NATIONAL ENERGY TECHNOLOGY LABORATORY

An Evaluation of Fracture Growth and Gas/Fluid Migration as Horizontal Marcellus Shale Gas Wells are Hydraulically Fractured in Greene County, Pennsylvania

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NETL-TRS-3-2014

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Cover Illustration: Three Marcellus Shale gas wells equipped with hydraulic fracturing wellheads in Greene County, Pennsylvania.

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An Evaluation of Fracture Growth and Gas/Fluid Migration as Horizontal Marcellus Shale Gas Wells are Hydraulically Fractured in Greene County, Pennsylvania

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Table of Contents

List of Figures

List of Tables

Acronyms, Abbreviations, and Symbols

Term	Description
bbl	Barrels, equal to 42 gallons (159 liters)
CI	Chemical ionization
gel	Carboxymethyl hydroxypropyl guar
EPA	United States Environmental Protection Agency
fL	Femtoliter, equal to 10^{-15} liters
ft	Foot, equal to 0.3048 m
GC	Gas chromatograph
GR	Gamma ray
Heel stage	In a horizontal well, the stage closest to the vertical section
iPPCH	Perfluoro-i-propylcyclohexane
IRMS	Isotope Ratio Mass Spectrometer
MC-ICP-MS	Multi-collector-inductively coupled plasma-mass spectrometer
MD	Measured depth
MSD	Mass selective detector
MSL	Mean sea level
NORM	Naturally-occurring radioactive materials
pad	Hydraulic fracturing fluid without proppant
PADEP	Pennsylvania Department of Environmental Protection
PDCB	Perfluorodimethylcyclobutane
PFC	Perfluorocarbon
ppg	Pounds per gallon
PMCH	Perfluoromethylcyclohexane
PTCH	Perfluorotrimethylcyclohexane
SIM	Selected ion mode
Slickwater	Hydraulic fracturing fluid that is predominantly water and friction reducer
SNR	Signal-to-noise ratio
Sr	Strontium
Toe stage	In a horizontal well, the most distal stage
TVD	Total vertical depth
USDW	Underground sources of drinking water
WVU	West Virginia University
Zipper frac	Multi-well sequencing of operations for 1) hydraulic fracturing and 2) plugging and perforation to improve efficiency

Acknowledgments

This work was completed as part of National Energy Technology Laboratory (NETL) research for the Department of Energy's (DOE) Complementary Research Program under Section 999 of the Energy Policy Act of 2005. The authors wish to acknowledge Roy Long (NETL Strategic Center for Natural Gas and Oil) and Elena Melchert (DOE Office of Fossil Energy) for programmatic guidance, direction, and support.

The authors also wish to acknowledge the natural gas industry for: 1) providing access to their wells for sampling and monitoring; 2) providing geological information for the site; 3) providing information relevant to the construction and completion of horizontal Marcellus Shale gas wells; and 4) providing production information for Upper Devonian/Lower Mississippian gas wells.

EXECUTIVE SUMMARY

This field study monitored the induced fracturing of six horizontal Marcellus Shale gas wells in Greene County, Pennsylvania. The study had two research objectives: 1) to determine the maximum height of fractures created by hydraulic fracturing at this location; and 2) to determine if natural gas or fluids from the hydraulically fractured Marcellus Shale had migrated 3,800 ft upward to an overlying Upper Devonian/Lower Mississippian gas field during or after hydraulic fracturing.

The Tully Limestone occurs about 280 ft above the Marcellus Shale at this location and is considered to be a barrier to upward fracture growth when intact. Microseismic monitoring using vertical geophone arrays located 10,288 microseismic events during hydraulic fracturing; about 40% of the events were above the Tully Limestone, but all events were at least 2,000 ft below producing zones in the overlying Upper Devonian/Lower Mississippian gas field, and more than 5,000 ft below drinking water aquifers.

Monitoring for evidence of fluid and gas migration was performed during and after the hydraulic fracturing of six horizontal Marcellus Shale gas wells. This monitoring program included: 1) gas pressure and production histories of three Upper Devonian/Lower Mississippian wells; 2) chemical and isotopic analysis of the gas produced from seven Upper Devonian/Lower Mississippian wells; 3) chemical and isotopic analysis of water produced from five Upper Devonian/Lower Mississippian wells; and 4) monitoring for perfluorocarbon tracers in gas produced from two Upper Devonian/Lower Mississippian wells.

Gas production and pressure histories from three Upper Devonian/Lower Mississippian gas wells that directly overlie stimulated, horizontal Marcellus Shale gas wells recorded no production or pressure increase in the 12-month period after hydraulic fracturing. An increase would imply communication with the over-pressured Marcellus Formation below.

Sampling to detect possible migration of fluid and gas from the underlying hydraulically fractured Marcellus Shale gas wells commenced 2 months prior to hydraulic fracturing to establish background conditions. Analyses have been completed for gas samples collected up to 8 months after hydraulic fracturing and for produced water samples collected up to 5 months after hydraulic fracturing. Samples of gas and produced water continue to be collected monthly (produced water) and bimonthly (gas) from seven Upper Devonian/Lower Mississippian gas wells.

Current findings are: 1) no evidence of gas migration from the Marcellus Shale; and 2) no evidence of brine migration from the Marcellus Shale.

Four perfluorocarbon tracers were injected with hydraulic fracturing fluids into 10 stages of a 14-stage, horizontal Marcellus Shale gas well during stimulation. Gas samples collected from two Upper Devonian/Lower Mississippian wells that directly overlie the tracer injection well were analyzed for presence of the tracer. No tracer was found in 17 gas samples taken from each of the two wells during the 2-month period after completion of the hydraulic fracturing.

Conclusions of this study are: 1) the impact of hydraulic fracturing on the rock mass did not extend to the Upper Devonian/Lower Mississippian gas field; and 2) there has been no detectable migration of gas or aqueous fluids to the Upper Devonian/Lower Mississippian gas field during the monitored period after hydraulic fracturing.

1. INTRODUCTION

Application of hydraulic fracturing technology towards natural gas extraction has increased the amount of natural gas available from United States shale gas resources. Although prior reports from industry show that fractures generated during hydraulic fracturing of Marcellus Shale remain thousands of feet below underground sources of drinking water (USDW) (Fisher and Warpinski, 2012), independent verifications of these observations are limited. This study is focused on: 1) determining the upward extent of hydraulic fracturing impact associated with six Marcellus Shale gas wells within a production pad in Greene County, Pennsylvania; and 2) determining whether induced fractures in conjunction with natural fractures and existing well penetrations provide pathways for fluid and gas migration to overlying formations at that location. The uppermost extent of induced fracture creation was determined using microseismic monitoring. Production/pressure histories and tracer analysis in an overlying gas field were used to monitor for potential gas or fluid migration.

This study monitored for inter-formational fluid and gas migration at depth (within the 2,100 ft to 8,200 ft depth interval) prior to, during, and after the hydraulic fracturing of six horizontal Marcellus Shale gas wells. Seven vertical gas wells completed in multiple, thin sands 3,800–6,100 ft above the six horizontal Marcellus Shale wells were monitored for tracer (carbon and hydrogen isotopes in the gas, strontium isotopes in the fluids), pressure, and production evidence that would indicate possible migration of fluid or gas upward from the hydraulically fractured shale formation below. This study also used geophones deployed in nearby vertical Marcellus Shale wells to detect and locate microseismic events that occurred during hydraulic fracturing. The point cloud of microseismic events was used to ascertain the maximum upward extent of brittle deformation caused by hydraulic fracturing.

Research conducted during this study was funded from oil and gas royalties legislatively directed to the Department of Energy under provisions of the Energy Policy Act of 2005, Title IX, Subtitle J, Section 999A-999H, Complementary Program. The work was performed by five teams with members from government, academia, and industry. The teams included:

1. Microseismic Monitoring – National Energy Technology Laboratory (NETL) and Weatherford
2. Pressure and Production History – NETL
3. Isotope Signature of Gas – West Virginia University and Isotech
4. Isotope Signature of Produced Water – University of Pittsburgh
5. Perfluorocarbon Tracers – NETL, ProTechnics, and SpectraChem

1.1 SITE DESCRIPTION

The research site is located in Greene County in southwestern Pennsylvania, a hilly, rural area comprised of hardwood forest and farm land (Figure 1). A repurposed airshaft from an abandoned and now flooded underground Pittsburgh Coal mine is the only visual reminder of prior industrial activity in the study area.

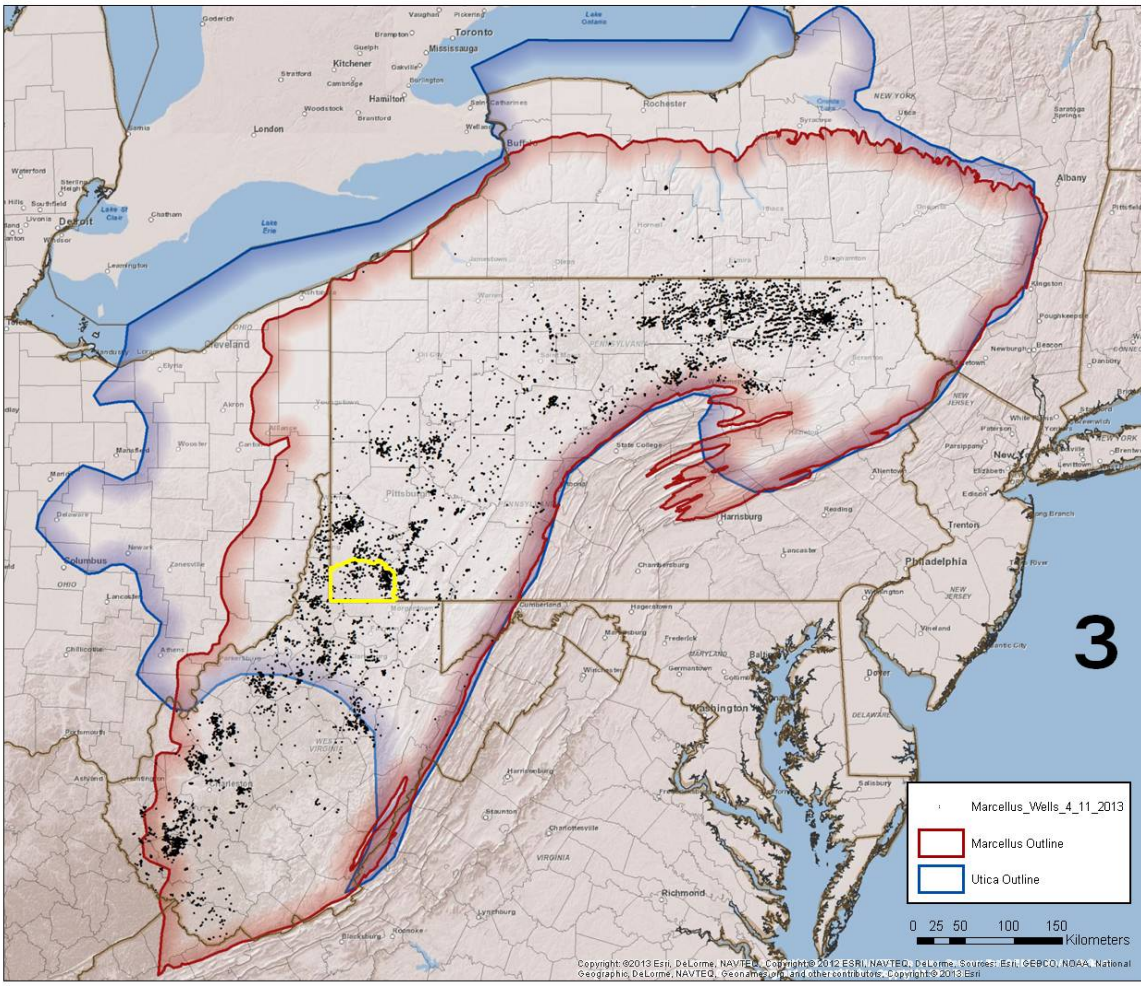


Figure 1: Map of east-central United States showing occurrence of Marcellus Shale (red shading) and Marcellus Shale wells (black dots). The occurrence of the Utica Formation is shown with blue shading. The study area is in Greene County, Pennsylvania (outlined in yellow).

1.1.1 Site Geology

The research site is located in the Waynesburg Hills section of the Appalachian Plateaus Physiographic Province of Pennsylvania. Topography of the area exhibits moderate relief and is typified by narrow hilltops and valleys separated by steep slopes. The area is drained by headwater streams of first and second order.

Surface geology comprises nearly horizontal beds of sandstone and shale of the Pennsylvanian/Permian age Waynesburg Formation. Freshwater aquifers were observed at depths of 124 ft, 610 ft, and 725 ft for a vertical Marcellus Shale gas well (MW-2) in the study area with surface elevation of 1,060 ft (Figure 2). The same well encountered a flooded underground mine in the Pittsburgh Coalbed at a depth of 570 ft (Figure 2). The mine is flooded with acidic, metal-containing water; a near constant water level within the mine is maintained by pumping and treatment. Nearly flat-lying strata persist from the surface to the lowermost units of

the Upper Devonian Bradford Group. However, Middle Devonian and older strata are offset by northeast trending faults as shown in reflection seismic section (Figure 3). Faults that offset the Marcellus Shale have impacted the placement of horizontal Marcellus Shale gas wells within the study area (Figure 4).

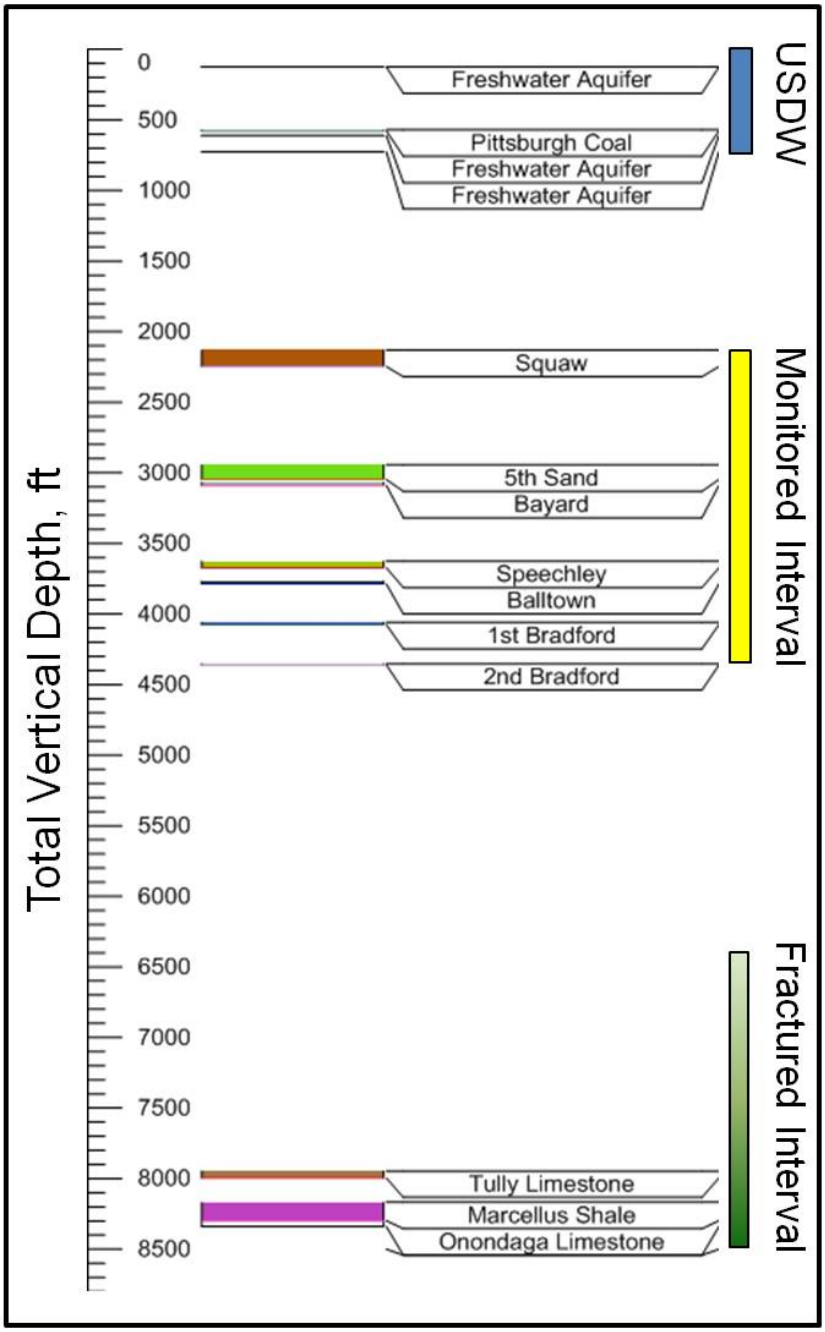


Figure 2: Vertical section from a Marcellus Shale gas well (MW-2) showing the depth relationship between the hydraulically fractured formation (Marcellus Shale), the monitoring zone (Upper Devonian/Lower Mississippian sands), and protected freshwater aquifers (USDW).

