembly and Niacine-Choline transport and metabolism; 8-9 percent), protein metabolism (6-8 percent), revealing the dominant roles of these categories in microorganisms from all samples (Figure 30). However, these broad categories are known to constitute dominant functional categories in many previous studies from very different environments (soil, marine samples, activated sludge, freshwater, and hypersaline environments), suggesting that the differences in metabolic profiles between these environments lies in the less-abundant functional gene categories. While the actual abundance of these dominant Level 1 functional categories across all three samples were similar (data not shown), normalization of gene abundance data shows a relative increase in each of these functional categories in the produced water samples as compared to the fracturing source water (Figure 30). This suggests that the genes necessary for survival are enriched in the produced water community, and from a genome perspective only the more adaptive microorganisms emerge in the produced water.

While comparison of gene abundance affiliated with the dominant broad Level 1 categories suggest similar functional profiles across samples, analysis of Level 2 functional categories within these Level 1 categories reveal sample-specific differences in metabolic capabilities (Figure 31). For instance, within the Level 1 carbohydrate metabolism category, genes related to more specific (Level 2) carbohydrate metabolism functional categories such as mono-, di-, oligo- and polysaccharides, and amino-sugars metabolism were present in higher relative abundance in the produced water samples (Figure 31). This correlates well with the expected higher concentration of carbohydrates and polysaccharides in produced water samples from addition of fracturing fluid amendments such as friction reducer and gel, as well as, organic compounds from the shale formation. These carbohydrates compounds, added during production of the hydraulic fracturing fluid as well as hydrocarbons from the subsurface, may serve as substrates for the growth of the microbial community.

Less abundant Level 1 functional categories of interest that show an overall increase in normalized abundance in produced water samples (Figure 31) included genes affiliated with stress response (3 percent), respiration (3-4 percent), iron acquisition and metabolism (1 percent), sulfur metabolism (1 percent), and dormancy and sporulation (0.2-1 percent). Analysis of Level 2 functional categories within these Level 1 domains also showed differences in metabolic potentials between these samples (Figure 32). For example, in the Level 1 domain of sulfur metabolism, the relative abundance of genes affiliated with Level 2 functional categories of inorganic and organic sulfur assimilation increased in produced water samples as compared to fracturing source water (Figure 32). The identification of bacteria affiliated with the classes *Clostridia* and *Gammaproteobacteria* that can metabolize inorganic sulfur compounds, and the higher concentrations of total sulfur in produced water samples (Table 6), compared well with detection and emerging abundance of these genes. Within the Level 1 domain of iron metabolism, contigs affiliated with siderophores, undetected in the fracturing source water, increased with time in produced water samples (Figure 32). Siderophores are strong chelators of ferric iron secreted and utilized by bacteria for iron metabolism. The relative increase in the abundance siderophore affiliated genes correlated with an increase in total iron concentrations with time in produced water (4.2-81.6 mg/L) (Table 6). Within the Level 1 dormancy and sporulation category, high relative abundance of Level 2 spore DNA protection related contigs in produced water Day 1 sample (Figure 32) suggested the potential for long term dormancy of cells through DNA protection. Further comparative genomics revealed that these genes were similar to those present in *Thermoanarobacter*, a bacterial order that constituted 16 percent of the total community in this sample, showing the robustness of this approach. An increase in relative abundance of spore forming bacteria and genes affiliated with sporulation and dormancy could indicate a potential response to commercial biocides and subsurface temperatures.

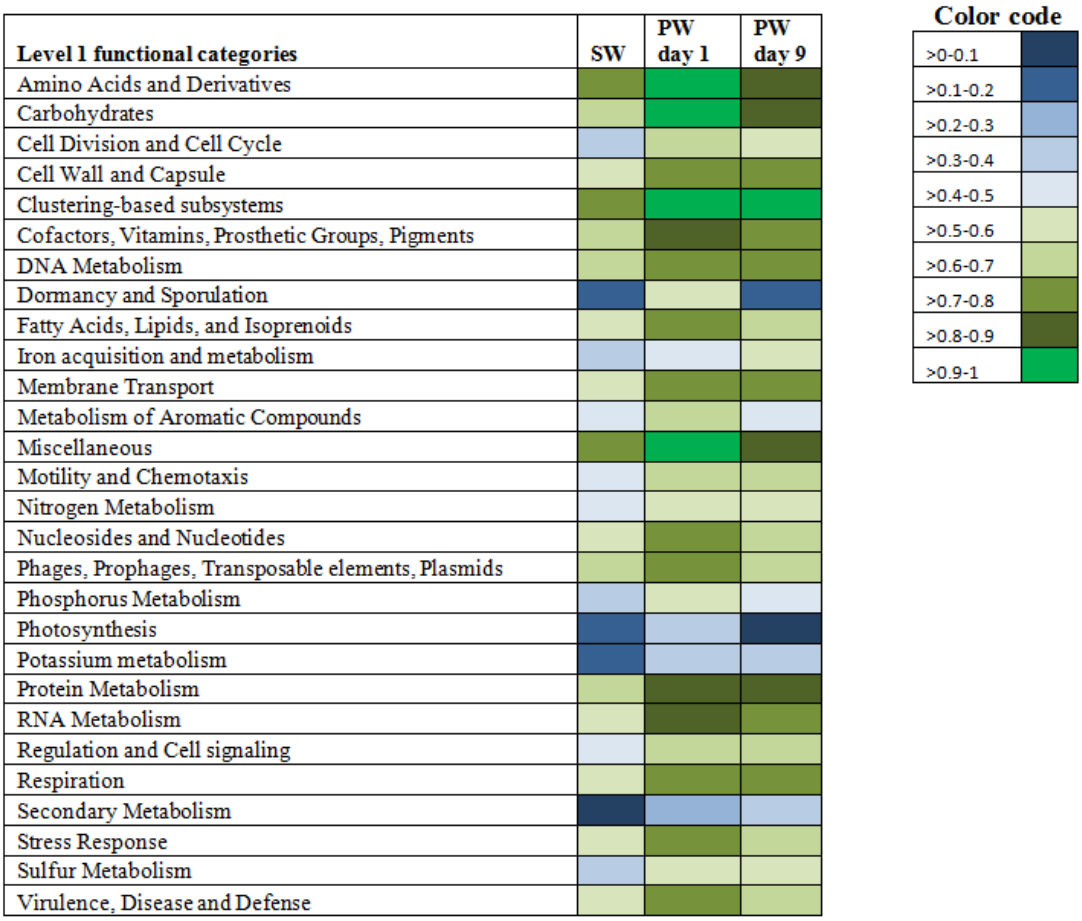


Figure 31: Normalized abundance (values of 0-1) of contigs (genes) belonging to Level 1 functional categories in source water (SW), produced water day 1 (PW day 1) and produced water day 9 (PW day 9). Functional annotations were assigned based on the Subsystems database.

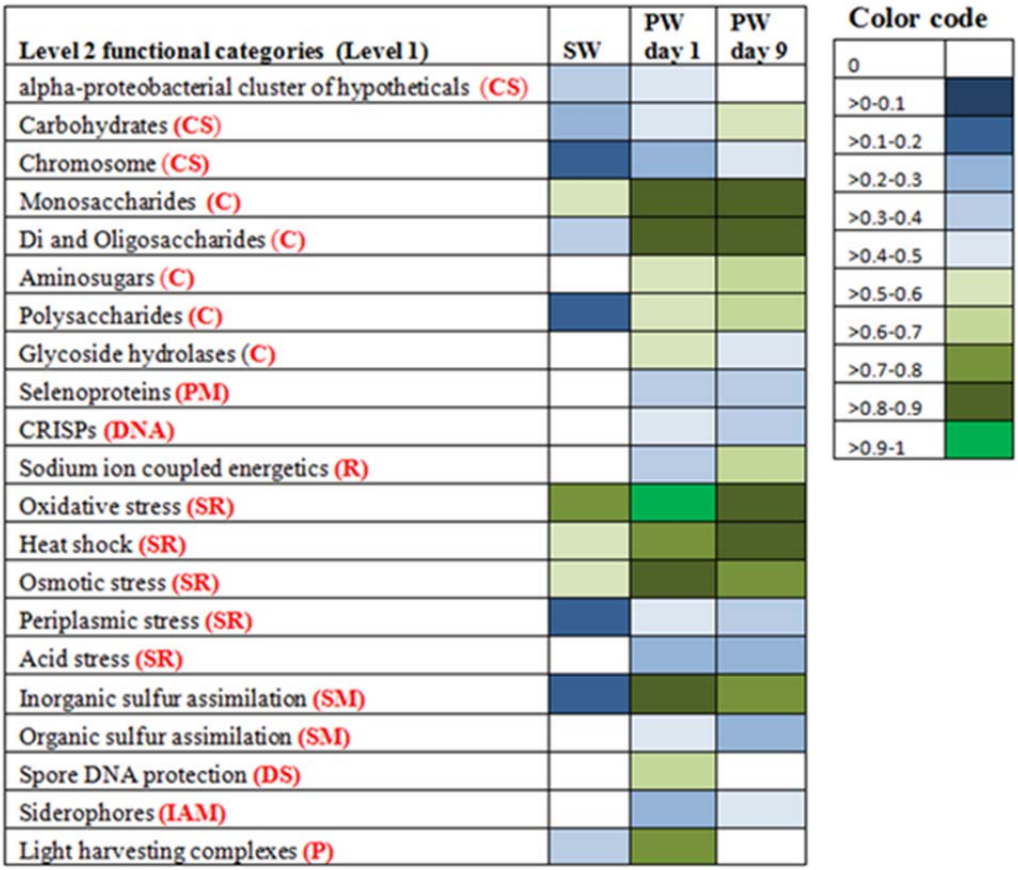


Figure 32: Normalized abundance (values of 0-1) of contigs belonging to selected Level 2 functional categories within associated Level 1 categories in source water (SW), produced water Day 1 (PW Day 1) and produced water Day 9 (PW Day 9). Functional annotations were assigned based on the Subsystems database. The affiliations of Level 2 categories to Level 1 categories are coded as follows CS- Clustering based subsystems; C- Carbohydrates; PM- Protein metabolism; DNA- DNA metabolism; R- Respiration; SR- Stress response; SM- Sulfur metabolism; DS- Dormancy and sporulation; IAM- Iron acquisition and metabolism; P- Photosynthesis.

Table 6: Chemical composition of source water and produced water (PW) samples Day 1 and Day 9.