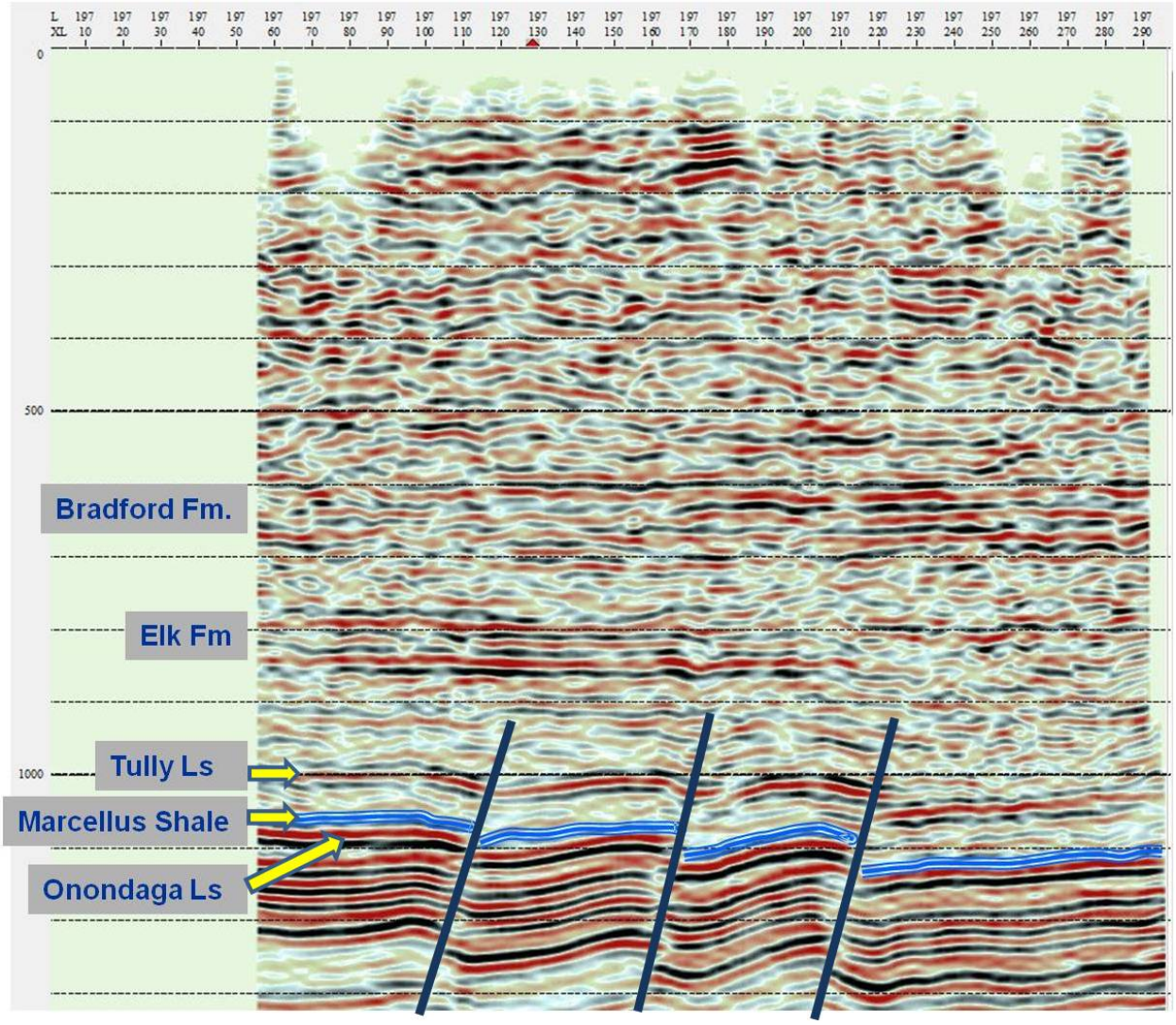


Figure 3: East-west seismic section looking north that shows fault offsets in the Tully Limestone, Marcellus Shale, and Onondaga Limestone of Middle Devonian age. Note that strata of the Upper Devonian age Elk Formation and Bradford Formation are not offset by faults. Ordinate axis is two-way travel time in milliseconds; abscissa is distance in 1,000-ft increments.

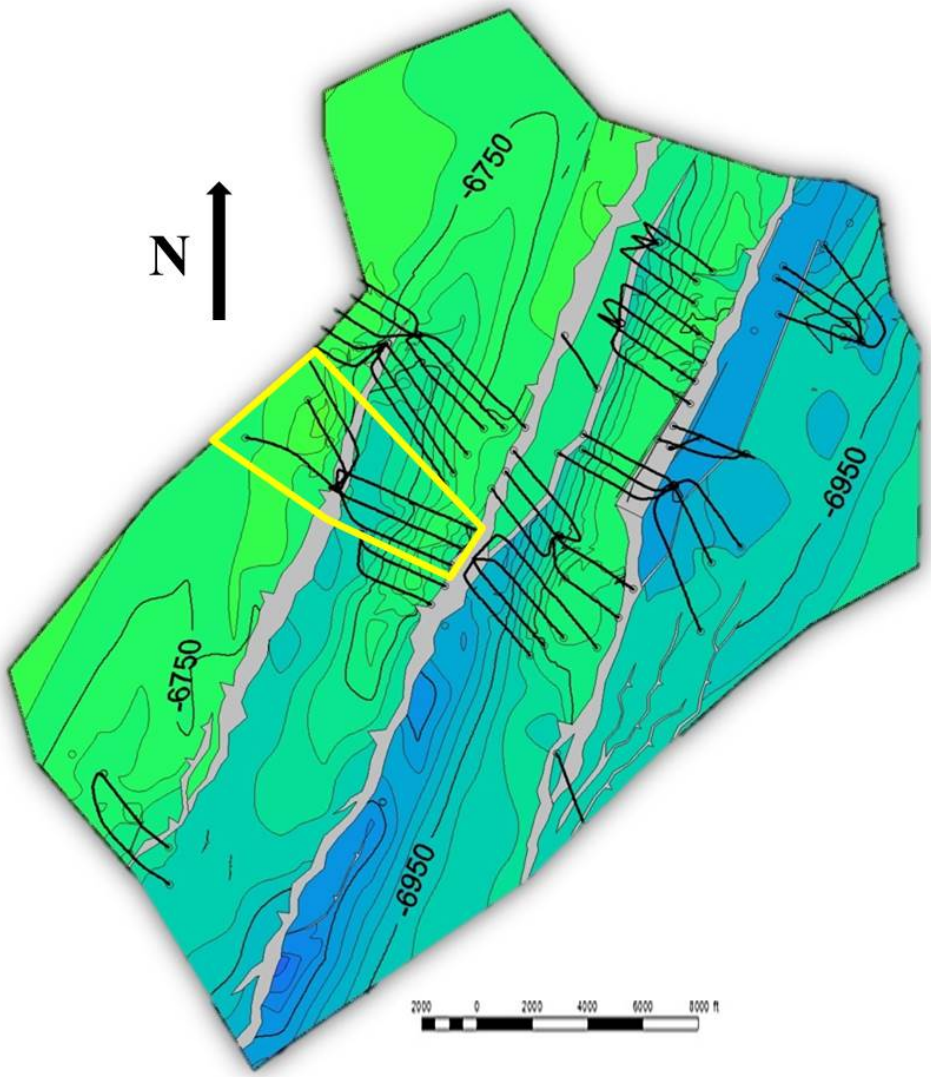


Figure 4: Structure contour map on a persistent limestone unit within the Middle Devonian age Marcellus Shale. Northeast trending gray areas depict fault zones present only in Middle Devonian and older strata; tooth marks point toward the fault block that has moved upward. Black lines show the location of horizontal Marcellus Shale gas wells. Area outlined in yellow contains the six horizontal Marcellus Shale gas wells investigated in this study. Contour interval is 25 ft. Lighter colors denote lesser depth.

1.1.2 Well Description

1.1.2.1 Marcellus Shale Gas Wells

Six horizontal Marcellus Shale gas wells had been drilled, but not hydraulically fractured, when this study commenced in March 2012 (Figure 4 and 5). At this location, the Marcellus Shale is approximately 8,100–8,200 ft below the surface and is vertically offset by northeast-trending, reverse faults that extend upward through the Tully Limestone into the Upper Devonian, but do not offset the Bradford Formation or overlying strata (Figure 3). The horizontal Marcellus Shale wells were drilled from a pad directly above the subsurface location of a reverse fault (fault does not extend to surface) and were landed in unfaulted segments of the Marcellus Shale to the northwest and southeast of the drill pad (Figure 4). Three southeastward-extending wells (Wells D, E, and F, Figure 4) terminate near a parallel northeast-trending fault zone located to the southeast (Figure 4). The locations of two vertical Marcellus Shale wells (MW-1 and MW-2) are depicted in Figure 5.

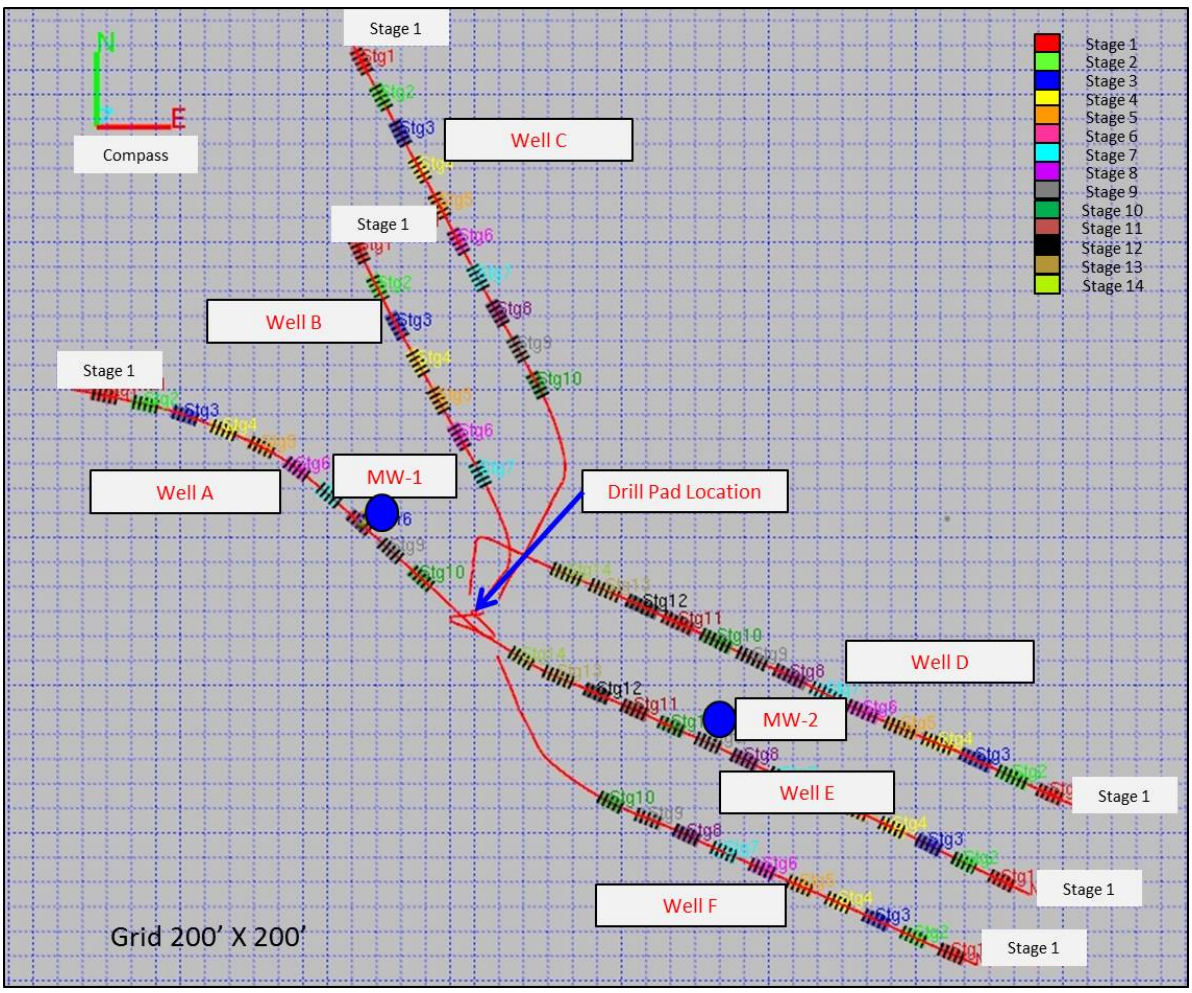


Figure 5: Map showing the locations of six horizontal Marcellus Shale gas wells (Wells A–F with stages depicted) and two vertical Marcellus Shale gas wells (MW-1 and MW-2) that served as microseismic monitoring wells.

Wells A and B were hydraulically fractured on April 24–29, 2012; only the first stage (toe stage) of Well C was completed at this time. Stages 2–10 of Well C were hydraulically fractured on May 2–6, 2012. Wells D, E, and F (that extend southeastward) were hydraulically fractured on June 4–11, 2012. A total of 65 stages were treated using conventional plugging and perforation through cemented casing. A "zipper-type" sequencing of treatment stages was used for Wells A and B, and then for Wells D, E, and F. Treatment was delayed for Well C, so that well was stimulated separately. Within each stage, perforation clusters were spaced about 110 ft apart with three clusters per stage. Each 2-ft perforation cluster used 0° phasing (all perforations pointed downward) at 5 perforation shots per foot, for a total of 10 shots per cluster. For Wells A, B, C, E, and F, the stage treatment design used "slickwater" (7,530 barrels or bbls), 100-mesh sand from 0.25 pounds per gallon (ppg) to 1.00 ppg, and 40/70-mesh sand from 1.00 ppg to 2.00 ppg (0.25 ppg increments). Total designed sand was 300,000 lbs/stage. For Well D, the treatment design was doubled, using 15,060 bbls of "slickwater" and 600,000 lbs of sand per stage. Chemicals added to fresh and recycled water for hydraulic fracturing included friction reducer, bactericide, scale inhibitor, and gel with breaker (also see Table 6 in Appendix E). The wells were drilled and hydraulically fractured by the operator.

1.1.2.2 Upper Devonian/Lower Mississippian Gas Wells

At the Greene County Site, a producing gas field overlies the horizontal Marcellus Shale wells and was used as the monitoring interval (Monitored Interval, Figure 2) between the hydraulically fractured zone (Fractured Interval, Figure 2) and a near-surface zone containing freshwater aquifers (USDW, Figure 2). Within the monitored interval, natural gas has been produced since 2006 from multiple completions in thin (<10-ft thick) sandstones within a 2,300-ft thick interval of sandstone, siltstone, and shale. The base of the monitored zone is about 3,800 ft above the underlying horizontal Marcellus Shale gas wells while the top of the zone is at least 1,300 ft below the deepest known freshwater aquifer at the site.

Vertical gas wells in the monitored zone were completed in the Squaw Sand of the Mississippian age Shenango Formation and multiple sands within the Upper Devonian age Venango and Bradford Formations (5th , Bayard, Speechley, Balltown, 1st Bradford, and 2nd Bradford sands) (Figures 2 and 6). Within the study area, there are seven vertical wells that were drilled and hydraulically fractured by the operator to produce natural gas from this zone. The vertical wells were drilled on 1,500-ft spacing based on the expectation of at least 750-ft radial fracture growth away from the vertical wells during hydraulic fracturing. Three wells completed in the monitored interval directly overlie horizontal Marcellus Shale gas Wells A and E that were hydraulically fractured (UD-1, UD-2, and UD-5; Figures 7 and 8); four wells (UD-3, UD-4, UD-6, and UD-7; Figure 7) are in offset positions from horizontal Marcellus Shale gas Wells D, E, and F.

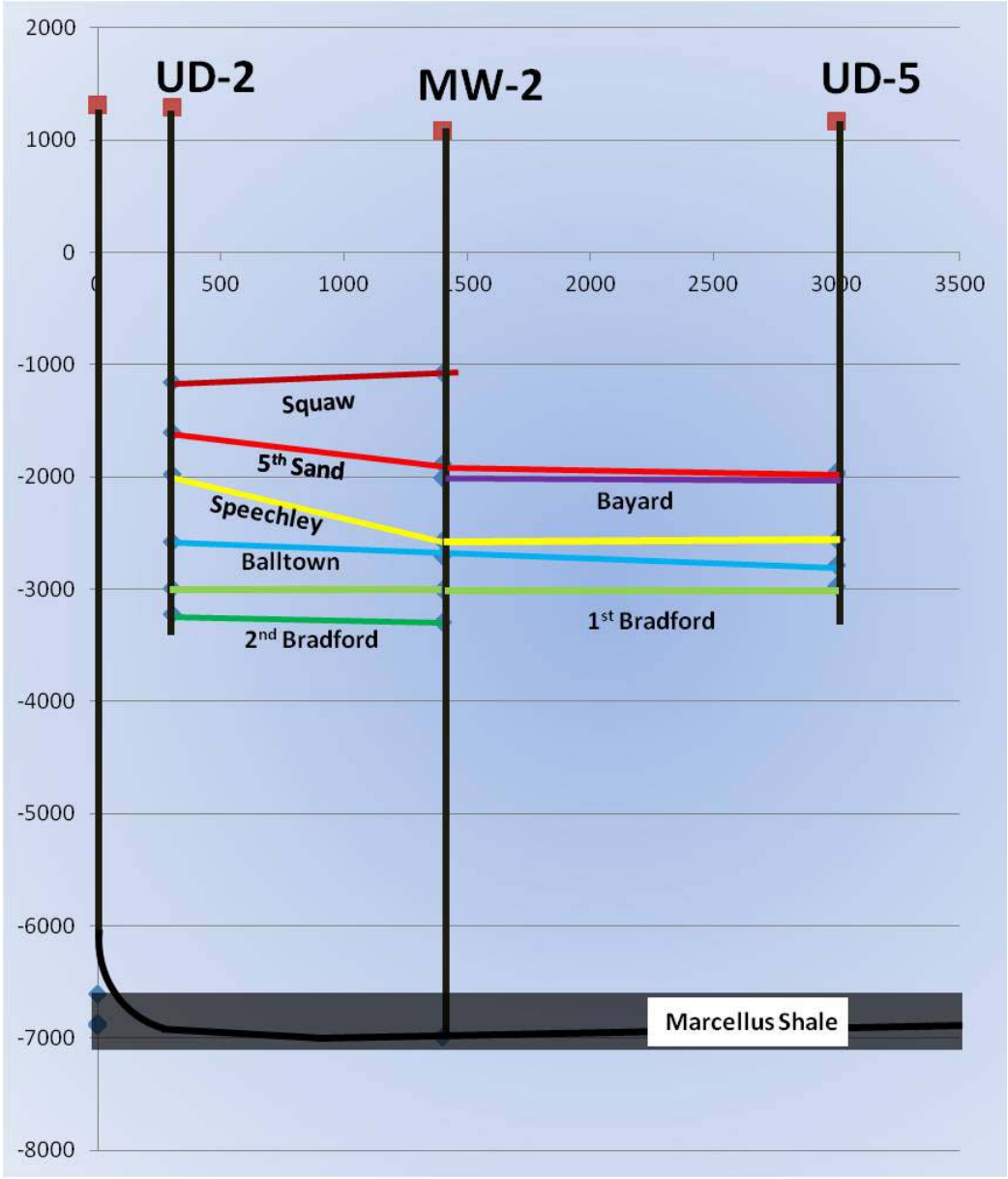


Figure 6: Schematic section along horizontal Marcellus Shale Well E showing vertical Marcellus Shale gas well (MW-2) and two Upper Devonian/Lower Mississippian gas wells (UD-2 and UD-5) that were completed in multiple zones. Distance and depth are in feet; sub-sea depths shown.

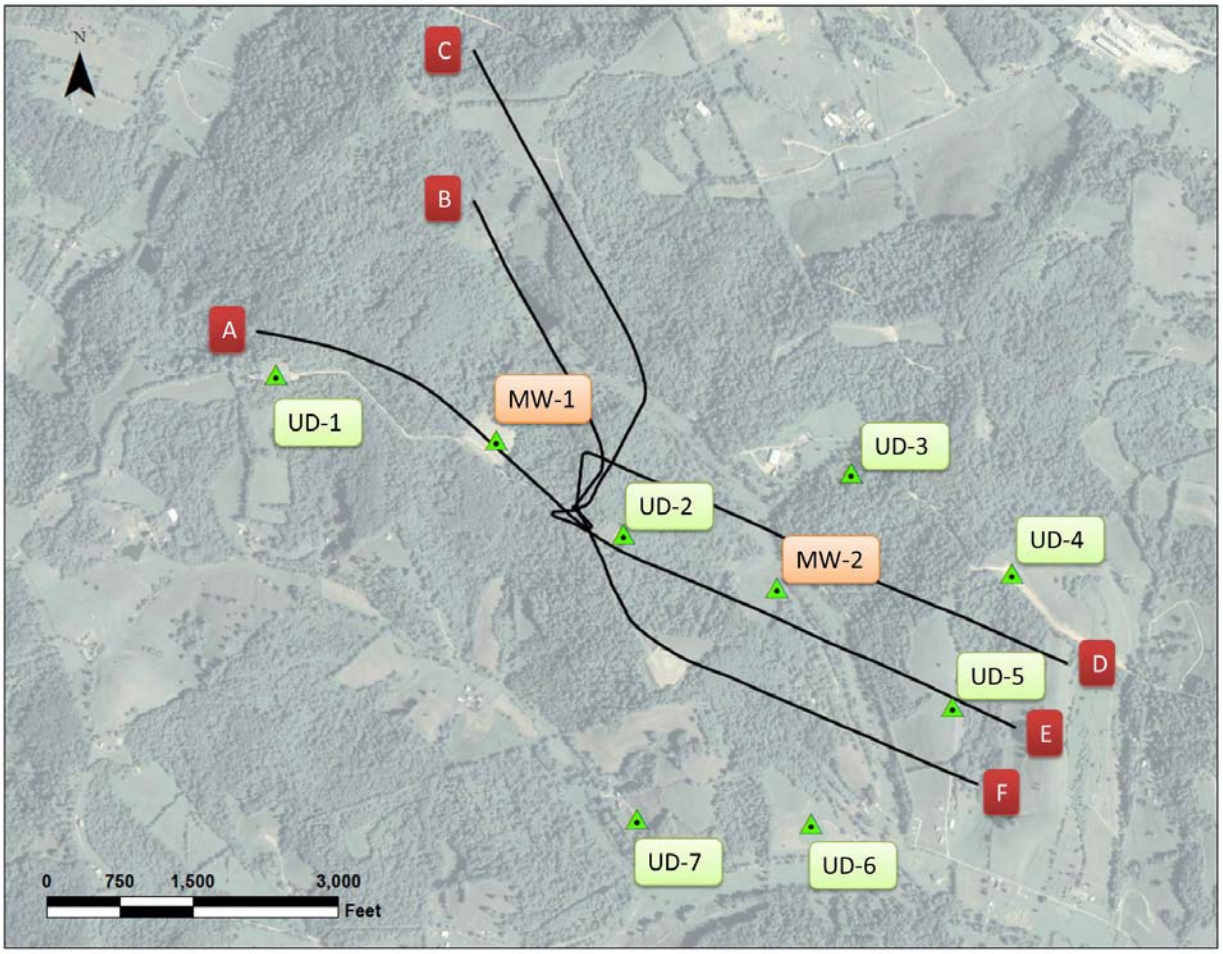


Figure 7: Map showing location of horizontal Marcellus Shale gas wells (black lines A-F), vertical Marcellus Shale gas wells (MW-1 and MW-2), and vertical Upper Devonian/Lower Mississippian gas wells (UD-1 through UD-7).

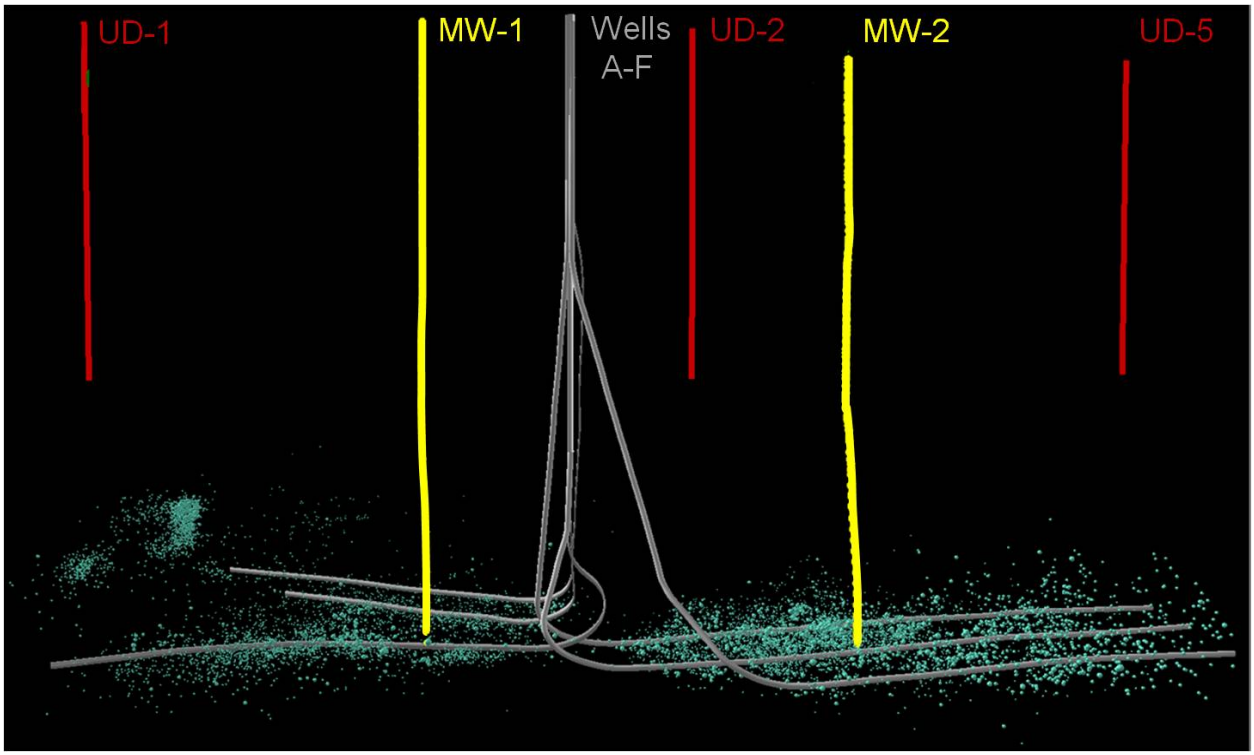


Figure 8: East-west section looking north that shows the spatial relationship between horizontal Marcellus Shale gas wells (A-F), vertical Marcellus Shale gas wells (MW-1 and MW-2), and vertical Upper Devonian/Lower Mississippian gas wells (UD-1, UD-2, and UD-5). Light blue spheres depict microseismic events located during the hydraulic fracturing of horizontal Marcellus Shale gas wells.

2. OBSERVATIONS

This study employed multiple lines of evidence to determine if fluids and gas from the hydraulically fractured Marcellus Shale had migrated at least 3,800 ft upward to a monitored conventional gas reservoir in the Upper Devonian and Lower Mississippian. This evidence was collected before, during, and after the hydraulic fracturing of six horizontal Marcellus Shale gas wells and included: 1) microseismic determination of the uppermost extent of the stress regime created by hydraulic fracturing; 2) pressure and production histories of Upper Devonian/Lower Mississippian wells; 3) chemical and isotopic analysis of the gas produced by Upper Devonian/Lower Mississippian wells; 4) chemical and isotopic analysis of water produced from Upper Devonian/Lower Mississippian wells (where fluid samples were available); and 5) monitoring for perfluorocarbon tracers in gas produced from two Upper Devonian/Lower Mississippian wells.

2.1 MICROSEISMIC MONITORING RESULTS

Microseismic monitoring of fracture growth was accomplished using a geophone array deployed in one of two vertical Marcellus Shale gas wells (MW-1 during the treatment of Wells A, B, and C; MW-2 during the treatment of Wells D, E, and F, Figure 5). The geophone array consisted of eight, three-component geophones spaced 100-ft apart (Figure 9 and10). The lowermost geophone was positioned approximately 100 ft above the bridge plug (at the top of the perforated zone in the Marcellus Shale) while the uppermost geophones were located in gray shale (Harrell and Brallier Formations) above the Tully Limestone (Figure 9). Microseismic monitoring during the hydraulic fracturing of 56 stages (all stages of Wells A, B, D, E, and F and Stage 1 of Well C) located 10,288 microseismic events (Figure 11) with moment magnitudes ranging between -3.15 and -0.56. A more detailed description of microseismic data acquisition, quality assurance, and results can be found in Appendix A.

Figure 11 is an east/west section that shows the vertical distribution of all located microseismic events. Most microseismic events were mapped below the Tully Limestone, considered by many to be an upper barrier to fracture growth from hydraulic fracturing in the Marcellus Shale (Harper and Kostelnik, 2013). However, in this study, many microseismic events also were located above the Tully Limestone and are of particular interest. For Wells A, B, and C (Figures 12 and 13), microseismic events above the Tully Limestone occur primarily as clusters of various geometries, but also as single, discrete events. However, for Wells D, E, and F (Figures 14 and 15), microseismic events above the Tully Limestone are isolated, widely separated events mostly associated with the pumping of toe stages. During the treatment of Wells A, B, and C (Stage 1 only for Well C), significant fracture growth above the Tully Limestone was inferred from event clusters located between 1,000 and 1,900 ft above the Marcellus Shale (Figures 16 and 17), a fracture height that is consistent with the inferred upper extent of pre-existing faults at the site, although no fault has been observed at this specific location. The uppermost events were separated from the gas producing zones of the Upper Devonian/Lower Mississippian wells by at least 1,800 ft of strata (see UD-1, Figure 8).

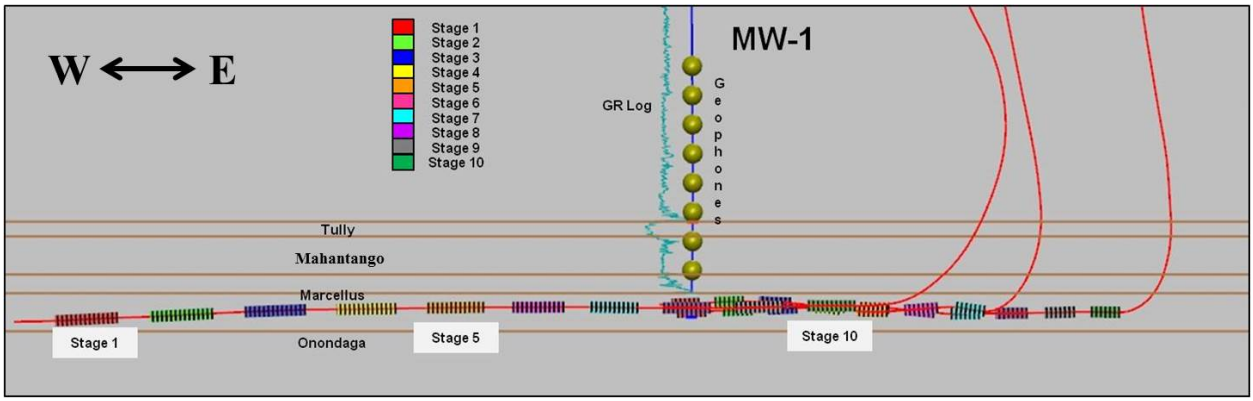


Figure 9: East/west vertical section looking north that shows geophone positions in monitoring Well 1 (MW-1) with respect to the stratigraphy interpreted from the gamma ray (GR) log for that well. Red lines represent the locations of horizontal Marcellus Shale gas Wells A, B, and C.

Figure 10: Deployment of geophones in vertical Marcellus Shale gas well (MW-1).

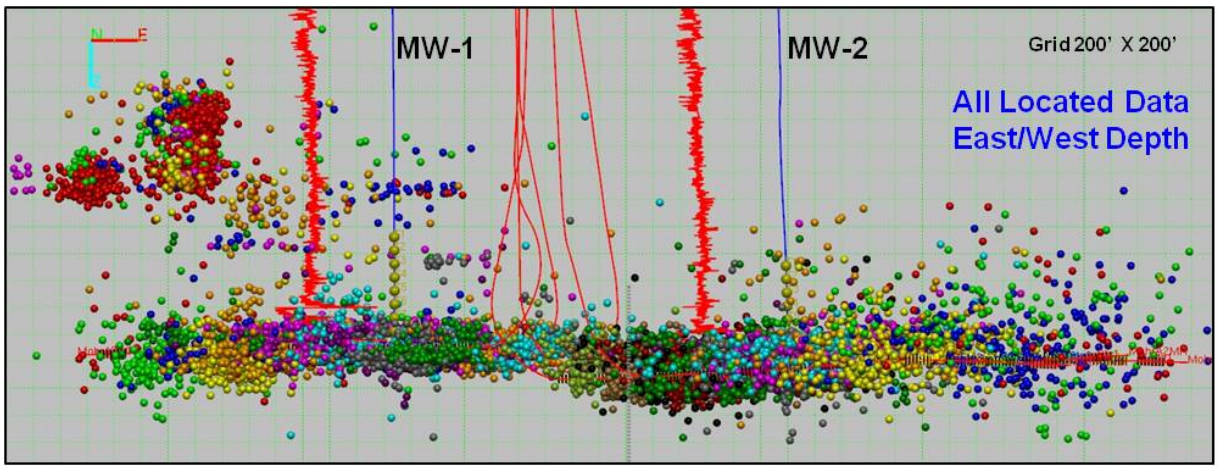


Figure 11: East/west depth section looking north that shows all microseismic events (small spheres, color coded to indicate specific frac stages) located during the hydraulic fracturing of horizontal Marcellus Shale gas Wells A, B, C (Stage 1 only), D, E, and F. Gold spheres on vertical blue lines (monitoring wells MW-1 and MW-2) depict geophone positions.

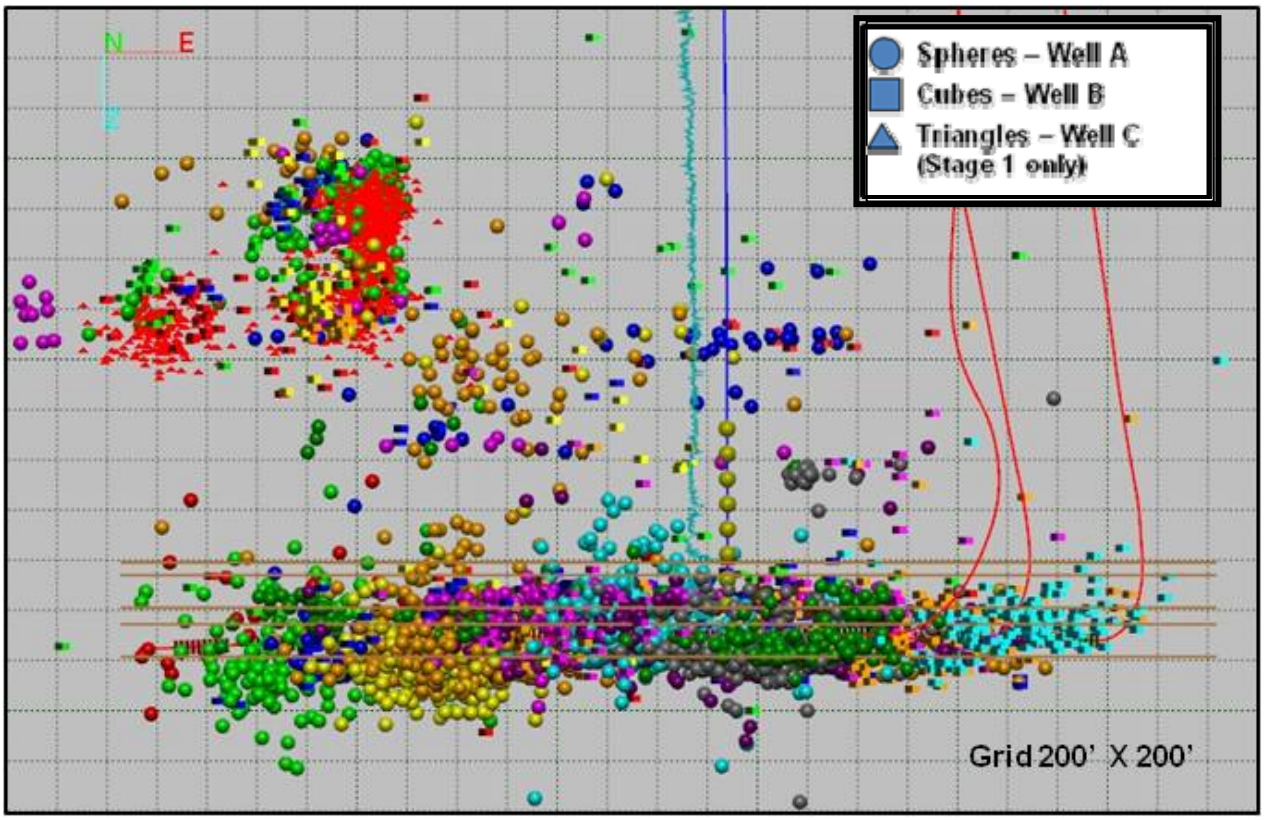


Figure 12: East/west depth section looking north that shows the vertical distribution of microseismic events located during the hydraulic fracturing of horizontal Marcellus Shale Wells A, B, and C (Stage 1 only). Gold spheres on blue line depict geophone positions.

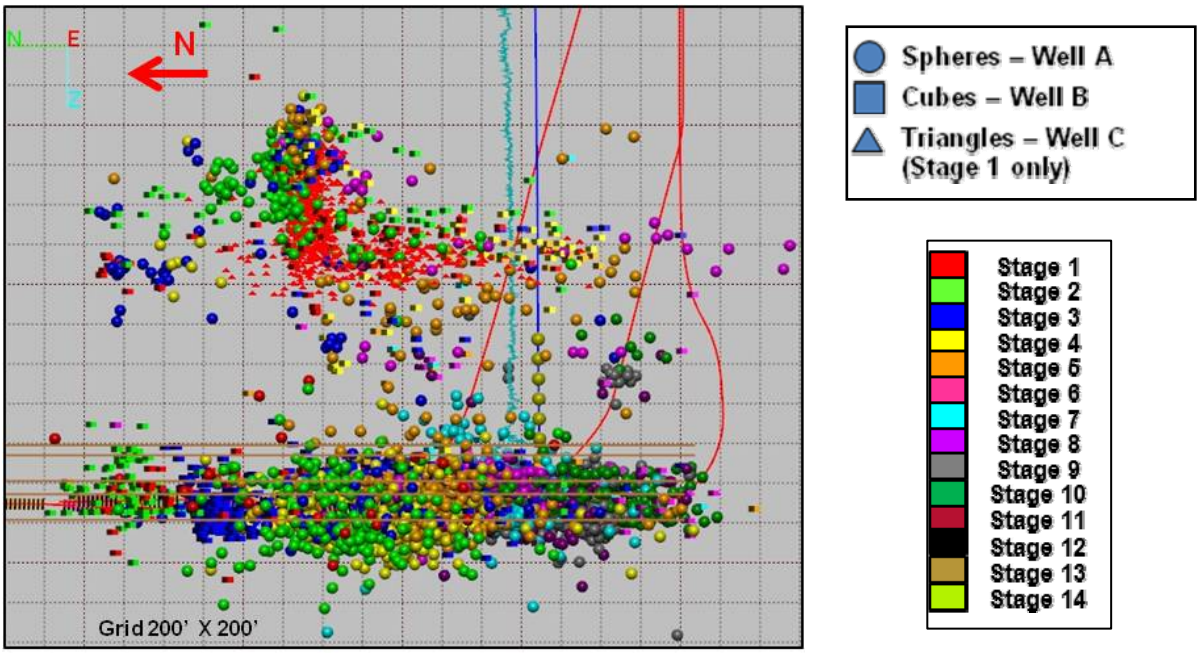


Figure 13. North/south depth section looking east that shows the vertical distribution of microseismic events located during the hydraulic fracturing of horizontal Marcellus Shale Wells A, B, and C (Stage 1 only). Gold spheres on blue line depict geophone positions.