	Concentration (mg/L)		
Element	Source water	PW day 1	PW day 9
Na^+	2953	13899	43094
Total Fe	BDL[1]	4.2	81.6
Total S	7.4	32.4	55.7
$SO4^{2-}$	6.2	31.7	9.3

[1]BDL- Below detection limits

Stability of Produced Water Treatment Residuals

The research objective is to characterize residual solids from the treatment and storage of produced water for potential release of toxic constituents to groundwater, soil or atmosphere. Sludge samples have been collected from a centralized facility that treats produced water for reuse in hydraulic fracturing. These samples are being subjected to simulated weathering protocols that are designed to mimic conditions in landfill disposal or burial at well site. Leachates/digests from simulated weathering procedures are being analyzed for chemical species (elements) of concern.

Biogeochemical Factors that Affect the Composition of Produced Waters and the Utility of Geochemical Tracer Tools

Source term data sets are needed to develop knowledge of parameters that may be important considerations when using alternative fracturing fluids, for use in modeling potential leachates from shale gas production waste solids, and to constrain field-based geochemical tracer measurements. The results of research activities described below will be used to inform geochemical monitoring strategies, manage potential risks associated with shale gas activities, and predict the longevity of gas production from hydraulically-fractured shale gas reservoirs.

Metal-Shale Interactions and Reactions

A primary goal for this research was to produce data sets to help identify biogeochemical processes that affect the mobilization of contaminants and tracers from shale gas reservoirs. This research focused on identifying geochemical signatures related to fluid-rock interactions of gas shale systems that result in the release of metals, organics, and naturally-occurring radioactive material (NORM). In addition, other geochemical tracers (e.g., isotopes and rare earth elements) were monitored as part of the characterization and experimental activities in order to better constrain their expected behavior in various field scenarios. Biological reactions also were investigated, as they could affect both the release of tracers and contaminants and overall system performance (e.g., integrity of metal casing in wells).

Efforts include the chemical and mineralogical characterization of natural samples (core, produced waters, and drill cuttings), development of techniques for analysis of trace elements in complex produced water matrices, and experimental work towards probing shale reaction mechanisms of importance in shale reservoir systems.

Development of Analytical Techniques for Trace Element Detection

Various methods may be employed to separate trace analytes from complicated environmental matrices. For example, analysis of rare earth elements (REE; a potential natural geochemical tracer) in produced waters from shale formations can be complicated by the high concentrations of chloride in these waters. In order to analyze rare earth element concentrations in our experimental samples, preconcentration techniques are undergoing development in order to better prepare the samples for ICP-MS analysis.

One technique is focused on using the seaFAST preconcentrator unit (Elemental Scientific). This uses column chemistry techniques to isolate analytes of interest from complicated fluid samples prior to injection into the ICP-MS instrument for elemental analysis. After calibration-testing the instrument, its robustness for analysis of complex samples was tested by analyzing REE profiles for acid mine drainage samples with published REE values. After modifying the procedure and optimizing instrument parameters, excellent agreement was obtained, as shown in Figure 33. Procedures for analysis of produced waters from shale formations containing extremely high Ba/REE ratios was undergoing development at the time of this report.

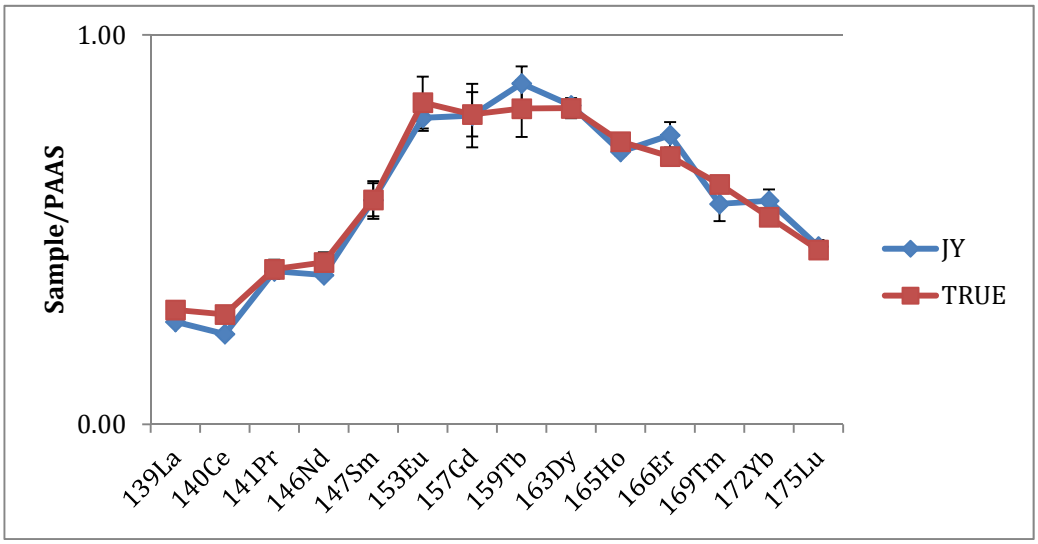


Figure 33: Comparison of acid-mine drainage sample generated using Seafast (JY) with published certified values (True).

In a complementary effort, the potential for using alternative liquid-liquid extractions for evaluating REE content in geologic fluids was investigated as part of the Geochemical Tracers project within this research portfolio (see description of project below, "Develop a Suite of Naturally Occurring Geochemical Tracer Tools that Verify the Sources of Fluids in Complex Geologic Systems"). These efforts will be coordinated as part of this project in future research.

Characterization of Elemental Profiles in Black Shale Samples

Characterization and evaluation of REEs and arsenic from various black shale formations was investigated through digestion and analysis of shale samples from a suite of samples obtained from six different locations in the continental United States (Kansas, Iowa, Oklahoma, Kentucky, North Dakota, and Pennsylvania), ranging in age from Devonian to Upper Pennsylvanian, and twenty Cretaceous black shale samples from the Demerara Rise. The ultimate goal of this approach is to unravel how the different depositional and post-depositional environments control the accumulation, diagenesis, and remobilization of metals in black shale systems, to develop a predictive model of remobilization propensity during shale gas development efforts.

Results to date indicate that total REE abundance (ΣREE) ranges from 35 to 420 ppm in organic rich samples from Stark and Hushpukney shales, Kansas. Post Archean Australian Shale (PAAS)-normalized REE concentrations ranged from 0.5 to 7, with the highest enrichments observed in the middle REE (MREE; Sm to Ho). Neither the ΣREE nor the MREE enrichments correlated with organic carbon concentrations or postulated depositional redox conditions. However, the high MREE enrichment is associated with samples rich in phosphorite, which selectively traps the MREEs. In contrast to the Stark and Hushpukney shales, the samples from the Marcellus formation do not show the MREE enrichment, consistent with the lower phosphorous content of these shales.

In the anoxic reducing environments in which black shales were deposited, sulfide minerals such as FeS_2 trap aqueous arsenic in the crystal lattice, but arsenic is also known to bind to the charged surfaces of clay minerals. The arsenic concentration data show that the highest abundances (up to 70 ppm) are found in sediments with the highest total sulfur concentration (to 2.6 ppm), but there was no clear correlation with organic carbon or aluminosilicate content. These results will be compared with ongoing flowback water

analyses from ten producing wells in Pennsylvania, and will be presented at the American Geophysical Union Fall Meeting (Yang et al., 2013).

Experiments to Probe Fracturing Fluid-Shale Reactions under Downhole Conditions

The rationale for this work is to provide insight into the processes that control contaminant liberation and migration to produced fluids in order to predict their composition and provide a means for risk assessment during exploration. This study also provides a basis for understanding the source of geochemical and isotopic tracers that have been used to identify surface and ground waters influenced by Marcellus Shale drilling activities. Experiments, containing a 20:1 fluid-rock ratio, were conducted at 275 bars (4,000 psi) (conditions present during Marcellus Shale drilling operations in Southwestern Pennsylvania). The experimental temperature of 130°C was chosen in order to drive mineral reaction kinetics while remaining in the same mineral reaction realm as modeled at 65°C (actual borehole temperature). Experimental run time was ~16 days (382 hours). To provide a basis of understanding for the impact that hydraulic fracture fluid has on the evolution of mineralogy and fluid chemistry, two experiments were run in parallel: one containing a modeled brine to simulate formation fluids (EPACT-1) and one containing a 7:3 mixture of brine-synthetic frac fluid (EPACT-2). The synthetic fracture fluid recipe was created after a survey of industry data found on fracfocus.org (Liu et al., in prep.).

The Marcellus shale sample was from the 7,846 foot depth of a core from Greene County, Pennsylvania. Synthetic brine was designed to mimic natural formation waters, as calculated through equilibrium modeling of interactions between the formation mineralogy with saline fluids. Formation mineralogy information was based on knowledge of the major and minor phases in the 7,846 foot sample being used for the experiments and results from Marcellus mineralogy in the literature. The starting fluid composition was based on information from Dresel and Rose brine review (Dresel and Rose, 2010). Calculations were performed using Geochemist's Workbench 9.0 standard edition using the thermo.dat database.

Dissolved inorganic elements were determined by ICP-OES and ICP-MS, and dissolved anions by ion chromatography. Samples for total carbon analysis were collected in glass gas-tight syringes and immediately measured by coulometric titration. Aliquots for organic measurements were stored in brown glass vials and refrigerated at 4°C until measurement by liquid chromatography-quadrupole time of flight mass spectrometry (LC-QTOF).

Both reacted and unreacted solid shale samples were examined using X-ray powder diffraction (XRD), optical microscopy, and secondary and backscatter scanning electron microscopy (SEM). Sr isotopes were analyzed using rapid-throughput column separation techniques and analyzed via multicollector inductively coupled plasma mass spectrometry (per methods described in Wall et al., 2013).

Results show that the EPACT-2 experiment (containing fracturing fluid) released elevated levels of certain elements relative to the EPACT-1 experiment (brine-only control experiment; Figure 34). Interpretation of the other analyses is ongoing, and a NETL Technical Report Series document is undergoing development to report full results (Hakala et al., in prep). Preliminary results from this experimental work were presented at the AAPG Annual Meeting during May 2013 (Hakala et al., 2013) and the Geological Society of America Annual Meeting during October 2013 (Wall et al., 2013). To date, geochemical modeling of the experimental results indicates that major mineral reactions are driven by low pH in the EPACT-2 experiment (a result of adding the synthetic hydraulic fracturing fluid containing hydrochloric acid).