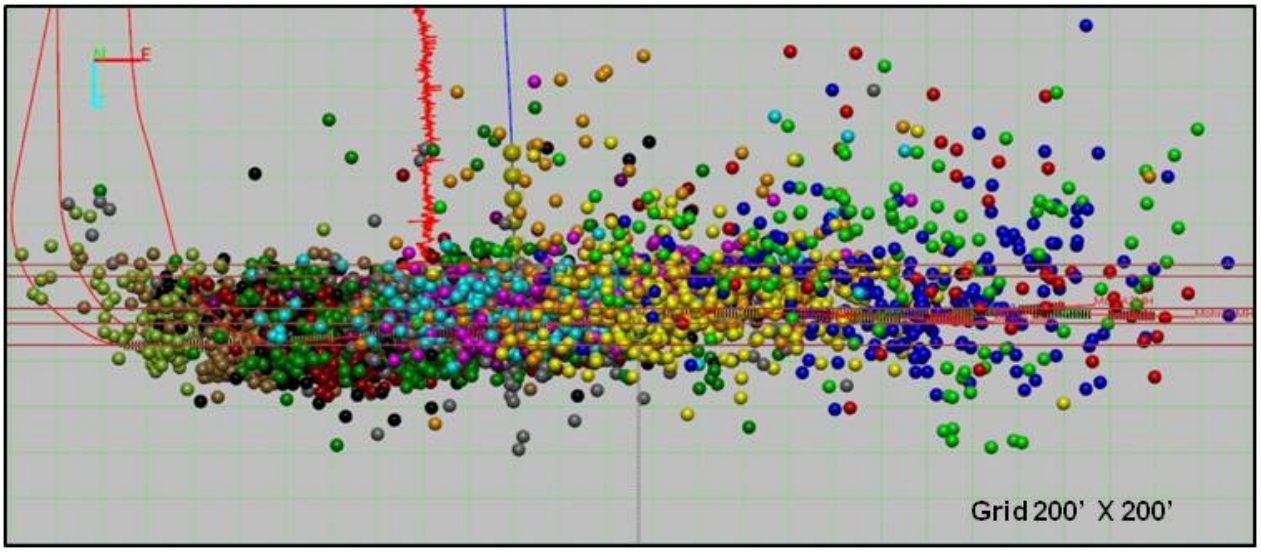
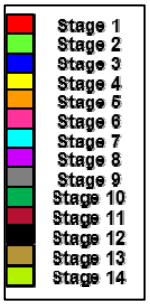


Figure 14: East/west depth section looking north that shows the vertical distribution of microseismic events located during the hydraulic fracturing of horizontal Marcellus Shale Wells D, E, and F. Gold spheres on blue line depict geophone positions.



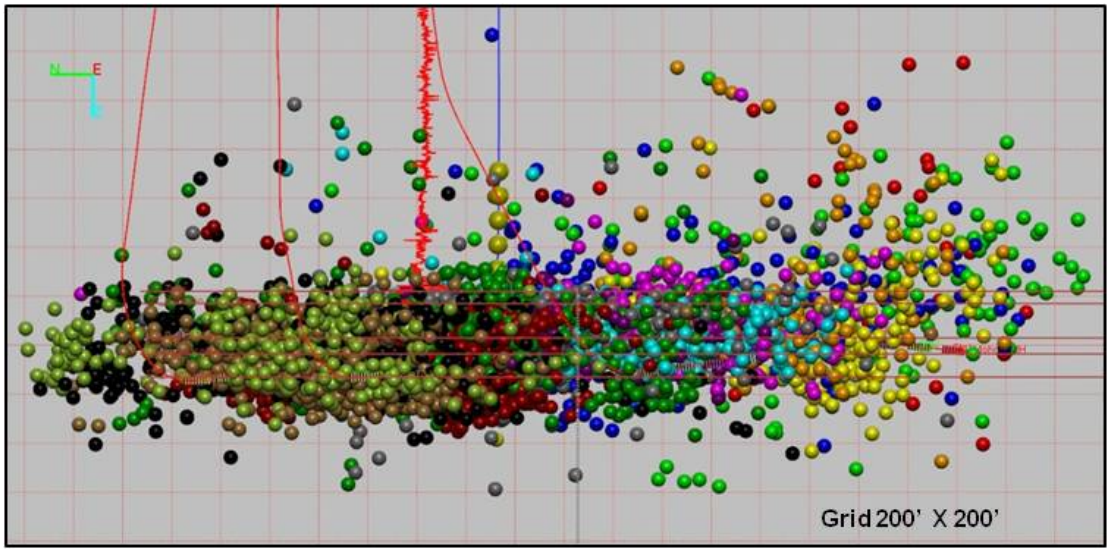


Figure 15: North/south depth section looking east that shows the vertical distribution of microseismic events located during the hydraulic fracturing of horizontal Marcellus Shale Wells D, E, and F. Gold spheres on blue lines depict geophone positions.

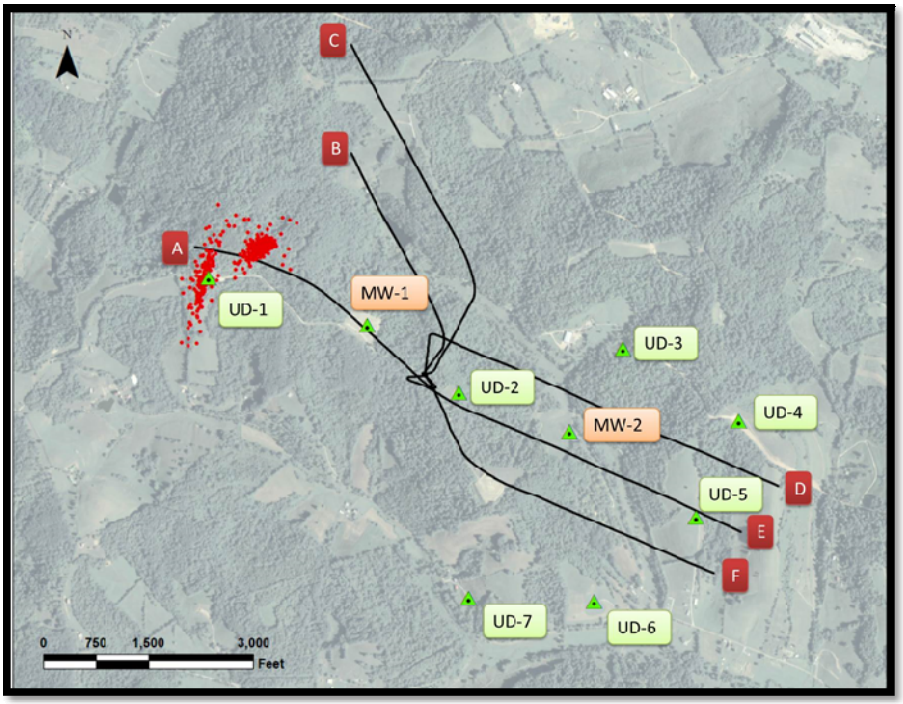


Figure 16: Map showing the spatial relationship between above-zone microseismic event clusters (red dots) located during the hydraulic fracturing of Well C, Stage 1 and overlying Upper Devonian/Lower Mississippian well, UD-1.

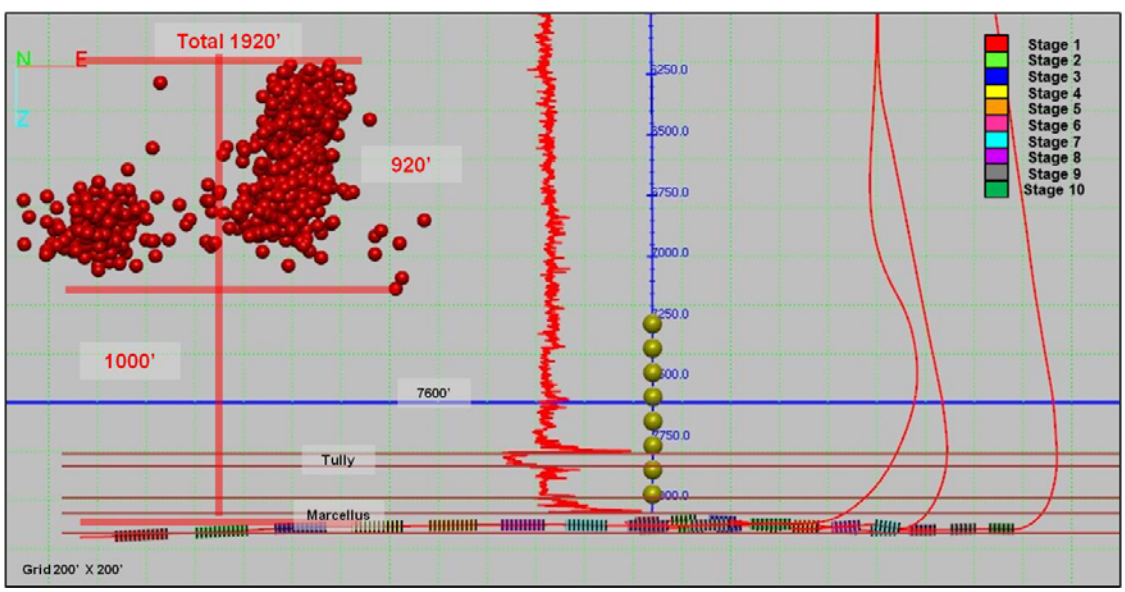


Figure 17: East/west vertical section looking north that shows two microseismic event clusters located during the hydraulic fracturing of Well C, Stage 1 (same events as Figure 16). Gold spheres on vertical blue line depict positions of geophones.

2.2 PRODUCTION AND PRESSURE HISTORY OF UPPER DEVONIAN/LOWER MISSISSIPPIAN WELLS

One method to detect possible upward gas migration from the hydraulically fractured Marcellus Shale is to examine the production and pressure histories of wells in the overlying Upper Devonian/Lower Mississippian gas field. Early production well head pressures of Marcellus Shale wells in the study area range between 1,500 and 2,000 psi; whereas the casing and/or tubing pressures of Upper Devonian/Lower Mississippian wells do not exceed 400 psi. The pressure differential between the two zones would be a driving force for accelerated gas migration from the Marcellus Shale to the Upper Devonian/Lower Mississippian monitoring interval (Figure 2) should a breach open in the seal provided by intervening strata.

The pressure differential between the Marcellus Shale and the Upper Devonian/Lower Mississippian reservoirs is at a maximum during hydraulic fracturing when high-pressure fluids are injected into the Marcellus Shale. After hydraulic fracturing, the pressure in the Marcellus Shale immediately begins to re-equilibrate to regional pressure gradient. Although pressure differential could provide the driving force for gas migration between the Marcellus Shale and the Upper Devonian/Lower Mississippian gas reservoirs, the permeability of natural and created pathways must be significantly increased for the gas migration to take place within the timeframe of this study. Gas migration between the Marcellus Shale and the Upper Devonian/Lower Mississippian reservoirs has occurred naturally on a geologic time scale[1] but slow, natural migration is not the focus of this study. This study is looking for evidence of more rapid gas migration over a period of 12 months that might be attributable to man-made changes to the seal provided by intervening strata (e.g. well penetrations and/or induced fracturing).

Production and pressure histories were obtained from the industry partner for three Upper Devonian/Lower Mississippian wells (UD-1, UD-2, and UD-5, Figure 7) that directly overlie horizontal Marcellus Shale wells which were hydraulically fractured during this study. Production and surface gage pressure records for the Upper Devonian/Lower Mississippian wells cover a time period starting at least 3 years prior to hydraulic fracturing (in the underlying Marcellus Shale), during hydraulic fracturing, and for 1 year after hydraulic fracturing (Figures 18, 19, and 20).

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[1] Natural gas in Upper Devonian/Lower Mississippian sandstone reservoirs migrated there from underlying carbonaceous shale units (Laughrey & Baldessare, 1998). The Burkett Shale and the Marcellus Shale are the closest organic-rich source rock for gas in the Upper Devonian/Lower Mississippian reservoirs at this site. This implies that the seal provided by strata between the Burkett Shale/Marcellus Shale and the Upper Devonian/Lower Mississippian gas reservoirs is not perfect and that significant amounts of gas have moved through this seal by natural processes over geologic time.

UD-1 is the Upper Devonian/Lower Mississippian gas well that is closest to the out-of-zone microseismic event clusters located during the hydraulic fracturing of horizontal Marcellus Shale Wells A, B, and C (Figures 8 and 16). Therefore, this is the well where the producing zones in Upper Devonian/Lower Mississippian are closest to known areas of fracture growth above the Tully Limestone; and where communication between the Marcellus Shale and the Upper Devonian/Lower Mississippian could most likely occur. Production history prior to hydraulic fracturing of the underlying horizontal Marcellus Shale wells shows a typical decline curve interrupted by spikes (periods of high pressure and no production) coincident with well shut-in periods. When underlying Marcellus Shale Wells A, B, and C were hydraulically fractured, gas production from UD-1 was at a minimum, but increased to a higher, more consistent level of production afterwards (Figure 18). It is worth noting that the orifice plate in the UD-1 flowmeter was downsized during the period of hydraulic fracturing in Marcellus Shale Wells A, B, and C. The new plate with its smaller orifice was more appropriate for the low-pressure, low-volume gas production from UD-1, and may be responsible for the more consistent gas production measurements after its installation.

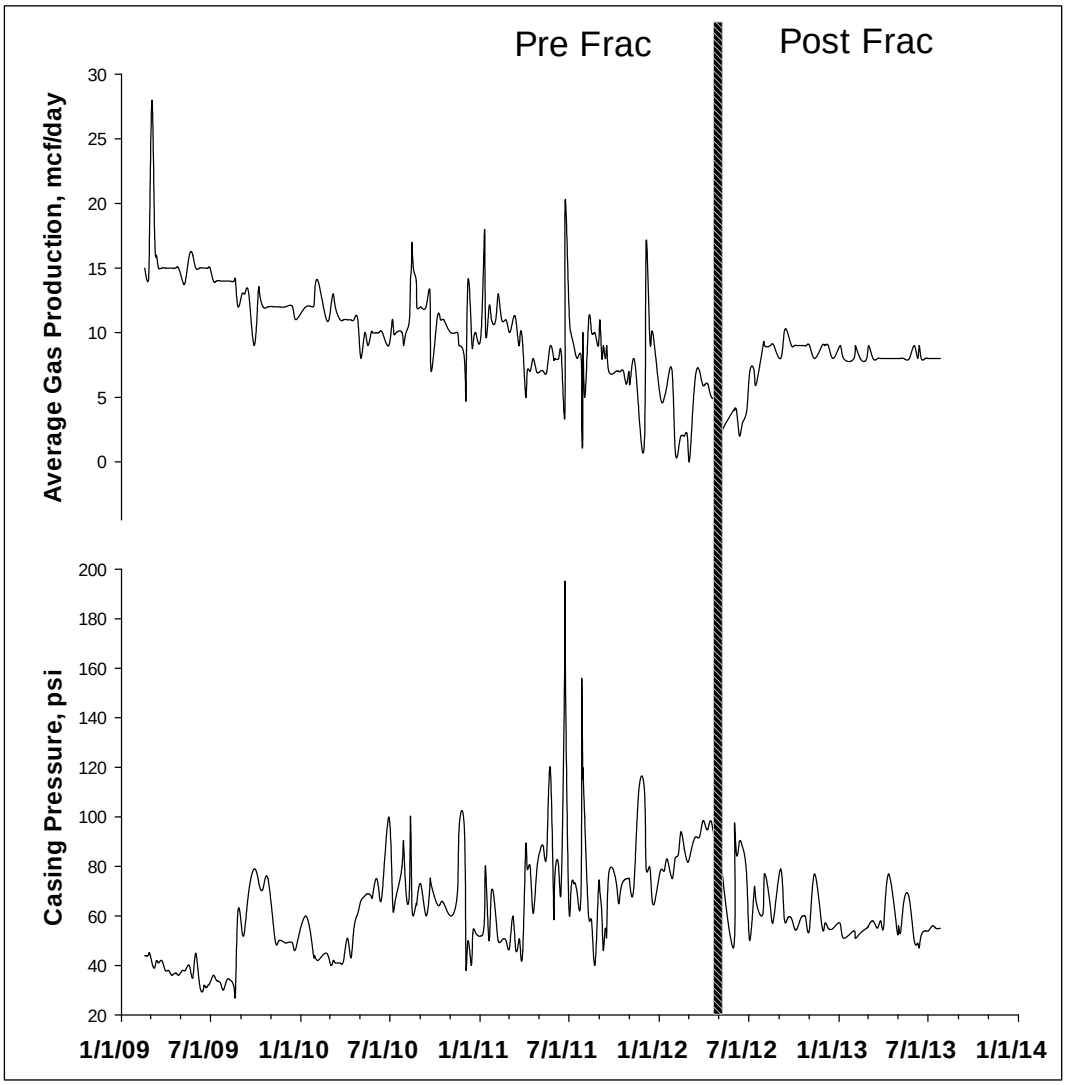

Figure 18: Gas production and casing pressure history for Upper Devonian/Lower Mississippian gas Well #1 (UD-1). Vertical line denotes the time period of hydraulic fracturing of horizontal Marcellus Shale gas Wells A, B, and C. Data spikes represent periods when well was shut in.

Upper Devonian/Lower Mississippian Well #2 (UD-2) is located near the near-vertical segments of horizontal Marcellus Shale Wells A, B, C, D, E, and F (Figure 8), a location that is useful for monitoring potential vertical migration of gas and fluids from the Marcellus Shale via the annuli of these wells. Microseismic results (Figure 11) show few events above the Tully Limestone in the vicinity of UD-2, suggesting that induced fracture growth remained within or close to the Marcellus Shale in this area.

The pre-frac and post-frac history of gas production, casing pressure, and tubing pressure from UD-2 (Figure 19) shows no evidence of sustained pressure and production increase after hydraulic fracturing that would indicate near-term communication with the over-pressured Marcellus Shale.

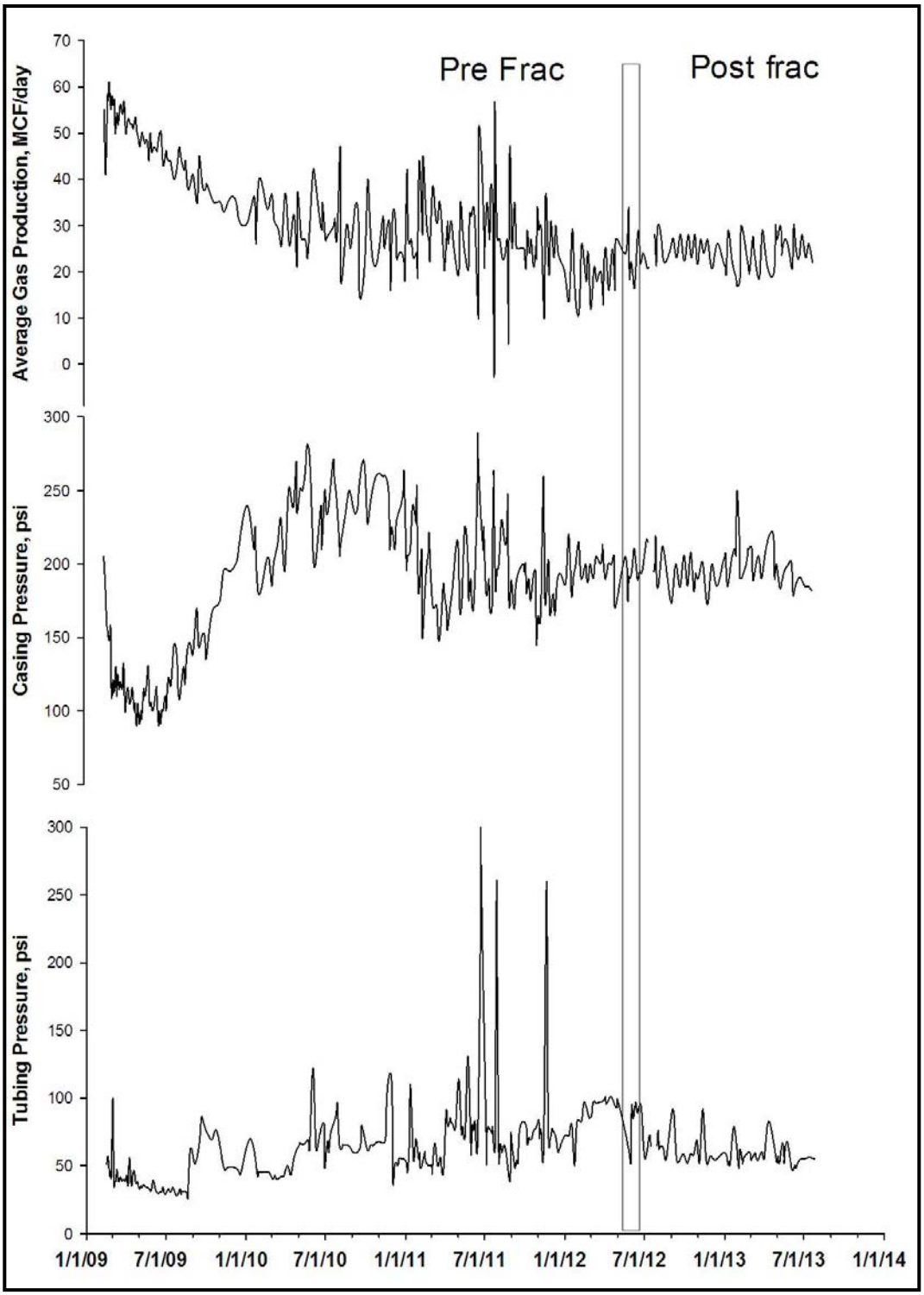

Figure 19: Production and pressure history for Upper Devonian Well #2 (UD-2). The vertical rectangle indicates the period during hydraulic fracturing of the Marcellus Shale.

Upper Devonian/Lower Mississippian Well #5 (UD-5, Figure 8) is located above Stage 2 of horizontal Marcellus Shale Well E where a fault, not recognized in reflection seismic data, was encountered during drilling. The observed fault, if open, would be expected to facilitate the flow of fracturing fluids away from the well. However, the limited number of microseismic events located above the Tully Limestone in this area were widely separated (Figure 14; light green events); there was no clustering of microseismic events in the vicinity of the observed fault that might indicate the dilation and extension of the fault caused by fluid injection. However, if the fault was open, fluid flow through the fault during hydraulic fracturing might be aseismic.

The production and pressure history of UD-5 (Figure 20) is typical for a low-pressure, low-production gas well. Within the timeframe of this study, there has been no increase in production and pressure that would suggest communication between the Marcellus Shale and the Upper Devonian/Lower Mississippian.

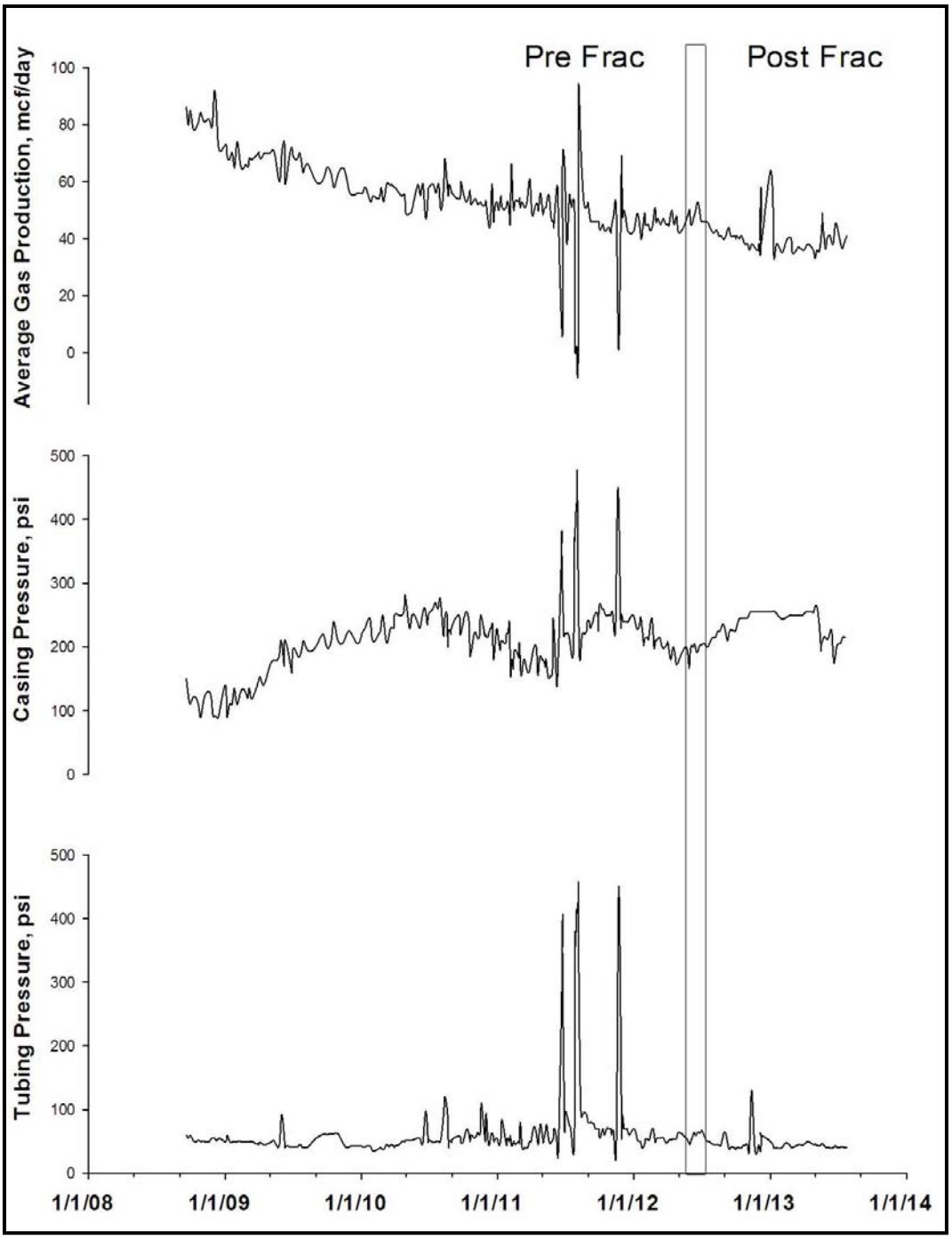

Figure 20: Production and pressure history for Upper Devonian/Lower Mississippian Well #5 (UD-5). The vertical rectangle indicates the period during hydraulic fracturing of the Marcellus Shale.

2.3 CARBON AND HYDROGEN ISOTOPE SIGNATURE OF GAS ($\delta^{13}C_{CH4}$ AND $\delta^{2}H_{CH4}$)

Samples of natural gas were collected from seven Upper Devonian gas wells (UD-1 through UD-7, Figure 7) and two vertical Marcellus Shale gas wells (MW-1 and MW-2, Figure 7). Sampling was bimonthly prior to hydraulic fracturing (in the underlying horizontal Marcellus Shale wells), monthly during hydraulic fracturing and for a period of 4 months after hydraulic fracturing, and then bimonthly for the next 4 months. Procedures for the collection and analysis of gas samples for carbon and hydrogen isotopes are described in Appendix B.

Between March 2012 and February 2013, the carbon isotope signature of gas ($\delta^{13}C_{CH4}$) for natural gas samples (Figure 21) collected from seven Upper Devonian/Lower Mississippian gas wells ranged from -43.81‰ to -43.06‰ (SD 0.17‰). The $\delta^{13}C_{CH4}$ for natural gas samples from two vertical Marcellus Shale gas wells (Figure 21) ranged from -38.55‰ to -37.49‰ (SD 0.29‰). Similarly, the hydrogen isotope signature of gas ($\delta^{2}H_{CH4}$) for natural gas samples (Figure 21) from seven Upper Devonian/Lower Mississippian gas wells ranged from -198.5‰ to -184.8‰ (SD 2.75‰); the $\delta^{2}H_{CH4}$ for two vertical Marcellus Shale gas wells ranged from -169.1‰ to -163.4‰ (SD 1.67‰). Both the $\delta^{13}C_{CH4}$ and the $\delta^{2}H_{CH4}$ signature of natural gas from the two vertical Marcellus Shale wells is distinctly different from that of gas samples from the seven Upper Devonian/Lower Mississippian wells, a characteristic that can be used to identify any mixing between the two gas reservoirs. Figures 22 and 23 are simple mixing curves that predict the percentage of Marcellus Shale gas that must be present in Upper Devonian/Lower Mississippian gas to be detected using gas isotopes. Mixing curves indicate that Marcellus Shale gas fractions of 10% or more can be detected using $\delta^{13}C_{CH4}$, while Marcellus Shale gas fractions of 30% or more can be detected using $\delta^{2}H_{CH4}$.

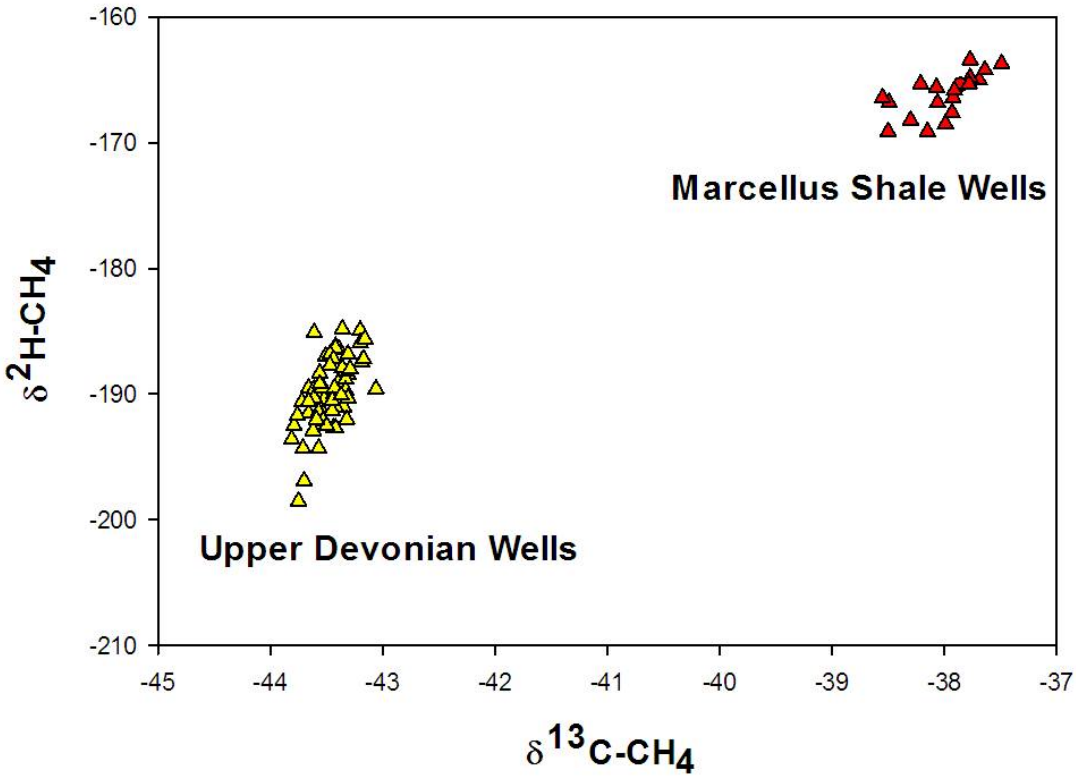

Figure 21: Crossplot of $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 for gas samples from Upper Devonian/Lower Mississippian wells and Marcellus Shale wells.

Figure 24 is a plot of $\delta^{13}C_{CH4}$ versus time for natural gas samples collected from the seven Upper Devonian/Lower Mississippian wells and the two vertical Marcellus Shale wells. Figure 24 shows that the $\delta^{13}C_{CH4}$ values of gas samples from Upper Devonian/Lower Mississippian wells have remained relatively constant and distinctly different from the $\delta^{13}C_{CH4}$ values of gas from Marcellus Shale wells before, during, and after hydraulic fracturing. Based on $\delta^{13}C_{CH4}$ results (Figure 24) and the mixing curve for $\delta^{13}C_{CH4}$ (Figure 22), there is no evidence of Marcellus Shale gas in the gas produced from the Upper Devonian/Lower Mississippian wells (minimum detection limit is 10% Marcellus Shale gas).

Figure 25 is a plot of $\delta^{2}H_{CH4}$ versus time for natural gas samples collected from the seven Upper Devonian/Lower Mississippian wells and the two vertical Marcellus Shale wells. Figure 25 shows that the $\delta^{2}H_{CH4}$ values of gas samples from Upper Devonian/Lower Mississippian wells also have remained distinctly different from the $\delta^{2}H_{CH4}$ values of gas from Marcellus Shale wells before, during, and after hydraulic fracturing. However, the $\delta^{2}H_{CH4}$ values for gas from Upper Devonian wells have a broad range, which requires a higher fraction of Marcellus Shale gas to be detected with confidence. Based on $\delta^{2}H_{CH4}$ results (Figure 25) and the mixing curve for $\delta^{2}H_{CH4}$ (Figure 23), there is no evidence of Marcellus Shale gas in the gas produced from the Upper Devonian/Lower Mississippian wells (minimum detection limit is 30% Marcellus Shale gas).

The $\delta^{13}C_{CH4}$ or $\delta^{2}H_{CH4}$ values of gas from the seven Upper Devonian/Lower Mississippian wells do not change during or after hydraulic fracturing of the underlying horizontal Marcellus Shale wells. A detectable shift in $\delta^{13}C_{CH4}$ or $\delta^{2}H_{CH4}$ values of Upper Devonian/Lower Mississippian gas would be expected if a significant fraction (~10%) of the gas produced from Upper Devonian/Lower Mississippian wells came from the gas liberated within the Marcellus Shale during the 2012 hydraulic fracturing operations.

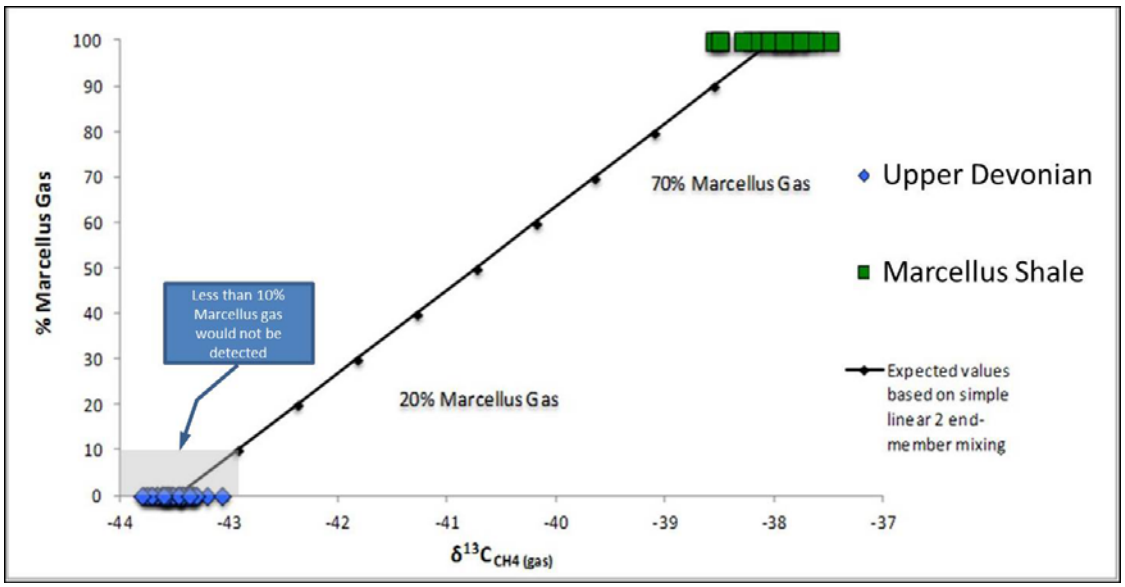

Figure 22: Simulated mixing curve that predicts $\delta^{13}C_{CH4}$ based on the percent Marcellus Shale gas that is mixed with Upper Devonian/Lower Mississippian gas.