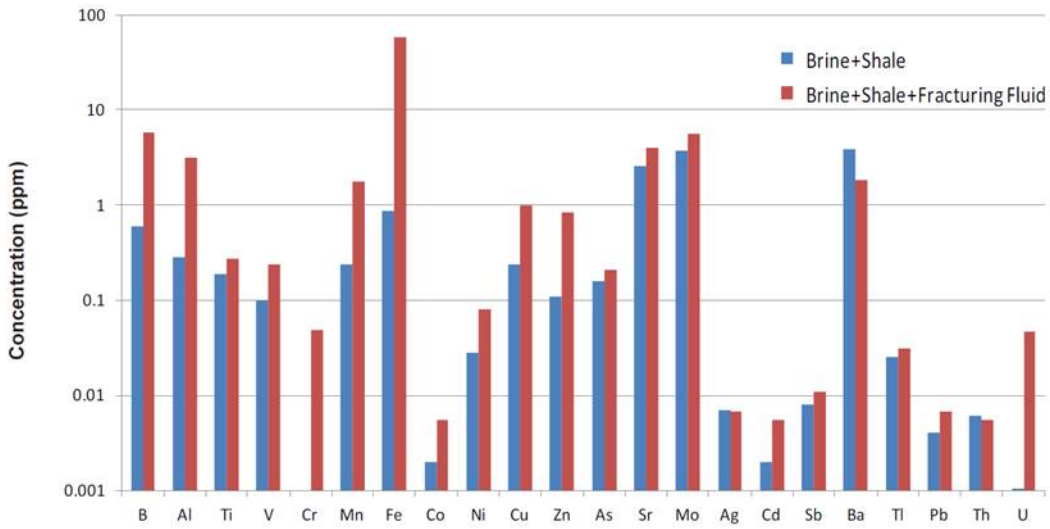


Figure 34: Metal and trace element concentrations after 15 days of reaction in the rocking autoclave show enrichment of most elements in the experiment containing fracturing fluid ("Brine+Shale+Fracturing Fluid" = EPACT-2) relative to the control experiment ("Brine+Shale" = EPACT-1). Cr only was detected in the experiment with fracturing fluid. Ba and Th are elevated in the control experiments.

Ion Exchange from Clay Minerals in Marcellus and Utica Shale Samples

One hypothesis used to explain the increase of salinity during flowback is that ion exchange processes are in part responsible for releasing salts into solution. In order to evaluate this hypothesis, ion exchange data were completed on approximately 40 Marcellus and Utica Shale samples. The values were obtained using a Cu complexing solution, and measured by UV-Vis spectroscopy. Results were compared to those obtained by a traditional Mg and Ca exchange method. The data show that cation exchange in both shales is low, and representative of shales dominated by illite and kaolinite rather than smectite and montmorillonite (Figure 35). These data are consistent with clay mineralogy obtained by quantitative XRD on the same samples.

To determine the contribution of cation exchange capacity (CEC) to salinities and cation compositions that form in fluids in contact with these shales, batch reactions at standard temperature and pressure were also completed. The concentrations of major cations (Na and Ca), which became elevated in batch fluids after 24 hours of reaction with the shale sample, could not be explained solely by cation exchange. Cation exchange could only account for <1 percent of the Ca and Na concentration increase in the batch fluids. Batch reactions were completed with 1 g solid material and 10 mL solution, and starting solutions of deionized water, 10 mM NaCl, and 10 mM $CaCl_2$ were used. These results were presented at the Geological Society of America Annual Meeting in October 2013 (Bank et al., 2013).

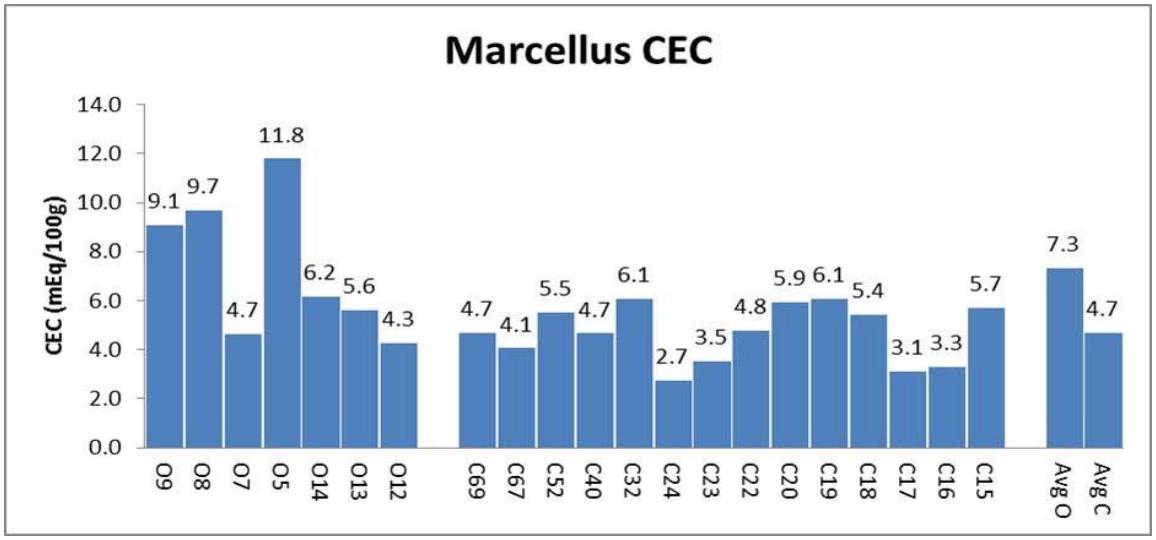


Figure 35: Cation exchange capacity (CEC) for Marcellus and Utica Shale samples. No trends were observed with total clay, total organic carbon, or Fe content. Correlation was observed with the amount of 2M1 illite (R^2=0.39). Some outcrops are less mature, with higher CEC.

Evaluating the Role of Microbiology on Chemical Reactions in Shale Reservoirs

Evaluating the role of microbially-mediated reactions is necessary to evaluate overall biogeochemical factors that can affect shale reservoir and produced water chemistry. In order to evaluate potentially important biogeochemical reactions, experiments were designed to examine the microbial communities that develop in Marcellus shale incubated with hydraulic flowback water under oxic and anoxic conditions. An osmopump sampler to be used for collecting experimental samples was constructed this year (Figure 36).

Figure 36: Osmopump to be used with the osmosampler.

Preliminary Geochemical Extractions on Marcellus Shale Drill Cuttings

In order to evaluate the potential effects of different storage and disposal conditions of drill cutting geochemistry, cuttings derived from both non-water-based and water-based drilling techniques were

subjected to various chemical extractions representing different chemical environments. Results show that pre-extraction, the cuttings solids had similar mineralogies (including the presence of framboidal pyrite); except for the following observations: non-water based drill cuttings contain a significant amount of barite, and water-based cuttings contain salts. Rainwater extractions demonstrated that certain elements are enhanced relative to deionized water extractions, and elements for future focus include: Se, Cr, and Cd. Results from an acid-base titration extraction show that trace metal concentration trends differ between water-based and non-water-based drill cuttings, which could affect how these solids are handled during waste management. Further work is needed to evaluate whether differences in leaching results from drilling fluid interactions with the shale, or whether leached metals are from the drilling fluids (and not the shale itself).

Effects of Different Fracturing Fluids on Fluid Flow Pathways, and Tracer and Contaminant Release

The objectives of this work are to understand: (1) the nature of chemical versus physical carbon dioxide, water, methane, frac, and brine fluid sorption; (2) the selectivity of Marcellus Shale lithotypes to sorption of the aforementioned fluids; and (3) the effects of fluid exposure to lithotype composition.

An extensive literature review on the geology of the Marcellus Shale Formation located in the Appalachian Basin has been completed (Dieterich, 2013). Experiments are in progress to evaluate geochemical interactions between representative Marcellus Shale outcrop samples and three fluids: (1) methane, (2) carbon dioxide, and (3) water vapor under high pressure. Sorption interactions are being monitored with attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR). Future experiments will evaluate the effect of fracture fluid reactions with shale on the ability for gases to sorb to shale surfaces.

Changes in shale surface morphology and pore structure due to shale-fluid interactions are being evaluated using Environmental Scanning Electron Microscopy (eSEM). Initial imaging of core shale samples has been completed. The core samples are now reacting with formation fracturing fluid that was collected at a Marcellus shale gas drilling site. The samples will be kept at 2,000 psig and 50ºC to mimic formation conditions. The samples will be taken out of the reactor after approximately three months, and reimaged in order to understand any alterations and geochemical reactions between the fracturing fluid and shale samples.

Geophysical and Geomechanical Factors that Affect Subsurface Fluid and Gas Migration

The objective of this effort is to use simulation to determine the risk of hydraulic fracturing contributing to vertical seepage of fluids through the subsurface into underground sources of drinking water (USDW). Target areas of investigation include: determining whether there is a reasonable risk for hydraulic fracturing fluids to reach groundwater aquifers through the natural system; whether hydraulic fracturing can create pathways for other *in situ* fluids to reach groundwater aquifers; and whether the risk to groundwater can be determined or detected before injection occurs or at least before the groundwater is impacted.

The work in this effort has been focused on the Marcellus shale. The Marcellus is one of the premier shale gas plays in the country and has close proximity to the Pittsburgh, Pennsylvania and Morgantown, West Virginia NETL sites. Additionally, NETL has access to several data sets within the Marcellus. The study being performed on the Marcellus in this work can be used as an outline for investigating the above questions in other shale plays.

Over the course of the past year, the NETL-RUA compiled a dataset of the geomechanical and geophysical properties of the Marcellus and overburden formations and associated geologic units for use in predicting subsurface migration of gas and fluids. Several of the parameters that were measured or collected and their typical values are shown in Table 7 below.

Table 7: Key mechanical properties for Marcellus and overburden layers

Layer	Depth at Bottom (ft)	Stress Gradient (psi/ft)	Stress (psi)	Young's Modulus (psi)	Poisson's Ratio	Fracture Toughness (psi-in^0.5)
Overburden	7528	0.770457	5800	2.00E+06	0.25	1500
Burkett Shale	7555	0.896	6769.28	3.68E+06	0.213	1480
Tully Limestone	7614	0.955	7271.37	4.93E+06	0.248	1120
Hamilton Shale	7765	0.894	6941.91	4.02E+06	0.209	1630
Upper Marcellus Shale	7880	0.874	6887.12	3.36E+06	0.201	1595
Cherry Valley	7885	0.934	7364.59	3.71E+06	0.26	1725
Lower Marcellus Shale	7915	0.859	6798.98	3.30E+06	0.187	1405
Onondaga Limestone	7932	1.006	7979.59	5.11E+06	0.249	955
Huntersville Chert	8108	1.01135	8200	5.00E+06	0.25	1000

We used the commercial code MFrac to generate a model of the Marcellus shale and underburden and overburden layers. It was used to simulate fracture propagation through the Marcellus and overburden formations during hydraulic fracturing with slickwater and proppant. One fairly consistent observation in the simulations was the presence of the Tully Limestone above the Marcellus shale, which often acts as a barrier to vertical hydraulic fracture growth (Figure 37).

Field data from a published study (Jacot, R. et al, 2010) where the microseismic data led to the conclusion that the hydraulic fracture had penetrated the Tully was used to calibrate the hydraulic fracture growth model. A model generated for that specific location was calibrated by matching the vertical and horizontal fracture extent. The properties needed for the match were within the range of properties collected in the data gathering phase. This model shows promise that it can help explain the microseismic data collected at other sites where events appear above the Tully. Simulations from this model also suggest that the use of different proppant types of the same mesh has a minor impact on propped fracture length. Based on

this study, we found that selecting a different proppant type of the same mesh size should not have a significant effect on fracture dimensions or the propped fracture length, but can certainly help to create greater fracture conductivity and increase fluid flow in the fracture.

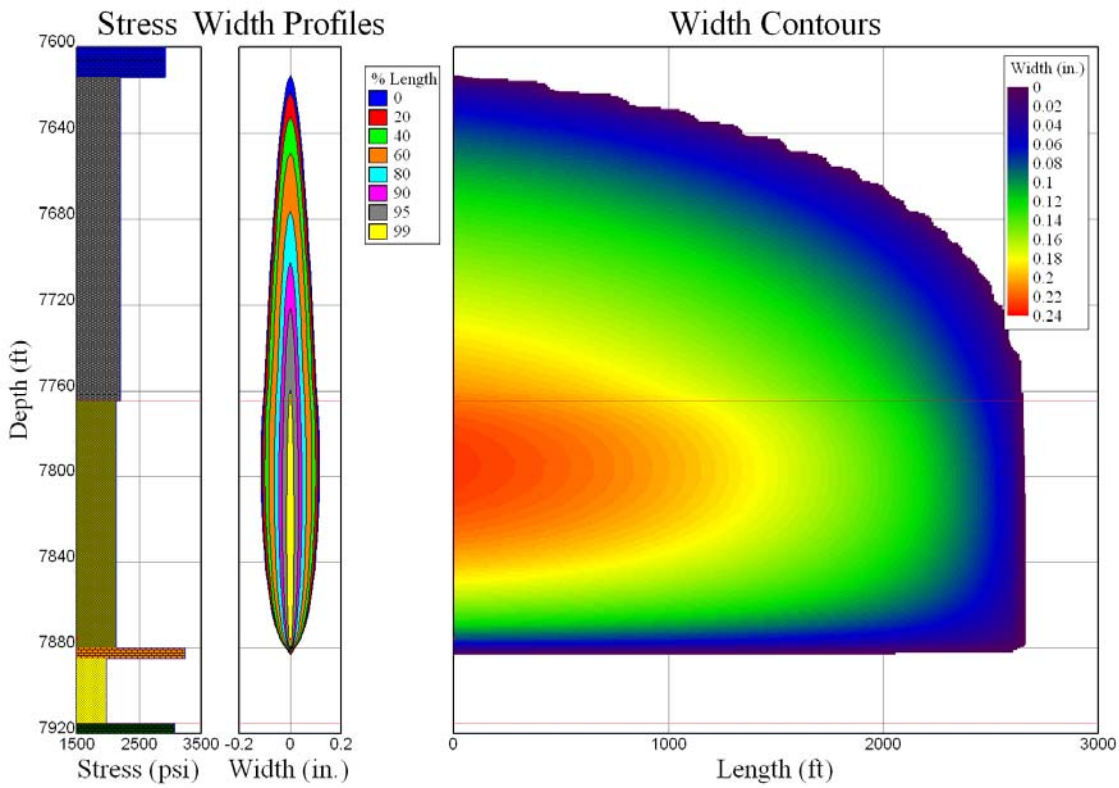


Figure 37: Simulation result showing fracture length, height, and width. The vertical fracture growth was halted within the Tully limestone, which is typical.

Finally, a simulation study was performed to investigate the potential vertical height of hydraulic fracturing using 600,000 gallons of water injected for each hydraulic fracturing stage. The five main properties which were considered for this study were: (1) horizontal stress gradient, (2) Young's Modulus, (3) Poisson's Ratio, (4) fracture toughness, and (5) fluid leakoff coefficient. A report has been drafted that outlines the findings from this study to date (Siriwardane et al., in preparation).

For the sensitivity study, a geologic column (Figure 38) with realistic thicknesses, depths, and properties for each layer were generated. A few hundred simulations were generated with the 600,000 gallons of injected volume, which is about the largest injected volume used anywhere in the Marcellus. The study to date showed that, at those volumes, it is common for the hydraulic fracture to extend vertically outside of the Marcellus. However, it is quite rare for a fracture to extend vertically through the Tully. Even when the hydraulic fractures extended beyond the Tully Limestone into other formations, they remained far from USDW (Figure 39). This figure shows that the clearance depth (distance from the ground's surface) is still quite deep, regardless of the formations' properties, as long as the Marcellus is suitably deep.

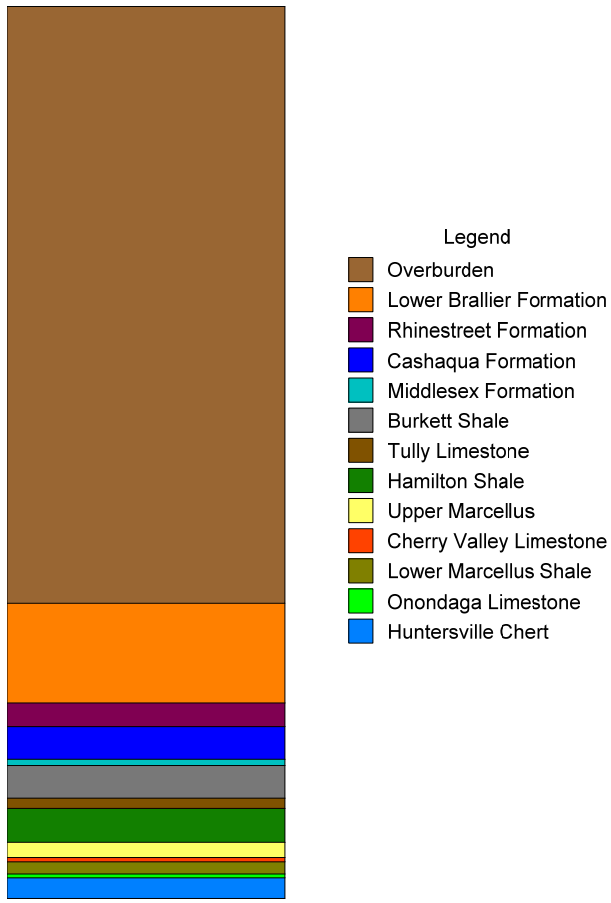


Figure 38: Geologic column generated for the simulation study.

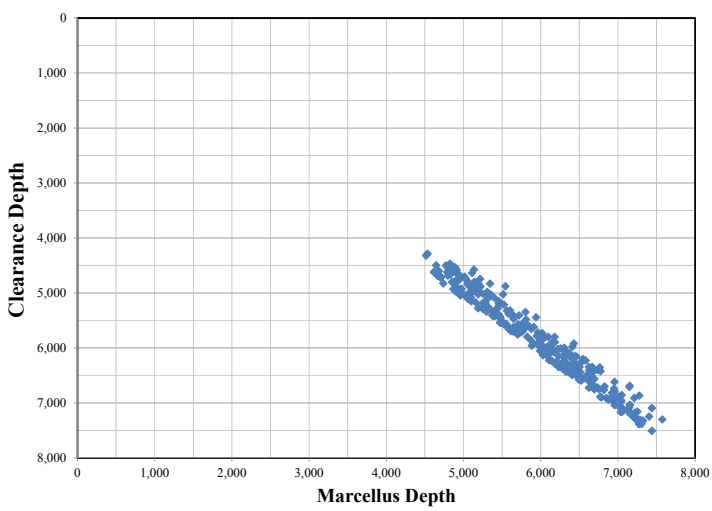


Figure 39: Fractures plotted as clearance depth (distance from ground surface) vs. Marcellus depth generated from simulation study of ~300 simulations of fracture growth.

Develop a Suite of Naturally Occurring Geochemical Tracer Tools that Verify the Sources of Fluids in Complex Geologic Systems

The objective of this effort is to develop a suite of naturally-occurring geochemical tracers that can be used to fingerprint the sources of fluids in complex geologic systems in order determine whether shale gas fracturing fluids have impacted groundwater.

Organic isotopes, inorganic isotopes, and rare earth element systems are used in geochemistry. Because each of these systems requires its own instrumentation and because each requires a different expertise, the following areas of the project are specific to the analytical techniques required for analysis. Each of the tasks includes the analysis of the isotopic composition of geologic end members, both fluids and solids, to provide for an interpretation of the source and reactivity of fluids. Fluid samples from Marcellus Shale flowback waters, Appalachian Basin gas field produced waters, regional groundwaters, surface waters, and other sources of water (e.g., acid mine drainage and coalbed methane produced waters) are examples of fluids analyzed for the different geochemical tracer systems described below.

Multicollector ICP-MS – Isotopes

Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) can be used to measure isotope ratios from liquid samples, reducing some of the analytical time required compared to traditional isotope analytical techniques such as thermal ionization mass spectrometry (TIMS). In order to advance the use of non-traditional isotopes as geochemical tracer tools, sample processing and isotope analysis time needs to be reduced in order to handle larger volumes of samples. Isotopes being considered within this effort include $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{238}U/^{235}U$, and $^{234}U/^{238}U$, and $^{7}Li/^{6}Li$.