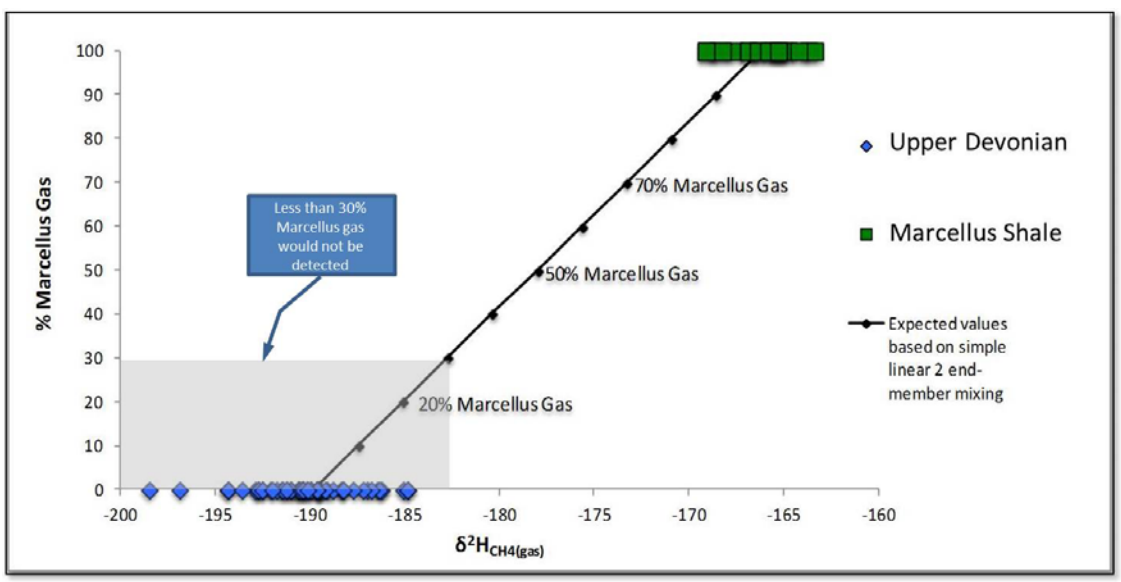

Figure 23: Simulated mixing curve that predicts $\delta^{2}H_{CH4}$ based on the percent Marcellus Shale gas that is mixed with Upper Devonian/Lower Mississippian gas.

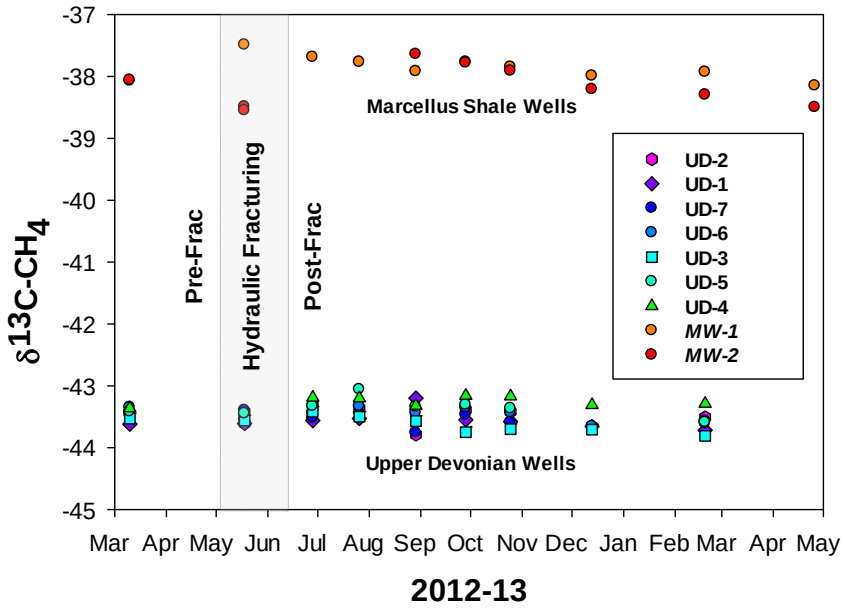

Figure 24: The $\delta^{13}C_{CH4}$ of natural gas samples collected from seven Upper Devonian/Lower Mississippian gas wells and two vertical Marcellus Shale gas wells versus time. Time period of hydraulic fracturing in underlying horizontal Marcellus Shale gas wells is shown by shading.

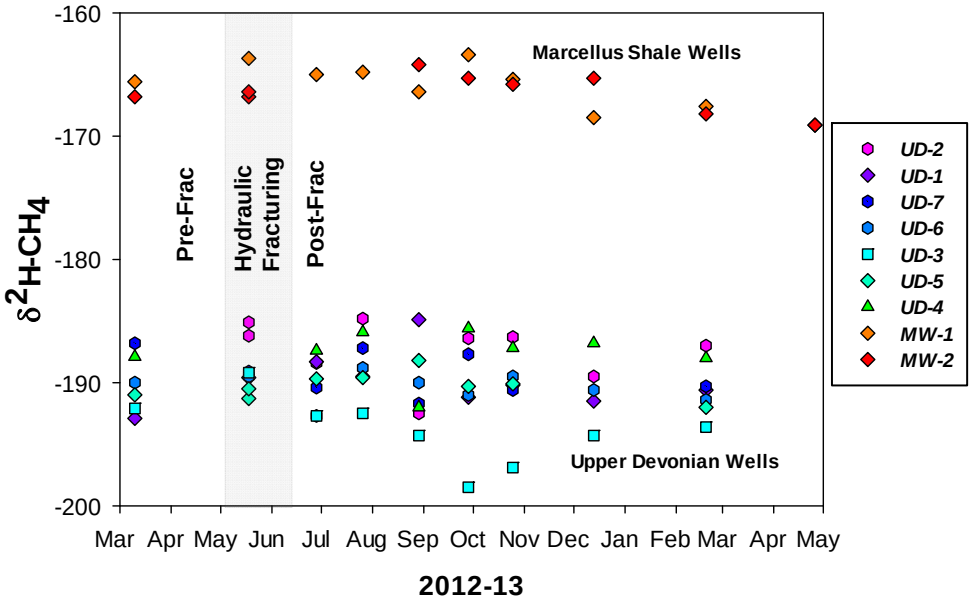

Figure 25: The $\delta^{2}H_{CH4}$ of natural gas samples collected from seven Upper Devonian/Lower Mississippian gas wells and two vertical Marcellus Shale gas wells versus time. Time period of hydraulic fracturing in underlying horizontal Marcellus Shale gas wells is shown by shading.

2.4 STRONTIUM ISOTOPE COMPOSITION OF PRODUCED WATER

Strontium (Sr) isotopes have long been used to track fluid–rock interaction and the origin of dissolved solids in geologic systems (Banner, 2004). Because ^{87}Sr is a radiogenic, relatively high-mass isotope produced by the decay of ^{87}Rb, the isotopic ratio of $^{87}Sr/^{86}Sr$ does not measurably vary with natural fractionation processes (e.g., temperature, biological activity, and evaporation), in contrast to lower mass systems such as C, O, and H. This allows use of the $^{87}Sr/^{86}Sr$ ratio as a natural tracer that can be used to identify source and quantify the extent of mixing and water-rock interaction (Capo et al., 1988; Stewart et al., 1988). Strontium isotope ratios can also be expressed using ε_{Sr}^{SW} notation, where the $^{87}Sr/^{86}Sr$ ratio of the sample is normalized to the globally uniform $^{87}Sr/^{86}Sr$ ratio of present-day seawater:

$$\varepsilon_{Sr}^{SW} = 10^4 \left(\frac{^{87}Sr/^{86}Sr_{sample}}{^{87}Sr/^{86}Sr_{seawater}} - 1 \right)$$

Produced water from Marcellus Shale gas wells across Pennsylvania fall within a relatively narrow range of Sr isotope values (ε_{Sr} = +14 to +42; $^{87}Sr/^{86}Sr$ = 0.7101-0.7121; Chapman et al., 2012; Capo et al., 2014) that are distinctly lower than Upper Devonian produced waters (Chapman et al., 2013; Kolesar et al., 2013; and this study). Figure 26 shows that $^{87}Sr/^{86}Sr$ values of Marcellus flowback/produced waters (lower left) differ significantly from brines from Upper Devonian/Lower Mississippian produced waters analyzed for this and other studies. The large difference between the $^{87}Sr/^{86}Sr$ ratio of the Marcellus Shale brines and the Upper Devonian/Lower Mississippian brines allow Sr isotopes to be a sensitive tracer of fluid migration between end members. Because Marcellus Shale produced waters also generally have Sr concentrations that are an order of magnitude greater than those of the Upper Devonian/Lower Mississippian waters in this region, $^{87}Sr/^{86}Sr$ ratios of the latter are particularly sensitive to small (>0.5%) intrusions of the former. Our measurement uncertainty is generally ≤ 0.2 ε units; a calculated mixing curve (Figure 27) indicates that infiltration of, for example, 5% Marcellus Shale brine into a unit bearing Upper Devonian/Lower Mississippian brine would result in a large shift of over 25 ε units. This provides a strong rationale for using Sr isotopes to monitor fluid migration as part of this study.

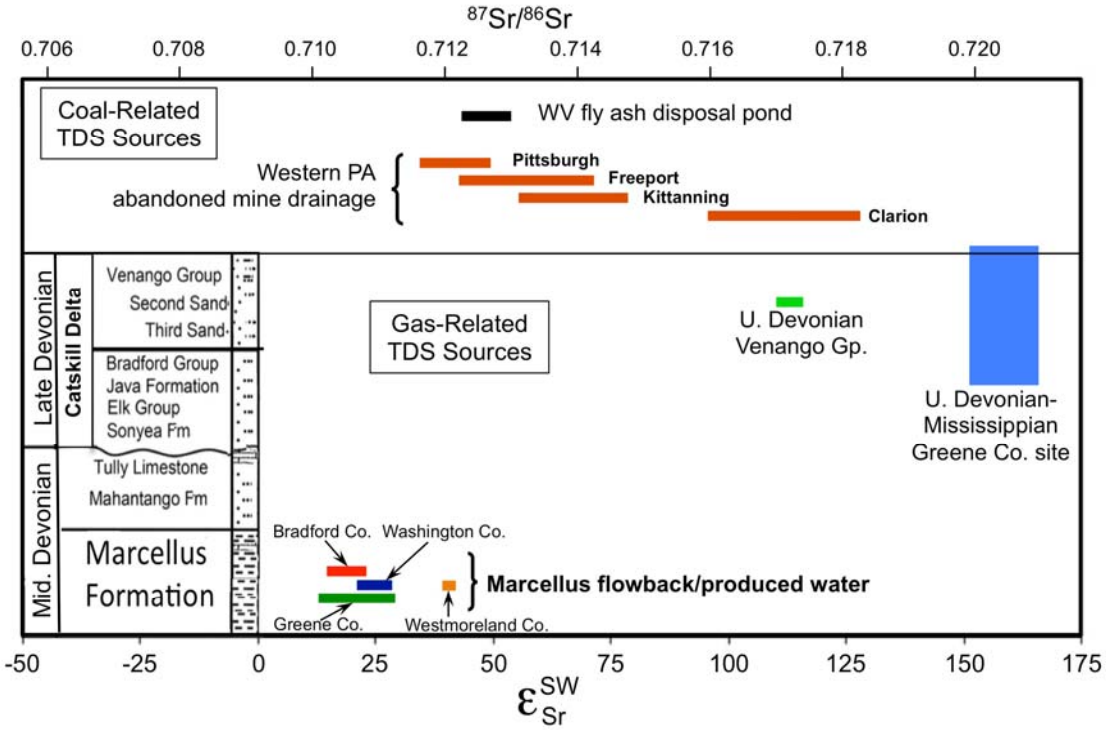

Figure 26: Variation in $^{87}Sr/^{86}Sr$ ratios of Marcellus produced waters, Upper Devonian and younger produced waters, and acid mine drainage. Data are from Chapman et al. (2012, 2013), Capo et al. (2014), Kolesar (2013) and this study. This figure is modified from Chapman et al. (2012).

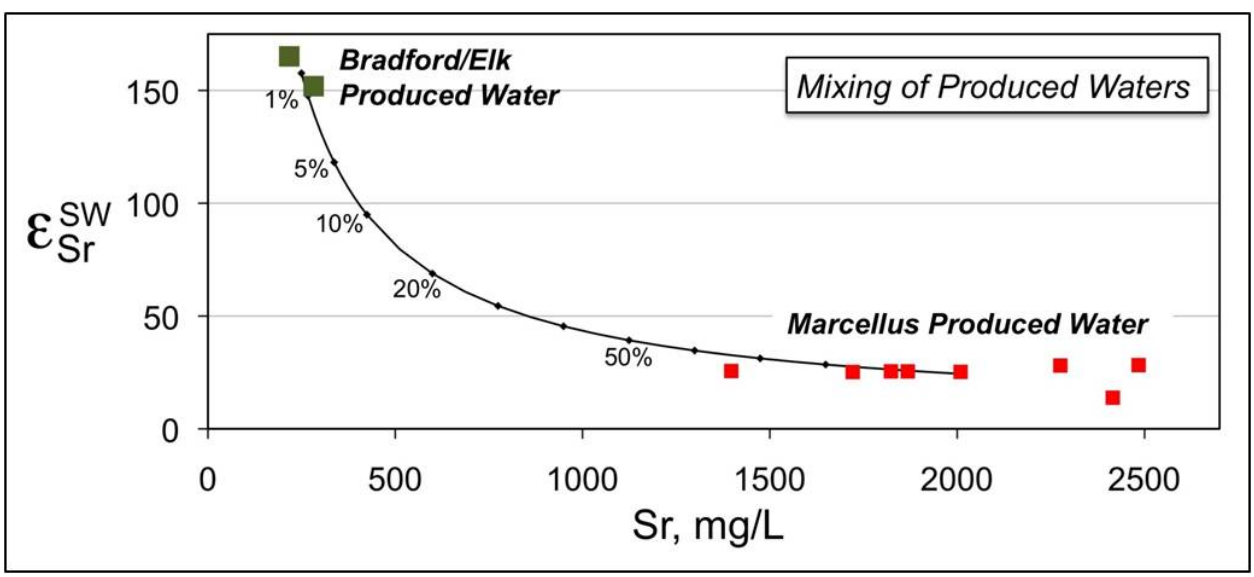

Figure 27: Strontium concentrations and isotope compositions of produced waters from Upper Devonian/Lower Mississippian gas wells and the Marcellus Shale. The mixing curve indicates the sensitivity of the Upper Devonian/Lower Mississippian waters to incursions of Marcellus-derived fluid at the Greene County study site.

This report shows results of Sr isotopic analysis of produced waters from: (1) three horizontal Marcellus shale gas wells spanning a period of up to 9 months following completion; and (2) five vertical wells completed in Upper Devonian/Lower Mississippian gas-bearing units, both before hydraulic fracturing (in the underlying Marcellus Shale) and for 5 months afterwards. Procedures for collection of produced water samples are described in Appendix C, and chemical separation and analytical methods used for Sr isotopic analysis are described in Appendix D.

The Marcellus produced water time series from horizontal Marcellus Shale gas Wells D, E, and F at the Greene County site follow the pattern described by Chapman et al. (2012), in which the Sr concentration increases at a consistent rate during the monitoring period. However, the $^{87}Sr/^{86}Sr$ ratio increases rapidly during the first 2 days of flowback, but then increases at a slower rate for the remainder of the monitoring period (Table 1; Figure 28). This is thought to reflect the mixing of hydraulic fracturing fluids with formation water, with the fraction of formation water increasing over time (Capo et al., 2014).

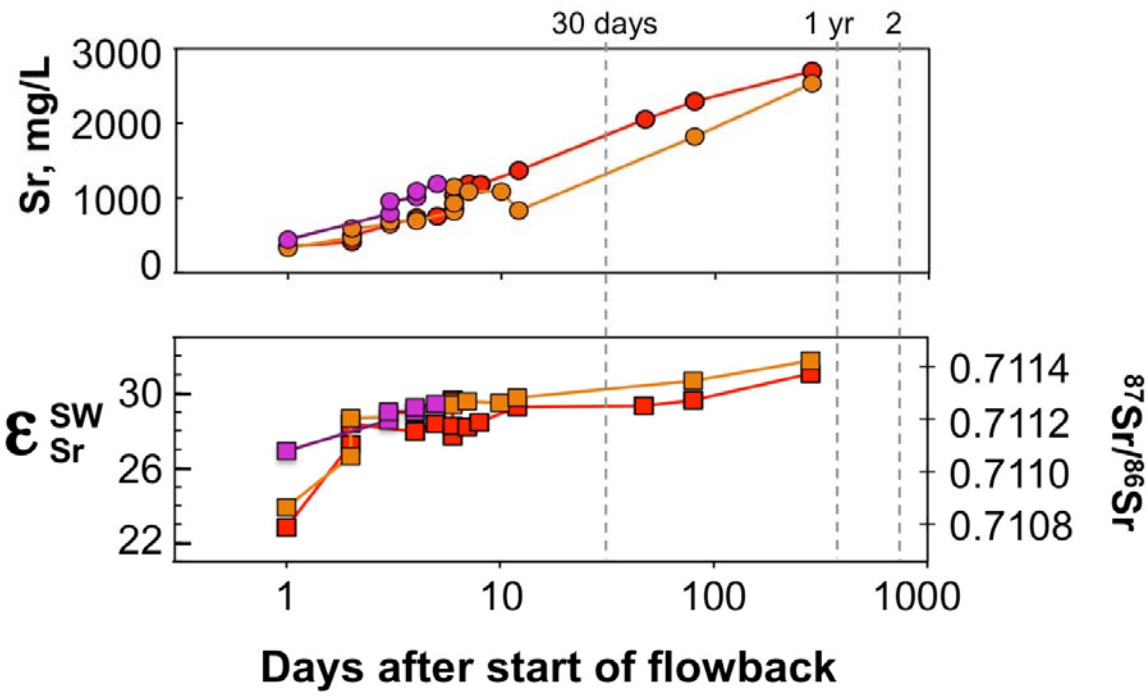

Figure 28: Change over time in Sr concentration and isotopic composition of flowback/ produced water from horizontal Marcellus Shale gas Wells D, E, and F at the Greene County study site. This figure is modified from Capo et al. (2014).

Table 1: Concentrations of Sr and Ca and Sr isotopic composition of flowback and produced water from horizontal Marcellus Shale gas Wells D, E, and F. Data from Capo et al. (2014).