Because of its abundance in natural waters and geologic samples, and because of its distinct signature in different geologic materials, $^{87}Sr/^{86}Sr$ was the initial system considered for development of a high-throughput sample processing technique. A column separation procedure coupled with analysis via MC-ICP-MS resulted in a ten-fold decrease in the amount of time for obtaining $^{87}Sr/^{86}Sr$ from complex natural brines. This work was accepted to the Journal of Analytical and Atomic Spectroscopy (Wall et al., 2013) and is being developed into a step-by-step laboratory procedure as a NETL Technical Report Series report (Wall et al., in preparation). In addition to Sr isotopes, U and Li systems are undergoing similar research and development to produce high-throughput methods for sample processing and analysis via MC-ICP-MS.

The characterization efforts for Sr, Nd, U, and Li end members in the Appalachian Basin were focused on: Marcellus Shale core residues from different locations, along with adjacent limestones and volcanic ashes; Upper Devonian, Bradford, and Venango Sands produced water samples; and produced waters from hydraulically-fractured Marcellus Shale. Data from these characterization analyses are currently being processed and developed into a database of Sr, Nd, and Li isotopic end members for the Appalachian Basin. Results from produced water analyses are presented in a prior section of this report ("Baseline Environmental Signals").

The use of $^{87}Sr/^{86}Sr$ as a tracer also was applied towards identifying inputs of bromide into the Allegheny Watershed, in collaboration with the Pittsburgh Water and Sewer Authority. Completion of isotope mixing models is underway at the time of this report.

IRMS – Isotopes

Stable isotopes of C, H and O are traditionally measured via isotope ratio mass spectrometry. Isotopes of these elements can provide information about the source of CO_2 and CH_4 in natural samples, and in this study were used to evaluate whether mixing occurred between the Marcellus Shale and overlying Upper

Devonian geologic units. Results from this effort were applied towards evaluating geochemical signatures as described above in the section on "Baseline Environmental Signals."

Liquid-Liquid Extraction Coupled with ICP-MS – Rare Earth Elements

Rare earth elements (REEs) can be used to identify waters sourced from different geologic end members. This effort started with a focus on understanding the overall abundance and statistical signatures that REEs can impart on waters of different types, and the literature review is being developed into a manuscript (Noack et al., in preparation). One finding from the literature review is that multiple REEs are needed in order to distinguish water types due to potential overlaps between individual elements.

Only 15 percent of studies in the current published literature addressed REE signatures in fluids that span the ionic strength range expected for Appalachian Basin brines. However, prior to working with field samples, methods for processing and analytical techniques for REEs from natural waters needed development. The focus of this effort centered on a liquid-liquid extraction technique after solid phase extraction techniques provided inconclusive results. The goal for the liquid-liquid extraction technique was to improve the mass balance obtained from this preconcentration step, in order to achieve reproducible REE partitioning into the extracted phase. The effort also focused on improving ICP-mass spectrometer tuning in order to analyze extracted samples effectively. Results to date demonstrate good reproducibility (Figure 40), and the error range for recovery (Figure 41).

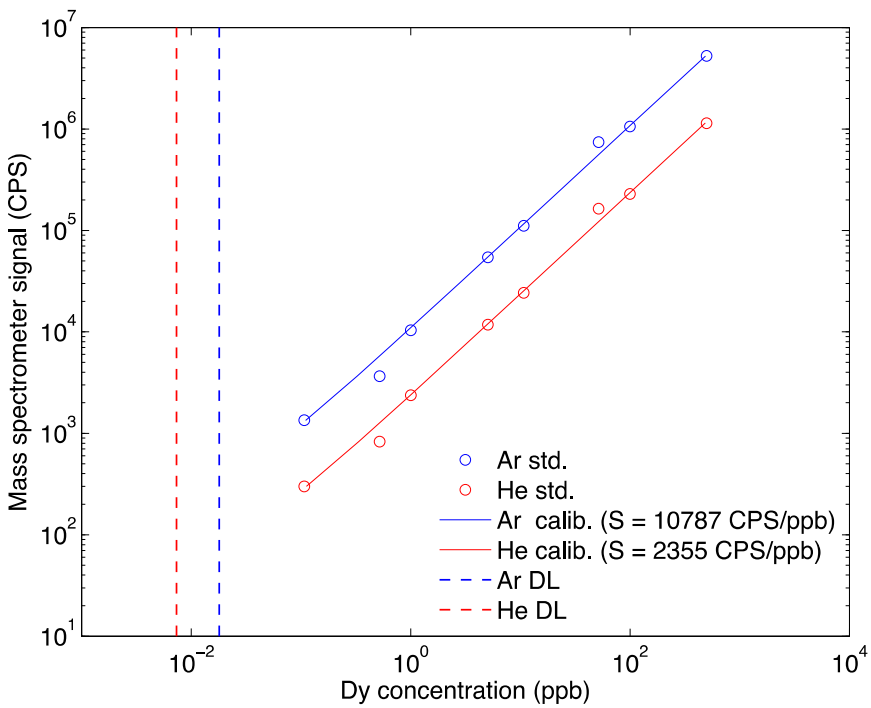


Figure 40: Calibration standards, fitted curves, and detection limits for analysis of Dy in 3 percent HNO_3 under two ICP-MS analysis modes. Standards prepared from 10 ppm mixed solution which includes all 16 REE, Th, and U. Analysis performed on August 9, 2013.

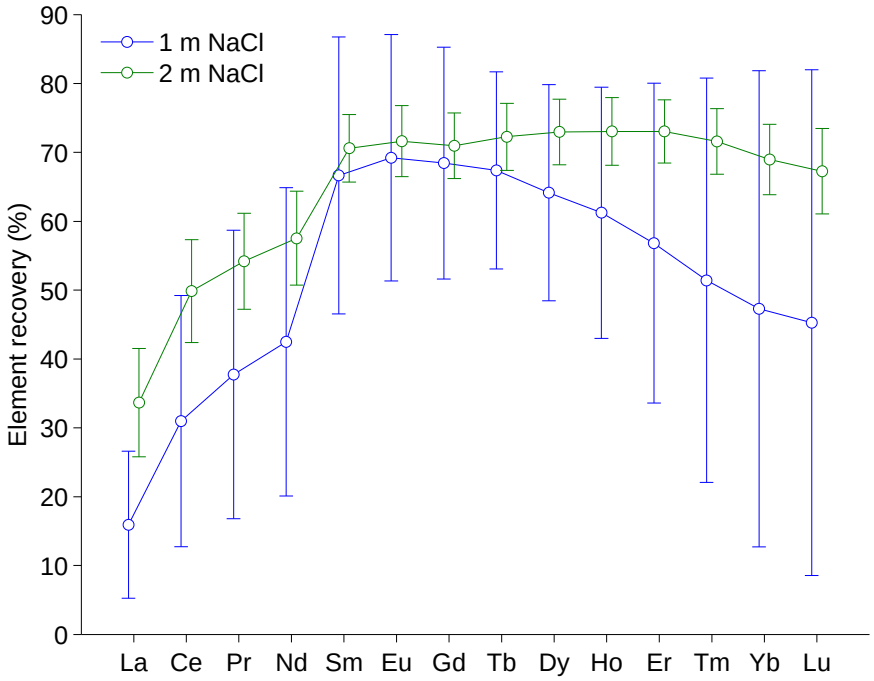


Figure 41: Recovery of REE from 100 ppb REE solutions of different ionic strength using miniaturized LLE methodology. Recovery calculated for argon-only (i.e. "no-gas") analysis mode of ICP-MS. Analysis performed on September 13, 2013. Marker is μ ± σ from triplicate experiments.

Integration of Multiple Natural Tracer Signals

Models were developed to explore the conditions that can differentiate sources of contamination by examining a suite of variables that can control the distinct $^{87}Sr/^{86}Sr$ ratios from different sources. The variables explored included leakage characteristics (leakage rates and leakage time duration), leakage source characteristics (Marcellus flowback water, acid mine drainage), and background groundwater composition.

Gas flow from Shallow Gas Formations

This project addresses the issue of regional gas flow from shallow gas formations into the wellbore environment during drilling and/or completion, and the effects of shallow gas on the hydration of wellbore cements. The objective of this project is to increase understanding of the complex downhole conditions during wellbore cement placement within shallow formations containing high-pressure gas by documenting downhole conditions and simulating those in a high-pressure chamber to support the development of engineered solutions to prevent adverse environmental impacts of gas migration along the wellbore annulus.

Laboratory investigations focused on two principal activities: (1) modifying the way the borehole simulator applies load to the curing cement and (2) repairing deficiencies in the way pore-pressure is measured within the borehole simulator.

Modification to Borehole Simulator

Some of the modification to the borehole simulator included a fabricated platen-cap with inner and outer O-rings. Test results of this modification are shown in Figure 42 and Figure 43.

Figure 42: Newly fabricate platen-cap for applying vertical load to the cement slurry.

Figure 43: Cap inserted into simulated formation.

Modification of the hydrostatic load, as it is applied to the curing cement, was necessary. Initially, the cap performed well under the applied hydrostatic pressure. As downward movement approaches 1-in, the water within the curing cement can push out of the slurry and into the simulated formation. As the hydrostatic pressure increases, the cap encounters resistance from the asperities in the simulated formation, causing sticking and rotation. The combination of high gas pressure and large cap displacements allow gas to pass through the O-ring seal. A void can develop beneath the cap, prohibiting the creation of a water tight seal (Figure 44).

Figure 44: Recent tests using the modified cap to apply mechanical load, simulating hydrostatic pressure.

Modifications to the borehole simulator to solve the above problem are in-progress and include:

- Replacing the upper portion of the simulated formation with a smooth-walled circular pipe (Figure 45).
- Polish the existing simulated formation to reduce the frictional resistance.
- Cast new samples with more uniform circle gap in the formation.
- Tighten the O-ring seal.

- Lower gas pressures applied to the cap.
- Fabricate a new plastic 2-inch thick plastic cap to replace the initial ¾-inch plastic cap shown in Figure 42.

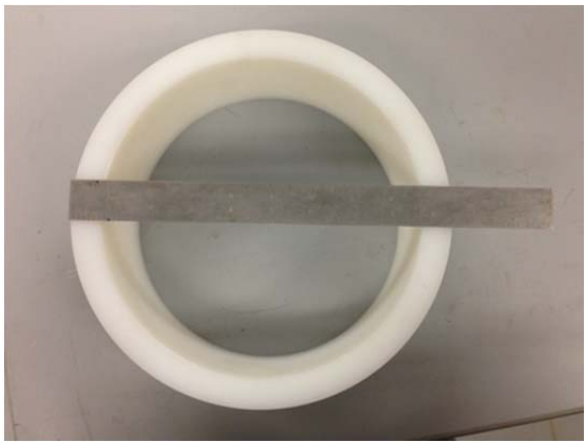


Figure 45: Smooth-walled circular wall placed within the top of the fabricated sandstone formation.

Repair Deficiencies in the Waypore Pressure Measured within the Borehole Simulator

The project team determined that the port used to measure pressure within the borehole simulator was not functioning correctly. Three corrective procedures are being implemented to improve the accuracy of the pore pressure measurements: (1) solid-prohibiting mesh barrier is applied to the outside port of the pressure transducer, (2) the receiving canal is filled with an incompressible oil, and (3) a more sensitive pressure transducer has been ordered.

Industry Supplied Cement Samples

A representative from Halliburton provided samples of cement for testing in September 2013.

Data Collection and Analysis of Case Studies and Cement Logs from Shallow Formation Gas Glow Occurrences

Compliance reports from the publically-obtainable PA-DEP well violations database, covering the date range of May, 2005 to March, 2013, were examined with a focus on unconventional drilling sites (Figure 46).

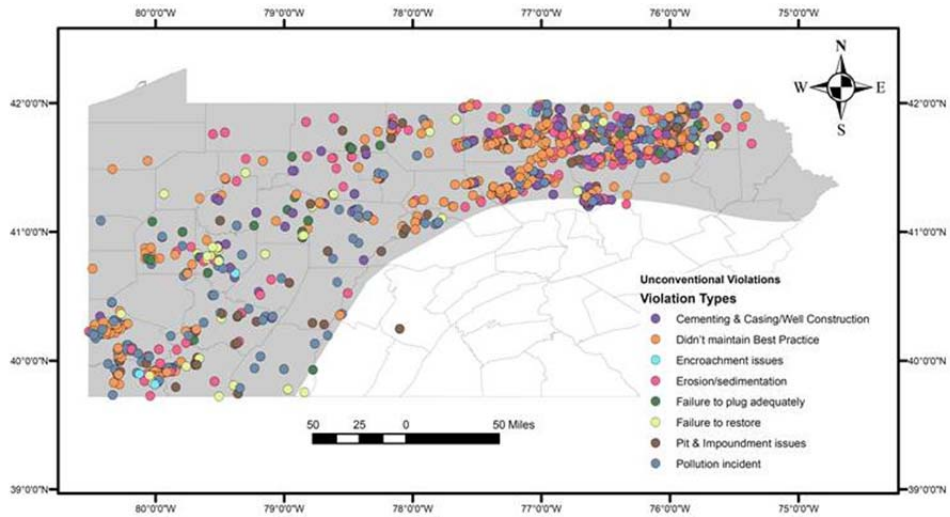


Figure 46: Unconventional drilling violation types in Pennsylvania (from PA-DEP Oil and Gas Compliance report May, 2005 to March, 2013)

Violations related to cementing and casing/well site construction issues are listed under the following sections of the governing laws:

- 207B – Failure to case and cement to prevent migrations into fresh groundwater.
- 78.73A – Operator shall prevent gas and other fluids from lower formations from entering fresh groundwater.
- 78.73B – Excessive casing seat pressure.
- 78.74 – Hazardous well venting.
- 78.81D1 – Failure to maintain control of anticipated gas storage reservoir pressures while drilling through reservoir or protective area.
- 78.81D2 – Failure to case and cement properly through storage reservoir or storage horizon.
- 78.83A – Diameter of bore hole not one inch greater than c/casing collar diameter.
- 78.83COALCSG – Improper coal protective casing and cementing procedures.
- 78.83GRNDWTR – Improper casing to protect fresh groundwater.
- 78.84 – Insufficient casing strength, thickness, and installation equipment.
- 78.85 – Inadequate, insufficient, and/or improperly installed cement.
- 78.86 – Failure to report defective, insufficient, or improperly cemented casing within 24-hours or submit plan to correct w/in 30 days.
- 79.12CW – Insufficient casing, BOP, cement, or wait on cement to prevent waste from conservation well.

Cementing and casing/well site construction violations are shown in Figure 47.

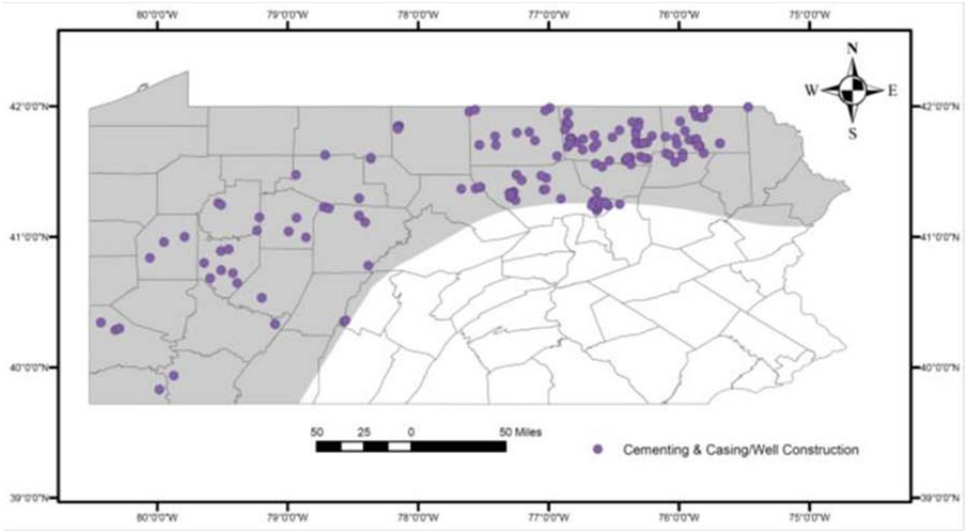


Figure 47: Cementing and Casing / Well Construction Violations in Pennsylvania.

Many of the violations shown in Figure 47 are not related to cementing issues. Figure 48 shows the location of cementing and casing violations that are potentially related to wellbore groundwater protection.

The wellbores shown in Figure 48 come from four violation codes with the most potential to affect wellbore groundwater protection (see list below).

Selected Violation Codes:

- 207B - Failure to case and cement to prevent migrations into fresh groundwater.
- 78.73A - Operator shall prevent gas and other fluids from lower formations from entering fresh groundwater.
- 78.73B - Excessive casing seat pressure.
- 78.83GRNDWTR - Improper casing to protect fresh groundwater.

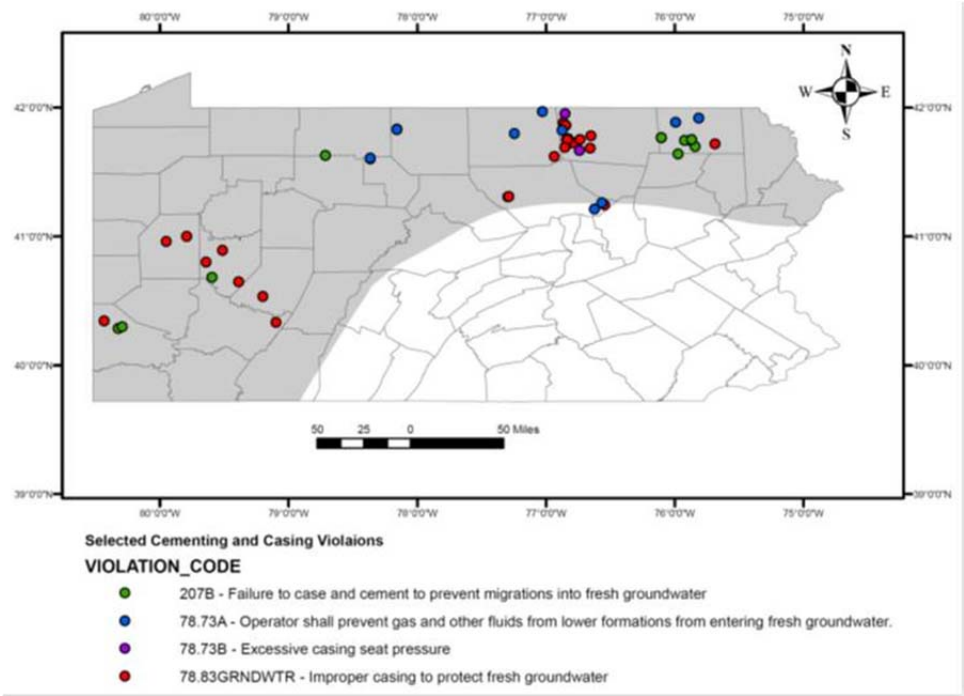


Figure 48: Location of selected violations in Pennsylvania.

Figure 49 and Figure 50 show the distribution of violations through time and by county. The year with the most violations was in 2010 (Figure 49) and Bradford county has the highest number of violations (38; Figure 50).

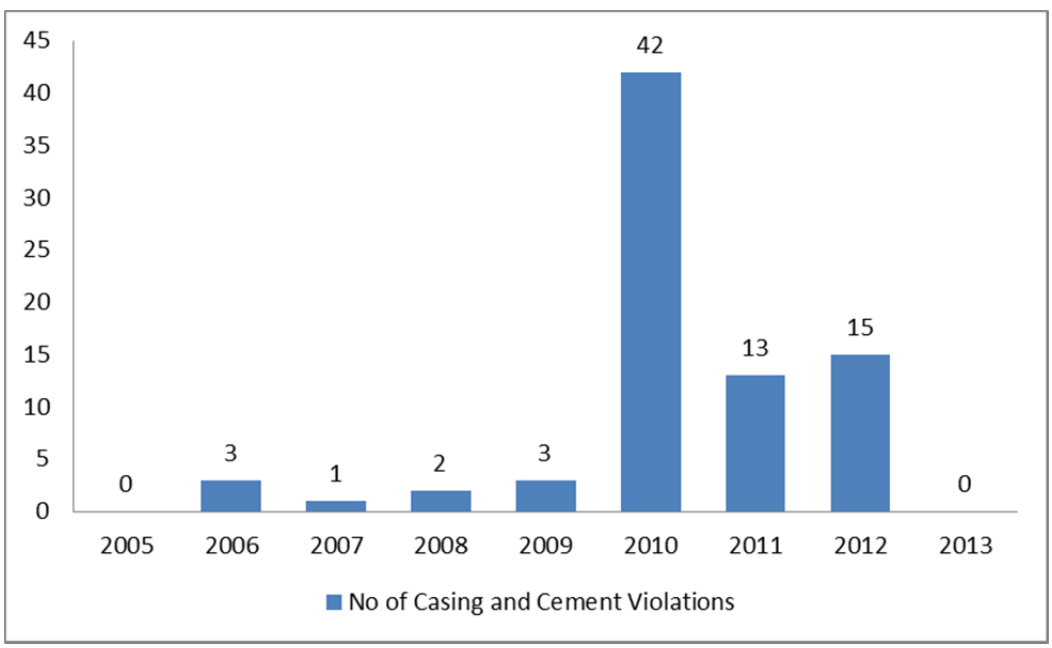


Figure 49: Number of casing and cementing violations by year.