Sample Name	Days after flowback	Sr ppm	Ca ppm	$^{87}Sr/^{86}Sr^{a,b}$			ε_{Sr}^{c}		
GREENE A									
GRN-A1-0001	1	353	2,154	0.710785	±	0.000010	22.83	±	0.14
GRN-A1-0002a	2	417	2,610	0.711099	±	0.000010	27.26	±	0.14
GRN-A1-0002b	2	498	3,143	0.711178	±	0.000010	28.37	±	0.14
				0.711166	±	0.000010	28.20	±	0.14
GRN-A1-0004	4	740	5,647	0.711149	±	0.000008	27.96	±	0.11
GRN-A1-0005	5	755	4,697	0.711177	±	0.000008	28.36	±	0.11
GRN-A1-0006a	6	855	5,481	0.711131	±	0.000010	27.71	±	0.13
GRN-A1-0006b	6	932	5,552	0.711269	±	0.000008	29.65	±	0.11
GRN-A1-0006c	6	1,037	6,120	0.711169	±	0.000010	28.24	±	0.13
GRN-A1-0007	7	1,190	13,806	0.711165	±	0.000008	28.19	±	0.11
GRN-A1-0008	8	1,183	7,480	0.711184	±	0.000008	28.46	±	0.11
				0.711184	±	0.000008	28.46	±	0.11
GRN-A1-0012	12	1,365	8,200	0.711241	±	0.000010	29.26	±	0.13
GRN-A1-0047	47	2,052	17,034	0.711246	±	0.000010	29.33	±	0.13
GRN-A1-0080	80	2,296	19,331	0.711267	±	0.000008	29.63	±	0.11
GRN-A1-0283	283	2,698	14,978	0.711368	±	0.000010	31.05	±	0.14
GRN-A2-0001	1	330	1,810	0.710861	±	0.000010	23.90	±	0.13
GRN-A2-0002a	2	471	3,293	0.711055	±	0.000010	26.64	±	0.13
GRN-A2-0002b	2	593	3,728	0.711199	±	0.000010	28.67	±	0.13
GRN-A2-0003a	3	645	3,974	0.711202	±	0.000010	28.71	±	0.13
GRN-A2-0003b	3	686	4,254	0.711215	±	0.000010	28.89	±	0.13
				0.711210	±	0.000010	28.82	±	0.13
GRN-A2-0004	4	698	4,360	0.711220	±	0.000010	28.96	±	0.13
GRN-A2-0006a	6	817	5,300	0.711251	±	0.000008	29.40	±	0.11
				0.711255	±	0.000008	29.46	±	0.11
GRN-A2-0006b	6	927	6,120	0.711259	±	0.000020	29.51	±	0.28
GRN-A2-0006c	6	1,149	12,899	0.711250	±	0.000003	29.39	±	0.04
GRN-A2-0007	7	1,086	7,608	0.711264	±	0.000008	29.58	±	0.11
GRN-A2-0010	10	1,085	12,221	0.711257	±	0.000011	29.49	±	0.16
				0.711285	±	0.000011	29.88	±	0.16
GRN-A2-0012	12	833	10,310	0.711276	±	0.000011	29.75	±	0.16
				0.711268	±	0.000011	29.64	±	0.16
GRN-A2-0080	80	1,823	15,846	0.711341	±	0.000008	30.67	±	0.11
GRN-A2-0283	283	2,531	14,851	0.711416	±	0.000010	31.73	±	0.14
GRN-A3-0001	1	444	2,856	0.711074	±	0.000010	26.90	±	0.14
GRN-A3-0003a	3	793	5,093	0.711192	±	0.000010	28.57	±	0.14
GRN-A3-0003b	3	957	5,867	0.711225	±	0.000010	29.03	±	0.14
GRN-A3-0004a	4	1,011	6,153	0.711225	±	0.000010	29.03	±	0.14

Sample Name	Days after flowback	Sr ppm	Ca ppm	$^{87}Sr/^{86}Sr^{a,b}$			$\varepsilon_{Sr}{}^{c}$		
GREENE A									
GRN-A3-0004b	4	1,093	8,955	0.711240	±	0.000008	29.25	±	0.11
GRN-A3-0005	5	1,187	9,302	0.711254	±	0.000008	29.44	±	0.11
[a]Reported $^{87}Sr/^{86}Sr$ normalized to SRM987 = 0.710240.									
[b]In-run uncertainty shown; estimated external reproducibility better than ±0.000016.									
[c]$e_{Sr} = (^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater} - 1)*10^4$; seawater ratio = 0.709166.									

To determine if hydraulic fracturing caused rapid incursions of formation waters from the stimulated zone into shallower reservoirs, Upper Devonian to Mississippian produced waters from wells directly overlying the laterals were sampled before and after hydraulically fracturing. As noted previously, incursion of only a few percent of Marcellus brines should cause a measurable shift in $^{87}Sr/^{86}Sr$ of the overlying formation waters. Pre- and post-frac isotopic variations for five overlying reservoirs (UD-2, UD-4, UD-5, UD-6 and UD-7) are shown in Figure 29. For the first 5 months of monitoring after hydraulic fracturing, the overlying reservoirs do not show detectable shifts toward Marcellus Shale (lower $^{87}Sr/^{86}Sr$) values outside of normal geological variation; thus, there are no indications of intermixing of Marcellus formation waters in water produced from the Upper Devonian/Lower Mississippian wells (Kolesar et al., 2013).

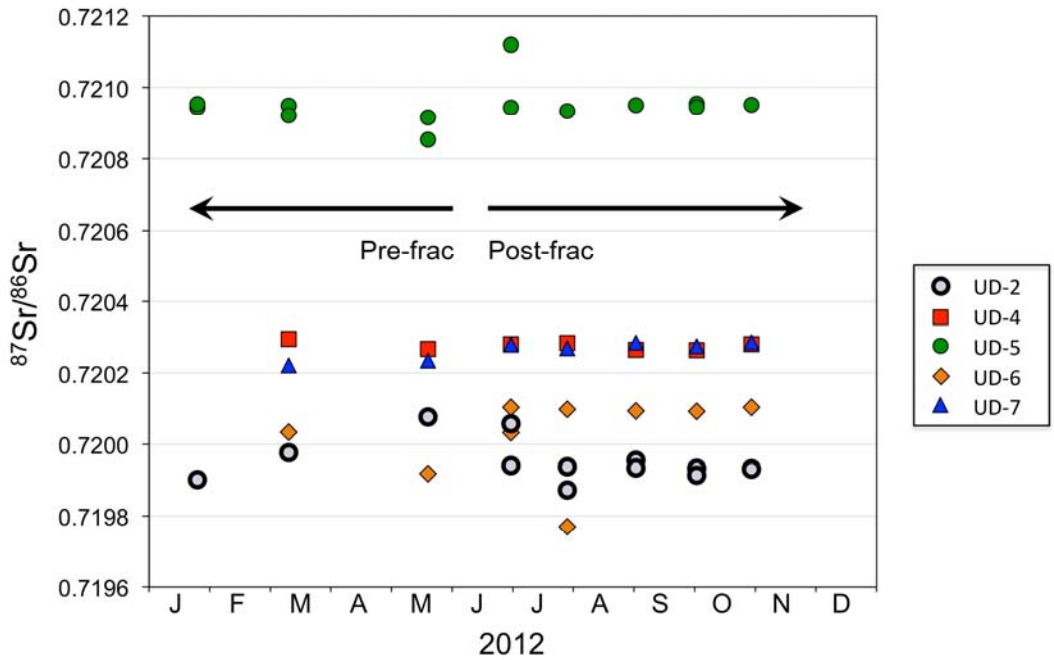

Figure 29: Variation in Sr isotope ratio of formation waters from Upper Devonian/Lower Mississippian units overlying hydraulically fractured Marcellus laterals. Measurement uncertainty falls within the size of the symbols. Following hydraulic fracturing, there is no significant downward shift toward Marcellus $^{87}Sr/^{86}Sr$ values (0.710-0.712) outside of normal geological variation.

2.5 PERFLUOROCARBON (PFC) TRACERS

The objective of this study was to inject perfluorocarbon (PFC) tracers into a horizontal Marcellus Shale gas well during hydraulic fracturing and then monitor for the presence of those tracers in gas produced from two overlying Upper Devonian/Lower Mississippian gas wells. A positive detection of PFC tracer in the gas from Upper Devonian/Lower Mississippian wells might indicate that gas had migrated up from the hydraulically fractured Marcellus Shale about 3,800 ft below.

PFC tracers were injected with hydraulic fracturing fluids into 10 stages (Stages 5–14) of the 14-stage, horizontal Marcellus Shale gas Well E (Figure 5 and Figure 30). PFC tracers were chosen for this application because they were expected to partition to the gas phase within the formation and move upward with the buoyant gas through created and natural fractures. PFC tracers were also chosen because of their exceptionally low detection volume of about 2 femtoliter (fL).

The study employed both active and passive monitoring to detect PFC tracers in gas produced from two Upper Devonian/Lower Mississippian wells (UD-2 and UD-5, Figure 5) that overlie horizontal Marcellus Shale gas Well E (where PFC tracers were injected during hydraulic fracturing). Active monitoring consisted of the frequent sampling of natural gas from UD-2 and UD-5 with subsequent gas analysis for the presence of PFC tracers. Passive monitoring was accomplished by placing a tube containing PFC absorbing material directly in the gas production

lines from UD-2 and UD-5. Periodically, the exposed sorbent tubes were exchanged for fresh tubes and the exposed tubes were analyzed for presence of tracer.

2.5.1 PFC Tracer Injection

ProTechnics injected four PFC tracers with the hydraulic fracturing fluids into 10 stages of Well E including: perfluoromethylcyclohexane (PMCH) was injected into Stages 5, 6, and 7; perfluorotrimethylcyclohexane (PTCH) was injected into Stages 8, 9, and 10; perfluorodimethylcyclobutane (PDCB) was injected into Stages 11, 12, and 13; and perfluoro-i-propylcyclohexane (iPPCH) was injected into Stage 14. For each Stage, 473 mL of the appropriate PFC tracer was introduced into hydraulic fracturing fluids between the blender and high pressure pumps. The tracer injection was timed to coincide with the pumping of the pad (post-acid and pre-proppant), which would allow the tracer to be carried away from the perforations to the most distant parts of created fractures. Within the formation, the PFC tracer was expected to form a non-aqueous, buoyant phase that would migrate to the uppermost extremities of created and existing fractures. More detailed information about the PFC tracer injection, including pad volume, total clean volume, and average pumping pressure and rate for the treatment of each stage of Well E is provided in Appendix E.

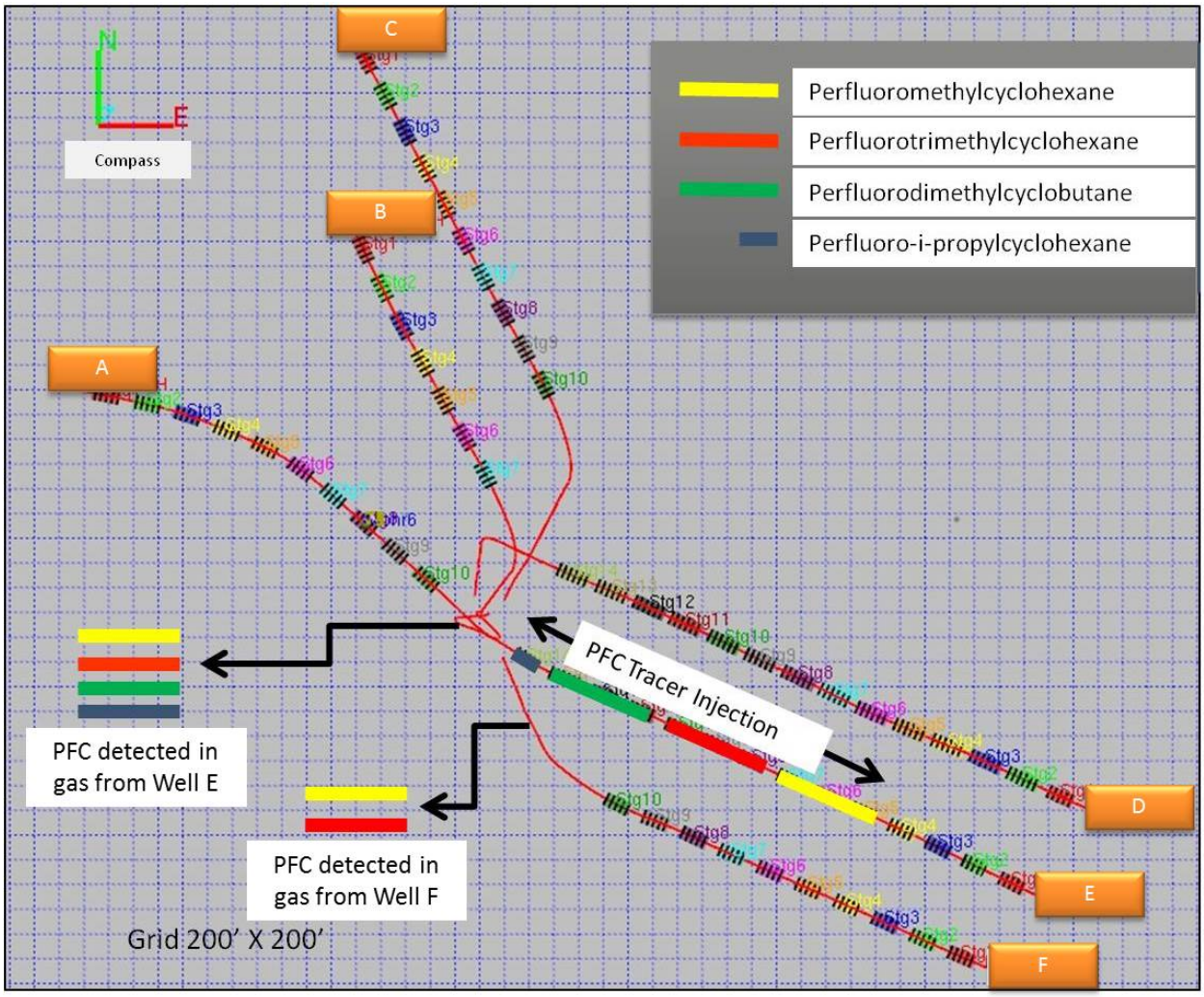

Figure 30: Map of horizontal Marcellus Shale wells showing where four PFC tracers were injected into Stages 5–14 of Well E. The identity of PFC tracers are denoted by color bars on the map overlying stages where injected. Also shown are color bars indicating the identity of tracers that were detected in gas produced from Wells E and F.

2.5.2 PFC Tracers - Atmospheric Background Levels

Gerstel® tubes containing PFC absorbing material were exposed to the atmosphere at UD-2 and UD-5 well locations and subsequently analyzed for PFC tracers. PFC tracer levels in the atmosphere were often near detection limits (Figures 31 and 32). Occasionally, high atmospheric concentrations of PFC tracers were detected, and may indicate times when the wind was blowing from directions where flowback/produced water (containing PFC tracers from injection well) was stored. Table 2 provides an assessment of the variability of atmospheric PFC tracer levels.

Table 2: Atmospheric concentration of PFC tracers at three well sites where natural gas was sampled and analyzed for presence of tracer. All values are in femtoliter (fL).

Well Location	Tracer	Average	Standard Deviation	Number of Samples	Maximum Values
UD-5	iPPCH	380	716	15	2,786
UD-5	PTCH	342	623	14	1,852
UD-5	PMCH	4	6	15	21
UD-5	PDCB	1,450	5,589	15	21,655
UD-2	iPPCH	1,211	3,199	17	12,915
UD-2	PTCH	1,645	4,749	17	18,883
UD-2	PMCH	4	12	17	48
UD-2	PDCB	525	1,554	17	5,803
MW-2	iPPCH	505	607	4	1,335
MW-2	PTCH	512	632	4	1,368
MW-2	PMCH	10	13	4	27
MW-2	PDCB	5	6	4	14

2.5.3 PFC Tracers in Gas Production from Horizontal Marcellus Shale Wells

All four PFC tracers were detected in the gas produced from the tracer injection well (Well E, Figure 31), which indicates that no tracer was completely and irreversibly sorbed by the formation. This measurement was necessary to ensure that some of the injected tracer would be free to move with the gas from the Marcellus Shale. Two PFC tracers (PMCH and PTCH) were detected in gas produced from an adjacent horizontal Marcellus Shale well (Well F) that is parallel to and approximately 750 ft offset from the tracer injection well (Figure 32). The presence of PMCH and PTCH in gas produced from Well F could be predicted based on the location of perforated zones in Well F, the location of Well E stages where PFC tracers were injected, and the azimuth of created fractures based on microseismic results (about 50–55°). This finding provided confidence that PFC tracers perform as expected within the stimulated zone.

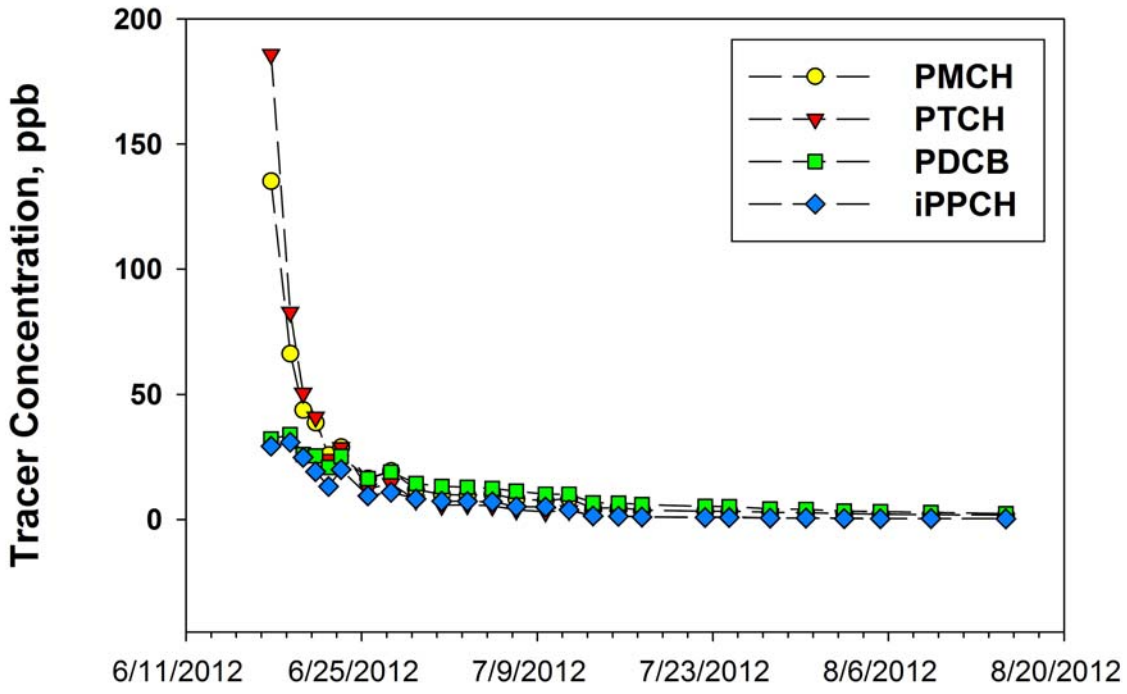

Figure 31: PFC tracer concentration in gas produced from horizontal Marcellus Shale Well E where tracers were injected.