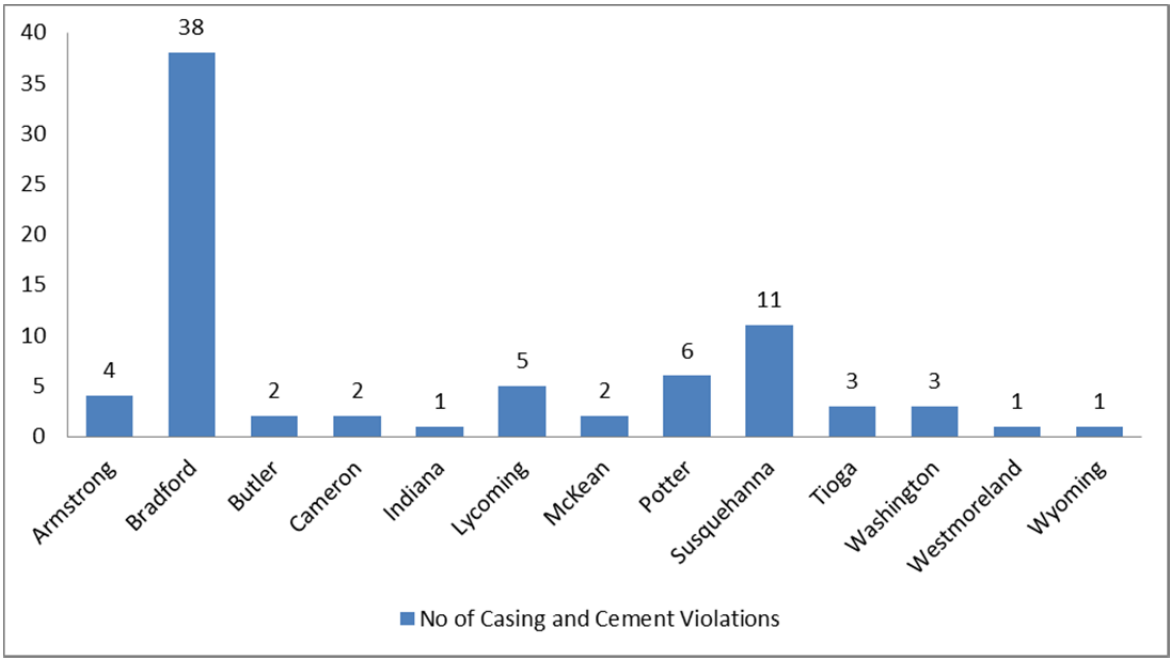


Figure 50: Cementing and casing violations by county.

The 79 cementing and casing violations that have the potential to impact wellbore groundwater protection will continue to be examined in greater detail.

Approach for Assessing Spatial Trends and Potential Risks with UCR Systems

The objective of this project is to develop a data framework and demonstrate a broad forecasting methodology that allows researchers, policy makers, regulators, or industry to evaluate potential risks and environmental impacts associated with development of unconventional hydrocarbon resources. In particular, this approach will capture field to regional-scale variability in hydrocarbon sources, migration pathways (anthropogenic and natural), and near-surface receptors such as groundwater and surface water systems.

Near surface receptors, such as groundwater reservoirs, are potentially impacted by unconventional hydrocarbon development activities. However, understanding the extent and probability of natural versus anthropogenic interactions between deeper hydrocarbon systems and shallow receptors remains unclear as demonstrated by field data and recent studies (e.g. Osborn et al., 2011, Molofsky et al., 2012, Susong, et al., 2012). This study is focused on evaluating the distribution and interaction between key subsurface systems, (1) hydrocarbon sources, (2) migration pathways, and (3) near surface receptors, in support of broad forecasting at the field to regional scale for risk and impact assessments. In particular, this study seeks to develop a science-based approach for integrating datasets associated with engineered-natural systems that can be utilized in a variety of basins and settings where subsurface hydrocarbon development and production activities may lead to impacts on near surface receptors.

In FY13 the project continued to focus on the compilation and standardization of key datasets to characterize hydrocarbon source, migration pathways (anthropogenic/wellbores), and receptors (groundwater systems); focusing on the Marcellus shale play in the West Virginia and Pennsylvania portions of the Appalachian Basin as a demonstration study area. Key accomplishments from this project in FY13 included development of an interpretation of the base of groundwater for West Virginia and Pennsylvania, produced using publically available subsurface data sources to be utilized as the receptor interval in the risk evaluation in this study. In addition, a geospatial analytical approach, the NETL Variable Grid Method (VGM) approach, supporting simultaneous display of spatial data trends and uncertainty was developed and has been selected for patent submission. Within NETL and the larger EPAct UCR Portfolio, this project continues to provide the spatial framework and data needed to support integrated risk assessments and modeling, comparison of field and laboratory analyses, including stable isotope and field monitoring efforts. Several knowledge transfer, derivative accomplishments, also resulted as part of this project including: (1) support for the development and release of NETL's Energy Data Exchange (EDX) version 2.0 in April 2013, (2) release of data-driven online applications that help support knowledge transfer of key unconventional resource datasets, including the Unconventional Resources Atlas that was initially released in 2012 but continues to be updated and augmented based on the data compiled for this project, and (3) the development and release of geoWELL to help support access to key subsurface information and data utilized by researchers through the UCR Portfolio as well as outside of NETL.

UCR Geospatial Evaluation Approach & Data Development Related

Largely publically available data and information was utilized for the Appalachian Basin, focusing on West Virginia and Pennsylvania to shake down and demonstrate the NETL VGM approach developed in part for this project. In FY13 data acquisition and evaluation activities focused largely on wellbore distribution analyses (through collaboration with ongoing research with the "Subsurface Fluid and Gas Migration Assessment" project described above) and to constrain the groundwater system as an example of a near surface receptor that could be impacted by historical and/or future UCR activities.

Information and interpretations to constrain the groundwater receptor for the Appalachian Basin in West Virginia and Pennsylvania were developed in FY13. The goal of this effort was to constrain the groundwater system utilizing largely existing, publically available data to interpret and constrain spatial

trends in the groundwater system in West Virginia and Pennsylvania (Figure 51). A TRS report is under development that will document and discuss the full approach and series of interpretations and analyses that were produced as part of this effort. An example interpretation from this effort is provided in Figure 52.

Building on the NETL VGM approach and development of key spatial layers to support individual and cumulative spatial risk and impact analyses related to UCR development, in FY13 the project team started focusing on how to concatenate multiple datasets to support cumulative spatial evaluations of attributes that could lead to increased impacts or risks associated with UCR resource development. Further development of this cumulative risk approach is one area of focus in FY14. The team will concentrate on finalizing this approach and through the rest of FY14 will develop the geospatial and statistical tool. Specifically, this tool will seek to communicate uncertainty and integrate multiple data-elements to support spatially distributed, cumulative risk evaluations.

Figure 51: Maps of the Marcellus Shale study area displaying data from selected sources used for the study. Moving from left to right, the USGS, PA DCNR and WV GES.

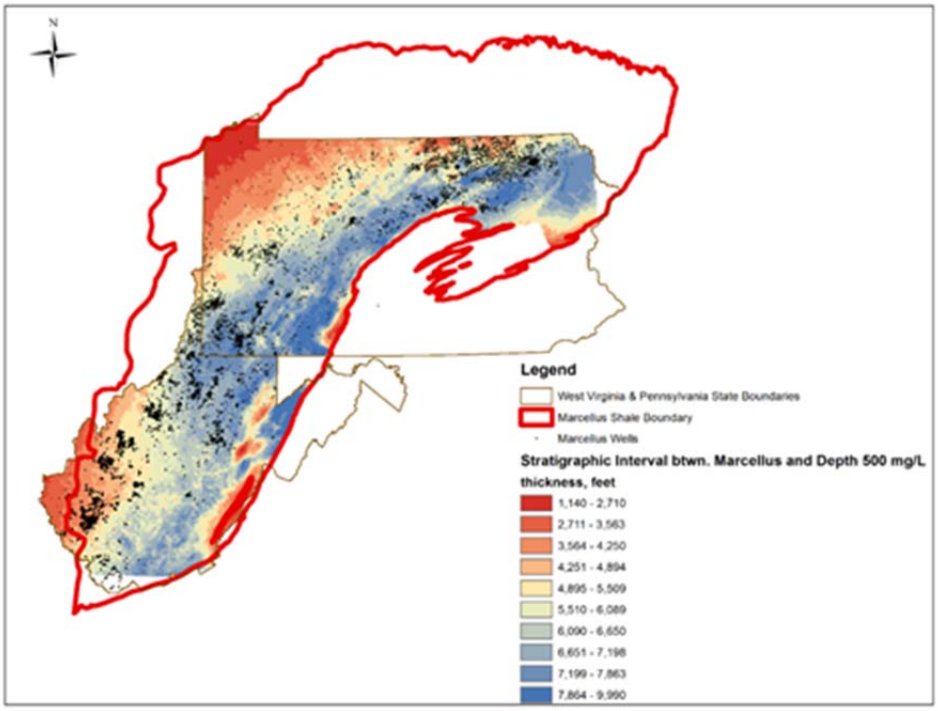


Figure 52: NETL ORD isopach map interpretation showing the stratigraphic interval between base of groundwater and top of the Marcellus Shale formation (from Vann, et al., in prep).

EDX and Knowledge Transfer Related

Release of EDX Version 2 included enhancements to allow UCR Portfolio Project teams to coordinate and collaborate more efficiently. https://edx.netl.doe.gov.

This project co-supports the development of NETL's Energy Data eXchange, an online coordination, collaboration, and knowledge transfer platform for NETL-affiliated research. In FY13, a dedicated portal summarizing the purpose, research, and products resulting from the NETL Complementary Program's Unconventional Resources Portfolio was produced. The research products page of the UCR Portfolio site is updated quarterly to reflect all new publications, presentations, datasets, and tools released via EDX. The UCR Portfolio page is available here: https://edx.netl.doe.gov/ucr/product_presentation.html.

This project also supported the development and release of the geoWELL tool as well as updates to the Unconventional Atlas Tool. A new tool, geoWELL, helps EDX affiliated researchers efficiently access subsurface geologic and wellbore data and information related resources. The geo- Water Energy Link Library, geoWELL is a map-based application that provides quick access to primary online sources of subsurface geologic and wellbore (oil, gas, and underground injection) information for appropriate United States state, tribal, and federal agencies. The geoWELL application will assist NETL researchers and analysts as they seek information about these systems to support ongoing and future studies related to risks, impacts, and resources associated with fossil energy research and development. The geoWELL application is an Energy Data Exchange (EDX) tool. See https://edx.netl.doe.gov/tools for information about this and other online tools and applications in the EDX.

The Unconventional Resources Atlas was originally released via EDX in 2012. However, in FY13 additional geospatial layers were fed to the EDX and UCR Atlas in compatible formats. The UCR Atlas

was also updated to provide additional functionality and compatibility with EDX as a whole. The UCR Atlas tool is available at https://edx.netl.doe.gov/tools.

Report of Invention was submitted to NETL for patent review for the "NETL VGM" approach developed under this project and in a complementary effort in the CO_2 Storage project. The VGM approach is up for review by the invention board in FY14-Q1.

A NETL TRS publication is under development and anticipated to be released in FY14 based on the work conducted in FY13 to produce the groundwater interpretation for West Virginia and Pennsylvania.

Hydrologic Factors Affecting Shallow Gas Migration

The objective of this task was to investigate the potential for shale gas well development to mobilize groundwater and stray methane gas in nearby water wells, and during FY13 work focused on the Marcellus Shale region. One objective of the study this year was to determine the potential for compressed air to enter aquifers from the air-percussion drilling technique commonly used for the vertical parts of shale gas wells. Compressed air trapped in a confined or semi-confined aquifer could potentially cause a surge in groundwater flow, resulting in the cloudy, bad-tasting water often reported in some water wells in shale gas development regions. Groundwater surges may also mobilize pre-existing methane gas in aquifers, leading to the build-up of stray gas in domestic water systems. Other potential sources of groundwater contamination, such as drilling fluids, surface leaks of tanks and impoundments, and chemical spills were also assessed to distinguish these compounds from those mobilized by pressurized air.

The approach attempted to use a combination of field data, laboratory studies and groundwater models to define and constrain the potential effects on groundwater from well drilling and hydraulic fracturing. Field and lab data supported the modeling efforts to provide reasonable inputs for the construction of realistic model scenarios. Model realizations helped to evaluate the potential impacts of well drilling on aquifers, and identify management strategies to mitigate them.

Groundwater modeling of the 2012 Sardis, WV incident with TOUGH-2 was successful. (In this incident, an air compressor was left running while drillers attempted to free a stuck drill bit from an uncased, shallow borehole, and water began flowing hours later from a number of unused wells several hundred meters from the drill site.) In collaboration with the Civil and Environmental Engineering Department at the New Jersey Institute of Technology in Newark, the development of a viable modeling realization reproduced the observed results fairly accurately. Fieldwork determined that the affected homes and the gas well lined up along the direction of a set of prominent natural fractures (joints) with an orientation of 110°, an aperture of 0.5-1 mm, and a mean spacing of 8.7 meters (median spacing of 6.2 meters). The subject aquifer is partially confined under an overlying shale that is eroded away about halfway between the gas well and water wells. Using these data along with known elements for the lateral distance, depth of the stuck drill bit, air pressure from the compressor, and reasonable estimates for the time needed to free the bit and groundwater travel time through the natural fractures, the model was able to generate results comparable to those that actually happened. Confidence in this particular scenario is high, and a technical paper has been published in the Journal of Environmental Engineering (Geng et al., 2013).

Laboratory-scale flow and transport experiments were carried out by a summer intern to investigate the entrainment and transport of contaminants in fractured aquifers (Giri, 2013). The velocity of water flow through fractures needed to entrain and transport gas bubbles clinging to the sides was surprisingly low. Additional tests are planned on samples of the Lock Haven and Catskill Formations, which make up the shallow aquifers at Dimock, PA, where a well vault exploded in 2009 because of methane gas buildup. The experiments will be aimed at determining if compressed air from nearby shale gas drilling operations could have mobilized pre-existing methane in the aquifer.

Contacts were made with a number of shale gas production companies in an attempt to obtain permission to access well sites for groundwater monitoring during gas well drilling. Cabot Oil and Gas responded that their sites would not be useful to our study because they no longer use compressed air for drilling based on earlier NETL presentations concerning the possible risks. Chesapeake Energy also reported that they have switched from air to mud for drilling their vertical holes based on NETL results.

Over the year, the fieldwork task evolved from a Department of Energy (DOE) drilling engineering site study to a prospective case study site for the EPA hydraulic fracturing drinking water investigation. The three agencies (EPA, DOE and DOI) agreed that the groundwater monitoring wells at a prospective site

would be installed by DOE. A spinoff study for a methodology to install monitoring wells without contaminating the aquifer with the same compounds that might be introduced from the gas well began in FY13 and has carried over to FY14. This is an especially sensitive and complex issue after the API review of EPA findings at the Pavillion, WY site indicated that many of the reported "contaminants" in the groundwater were actually additives to the drilling mud and cement, or coatings on the casing that entered the aquifer when the monitoring wells were drilled. Several drilling experts at NETL have been engaged to address this complex problem. A groundwater monitoring plan has been developed, and is being reviewed as we continue to seek site access.

Groundwater contaminant hydrology experts have strongly advised the use of a multilevel sampler in groundwater monitoring wells adjacent to a shale gas drill pad. DOE has been seeking an existing, open-hole completed water well for a field test of the Schlumberger "Westbay" groundwater sampling system. EPA has concerns about how the system will perform in terms of the purge volumes and sample delivery needed for compliance with their Quality Assurance Program Plan (QAPP). Schlumberger has offered assurances that the Westbay will perform adequately, but a field test before trying this at an actual gas well drill site is needed. Earth Data Northeast, the local distributor for Westbay, offered access to a groundwater monitoring well on a Superfund site in Maryland for DOE and EPA scientists to observe the installation of the multilevel sampler and assess the performance for the EPA water sampling QAPP. This will save a significant amount of time and expense compared to installing a unit in our own test well.

The fieldwork task has been delayed repeatedly because of difficulties obtaining access to a shale gas well site. We are continuing to pursue this on several fronts, with the intent of gaining access to a site that can be used for a joint DOE-EPA-DOI study. However, at this point a location that is suitable for the DOE efforts only will still be acceptable. In addition to discussions with industry, NETL has been seeking to collaborate with a number of universities that have proposed "transparent wells" on their lands. These include West Virginia University, Ohio State University, and University of Tennessee. None of these universities have so far been able to sign an agreement with a driller for a well where extensive research can be carried out during drilling and production. Due to challenges in finding a suitable field site for installation of monitoring wells, the fieldwork portion of this project was reviewed by the Team Technical Coordinator (TTC) and Technical Coordinator (TC), and a plan to move forward is now focused primarily on lab analyses and developing groundwater models as a framework to test different contaminant and gas migration scenarios, which will be populated with data as field sites and/or field data sets become available.

Natural attenuation studies have been initiated in the lab to investigate the processes and rates of natural breakdown of contaminants in groundwater, and reactive transport models are being used to determine the potential for contaminants to reach the accessible environment. Field instrumentation is also being assessed in the laboratory to determine the sensitivity and response for the detection drilling fluids and frac chemicals in surface water and groundwater.

3.0 Conclusion

Research efforts performed through the EPAct Complementary program UCR portfolio focused on field, laboratory, modeling, and data synthesis efforts to evaluate the geologic and environmental response to developing hydraulically-fractured shale reservoirs. Future research is planned to continue building on the results presented here to provide the technical basis for understanding fugitive emissions and air quality; produced waste management; subsurface gas and fluid migration; and the potential for ground motion associated with development of unconventional energy resources.

4.0 Technology Transfer

Presentations

Capo, R., "Data from Marcellus Produced Water Time Series Samples from Meadows, Blaker, and Mohr Horizontal Wells," presented at the AAPG Annual Convention and Exhibition, Pittsburgh, PA, May 19-22, 2013.

Gregory, K., "Microbial Ecology of Flowback and Produced Water from Hydraulic Fracturing for Gas Production from Shale," presented at the American Institute of Chemical Engineers (AIChE) Annual Meeting, Pittsburgh, PA, October 30, 2012.

Gregory, K., "Produced Water Management: Importance of Microbial Ecology for the Fate of Naturally Occurring Radioactivity," submitted for presentation at the Engineering Conferences International's Overcoming the Environmental and Community Challenges of Hydraulic Fracturing for Shale Gas, Boulder, CO, August 4-8, 2013.

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Karamalidis, A., Dzombak, D.A., and Noack, C.W., "Rare Earth Elements in Aqueous Media: Implication for Shale Gas Development," submitted to the World Environmental and Water Resources Congress, EWRI, Cincinnati, OH, May 19-23, 2013.

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Tools Developed and Released via NETL's EDX (*https://edx.netl.doe.gov*)

In FY13, a dedicated website was developed for the UCR portfolio to communicate to the public the purpose, background information, and results of work conducted by the EPAct UCR Portfolio: *https://edx.netl.doe.gov/ucr*

North America Atlas of Unconventional Hydrocarbon Resources is an interactive web map application developed by the West Virginia GIS Technical Center (WVGISTC) to depict geologic basin, oil and gas plays and unconventional well locations in an online map environment.

geoWELL was developed in collaboration with the UDW Portfolio. geoWELL is a map-based application that provides quick access to websites of primary sources of subsurface geologic and wellbore information for appropriate U.S. state, tribal and federal agencies.

Energy Data Exchange is a tool to support coordination and collaboration across research efforts that require a common set of information related to subsurface energy resources. The UCR Portfolio supports ongoing development of the system as a whole, as well as addition of key content that is provided through NETL's EDX.

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