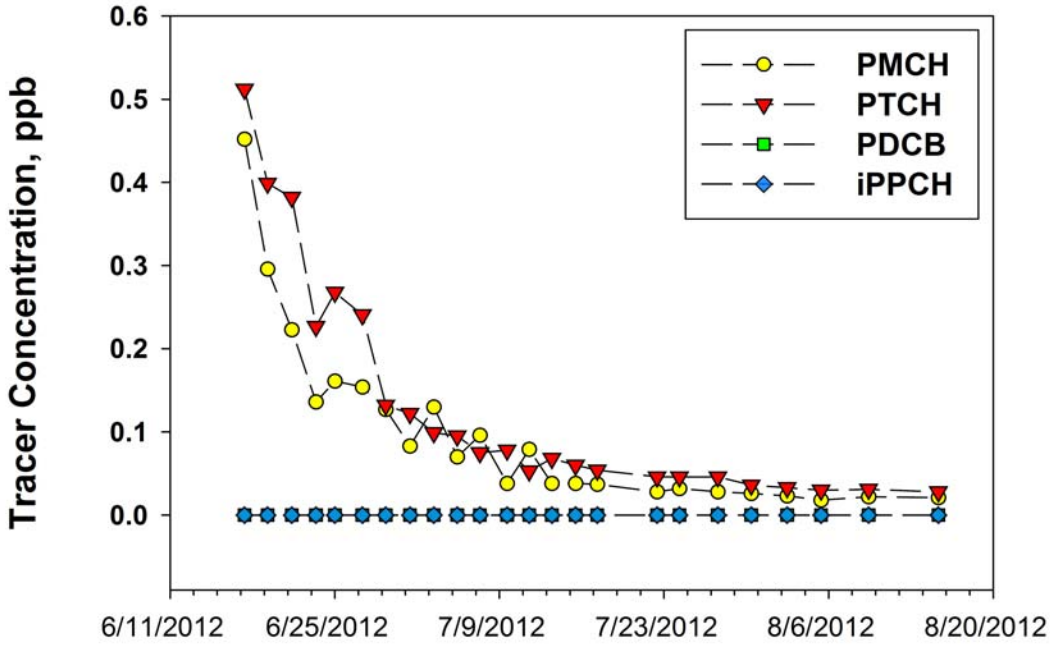

Figure 32: PFC tracer concentration in gas produced from horizontal Marcellus Shale Well F, which is offset 750 ft from the tracer injection well.

2.5.4 PFC Tracer Monitoring in Upper Devonian Gas Wells UD-2 and UD-5

The lowermost producing zone in the Upper Devonian/Lower Mississippian gas Wells UD-2 and UD-5 is at least 3,800 ft above horizontal Marcellus Shale Well E where PFC tracers were injected. Both UD-2 and UD-5 overlie hydraulically fractured stages of horizontal Marcellus Shale Well E, although only the stages beneath UD-2 were injected with PFC tracers.

Active monitoring commenced 6 days after the hydraulic fracturing of Well E was completed and consisted of collecting gas samples from UD-2 and UD-5 wells at 2-day intervals for 14 days, 4-day intervals for 20 days, and approximately 6-day intervals for the remainder of the 2-month monitoring campaign. A total of 17 gas samples were collected from each well by ProTechnics and analyzed for the presence of PFC tracer by Spectrachem. Spectrachem designated any tracer concentration exceeding 0.05 ppb as a positive detection of that tracer. No PFC tracers were detected in the gas samples from UD-2 and UD-5 (detection limit = 1 ppt).

To augment the PFC monitoring performed by ProTechnics, NETL placed Gerstel® tubes containing PFC-absorbing material directly in the gas production lines from UD-2 and UD-5. When inserted in the production line, only one end of the Gerstel® tube was open to the gas (not a flow-through configuration). Weekly at first and then monthly, the sorbent tubes were replaced with fresh tubes and the exposed tubes were analyzed for presence of PFC. The volumes of PFC tracers recovered from exposed UD-2 and UD-5 sorbent tubes are presented as “natural gas” values (black diamonds) on time series graphs (Figures 33 and 34, respectively). Also shown are “atmosphere” values (red circles), which are PFC tracer volumes recovered from sorbent tubes

that were exposed to the atmosphere at the UD-2 and UD-5 locations for the amount of time that the "natural gas" tubes were exposed to the atmosphere during tube exchange. Sometimes, when the atmosphere contained high levels of PFC tracers, the "atmosphere" values were higher than the "natural gas" values. In such cases, the "natural gas" value was considered a "no detect" irrespective of its magnitude.

Watson et al. (2007) recommended 10-times background level as the lower limit of confidence for PFC tracer detection. Using this criterion, there were no "positive" PFC tracer detections in UD-5 and a possible detection of only PMCH in UD-2. For UD-2, the PMCH "natural gas" value was 10 times greater than background values at two samplings (Figure 33). However, it should be noted that the "positive" detections of PMCH were from sorbent tubes that had been exposed to gas for month-long periods. Long exposure to gas resulted in the formation of moisture and hydrocarbon condensate in the sorbent tube. During PFC analysis, the condensates may have interfered with the analysis and resulted in false positive detections. This was not investigated because there are other indications that the sorbent tubes were not performing as expected.

This study provides evidence that sorbent tubes exposed to the natural gas stream may not be able to sorb the PFC tracer. In Figures 33 and 34, there are numerous instances where the "atmosphere" tube contained detectible amounts of PFC, but no PFC was detected in the sorbent tube that had been exposed to the natural gas flow. Both the "atmosphere" tube and the "natural gas" tube were exposed to the atmosphere for exactly the same time period. At a minimum, the "natural gas" sorbent tube should have contained the same amount of PFC tracer as the "atmosphere" tube. Visible moisture and hydrocarbon condensates are thought to have interfered with PFC sorption, but this hypothesis was not tested. If, and to what degree, moisture and hydrocarbon condensates interfered (either positively or negatively) with the sorption/desorption of PFC tracers and PFC analysis results is not known.

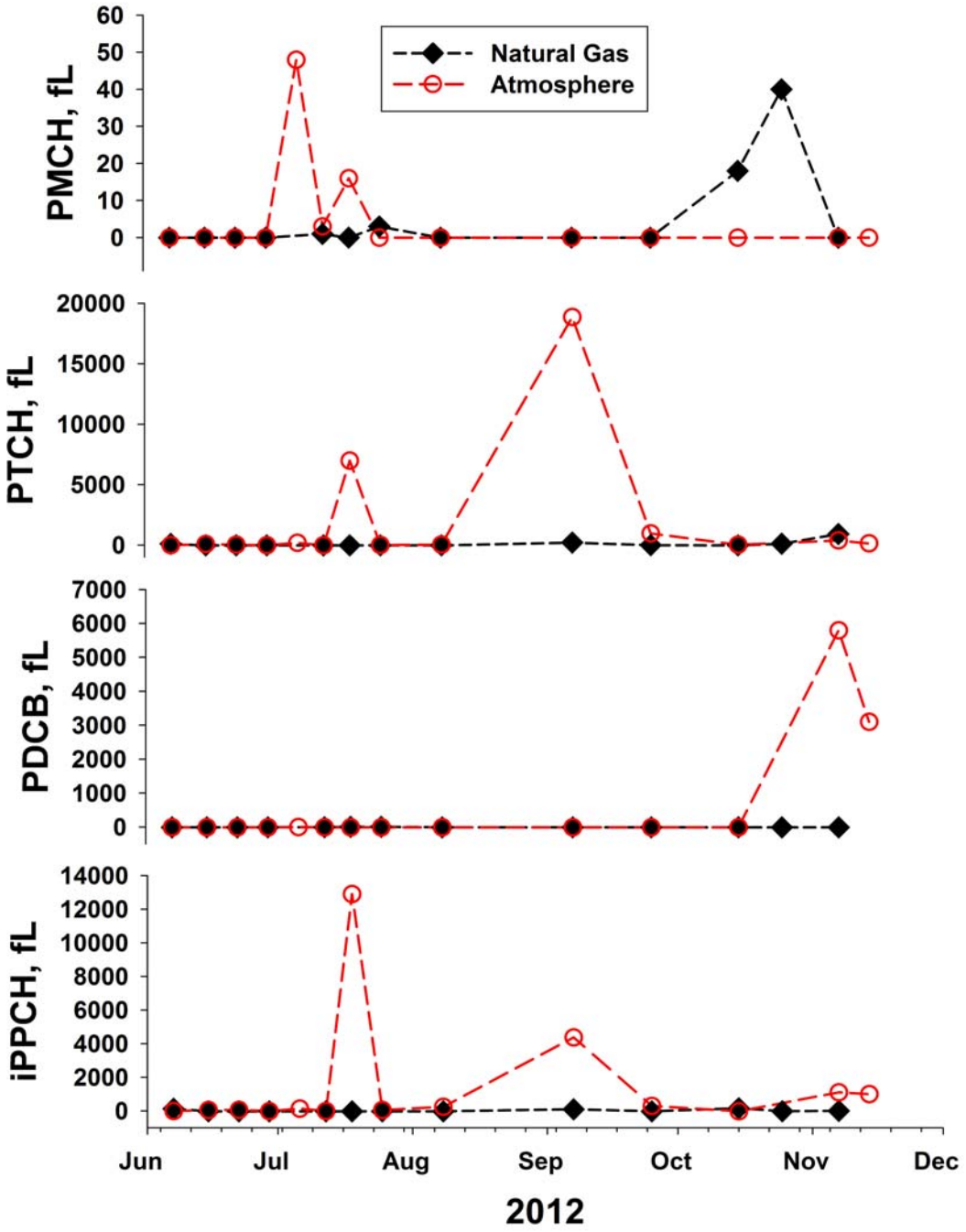

Figure 33: Volume of PFC tracer recovered from sorbent tubes that had been exposed to natural gas from Upper Devonian/Lower Mississippian Well UD-2 (black diamonds), or from sorbent tubes that had been momentarily exposed to the atmosphere at the UD-2 location (red circles).

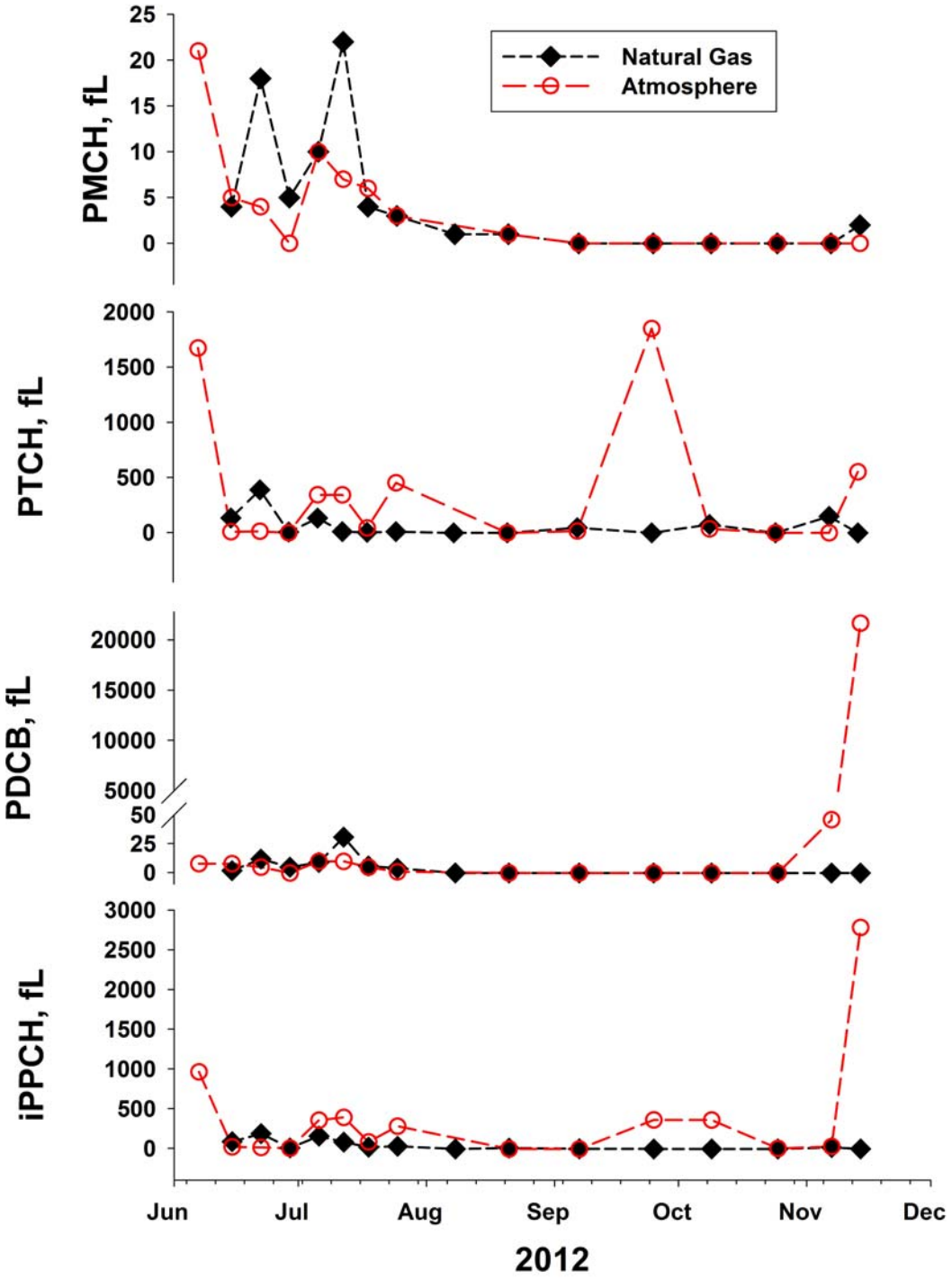

Figure 34: Volume of PFC tracer recovered from sorbent tubes that had been exposed to natural gas from Upper Devonian/Lower Mississippian Well UD-5 (black diamonds), or from sorbent tubes that had been momentarily exposed to the atmosphere at the UD-5 location (red circles).

3. CONCLUSIONS

The research objective at the Greene County site was to assess the extent and nature of fluid and gas migration from a six-well, hydraulically fractured Marcellus Shale development site. This objective was addressed by examining five independent methods that were available using existing well infrastructure at the site. The methods employed: 1) microseismic monitoring from geophones deployed in vertical Marcellus Shale wells; 2) production and pressure histories from shallower Upper Devonian/Lower Mississippian gas wells; 3) chemistry and isotopic composition of natural gas from Upper Devonian/Lower Mississippian and Marcellus Shale gas wells; 4) chemistry and isotopic composition of produced water from Upper Devonian/Lower Mississippian and Marcellus Shale gas wells; and 5) monitoring of gas produced from Upper Devonian/Lower Mississippian wells for the presence of perfluorocarbon tracers that had been injected with the hydraulic fracturing fluid into a horizontal Marcellus Shale gas well. The five methods were pursued in parallel by five teams that included researchers from government, academia, and industry. The teams included:

1. Microseismic Monitoring – NETL and Weatherford
2. Pressure and Production History – NETL
3. Isotopic Signature of Natural Gas – West Virginia University and Isotech
4. Isotopic Signature of Produced Water – University of Pittsburgh
5. Perfluorocarbon Tracers – NETL, ProTechnics, and SpectraChem

Overall conclusions pertaining to whether fluid and gas has migrated upward from the hydraulically fractured formation to the monitoring zone were made by NETL based on evidence provided by each team.

3.1 MICROSEISMIC MONITORING

Microseismic events observed during hydraulic fracturing at the Greene County site were primarily located in formations below the Tully Limestone for horizontal Marcellus Shale Wells D, E, and F. However, for Wells A, B, and C, microseismic events located above the Tully Limestone formed clusters that were 1,000 to 1,900 ft above the well. The maximum heights of these clusters are consistent with the likely uppermost extent of reverse faults (as mapped by 3-D surface seismic). Because no fault was observed at this specific location, this suggests that pre-existing fractures or small-offset (sub-seismic) faults may have focused the energy of hydraulic fracturing on certain areas and that microseismic event clusters occur where pre-existing faults or fractures terminate below younger, undisturbed strata in the Upper Devonian. Microseismic results suggest that the Tully Limestone did not always act as an upper frac barrier at this site. Above-Tully Limestone events were observed during the hydraulic fracturing of all stages of horizontal Marcellus Shale Wells A and B, and Stage 1 of Well C. For horizontal Marcellus Shale Wells D, E, and F, above-Tully Limestone events were mostly limited to Stages 1, 2, and 3. Although microseismic events were observed higher than would be expected based on the assumption that the Tully Limestone is an upper frac barrier, the uppermost microseismic events were at least 1,800 ft below the lowermost producing zone in the Upper Devonian/Lower

Mississippian gas field. Hence, microseismic data suggest that the creation of new fractures or the reactivation of existing faults or fractures was constrained to strata below the Upper Devonian/Upper Mississippian gas field.

3.2 PRESSURE AND PRODUCTION HISTORY OF UPPER DEVONIAN GAS WELLS

Results of the pressure and production history from Upper Devonian/Lower Mississippian gas wells showed no detectable increases in the gas pressure and gas production that would be expected if hydraulic fracturing in the Marcellus Shale had provide fracture pathways that connected the two reservoirs.

The gas pressure and production history data of Upper Devonian/Lower Mississippian Wells UD-1, UD-2, and UD-5 was consistent with the routine operation of low-pressure wells. There were no pressure or gas production increases in the Upper Devonian/Lower Mississippian Wells during or 1 year following hydraulic fracturing of the Marcellus Shale below that would suggest communication with the over-pressured Marcellus Shale.

3.3 CARBON AND HYDROGEN ISOTOPE SIGNATURE OF GAS ($\delta^{13}C_{CH4}$ AND $\delta^{2}H_{CH4}$)

Results of the carbon and hydrogen isotope analysis of gas produced from Upper Devonian/Lower Mississippian wells demonstrated that hydraulic fracturing of the Marcellus Shale did not provide fracture pathways that allowed detectable amounts of gas from the Marcellus Shale to migrate to the Upper Devonian/Lower Mississippian gas field.

The carbon isotope ($\delta^{13}C_{CH4}$) and hydrogen isotope ($\delta^{2}H_{CH4}$) signature of natural gas from the Upper Devonian/Lower Mississippian are quite distinct from the carbon and hydrogen isotope signature of Marcellus Shale gas. This study took advantage of those differences to detect the possible upward migration of Marcellus Shale gas by monitoring $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ for gas produced from seven Upper Devonian/Lower Mississippian wells. A positive shift in $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values for gas from Upper Devonian/Lower Mississippian wells was expected if there was intermixing of Marcellus Shale gas. The $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values for gas produced from Upper Devonian/Lower Mississippian wells have remained constant during and following the hydraulic fracturing of the Marcellus Shale. Therefore, $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ results did not detect the presence of Marcellus Shale gas in the gas produced from the seven Upper Devonian/Lower Mississippian wells.

3.4 STRONTIUM ISOTOPE SIGNATURE OF PRODUCED WATER

Results of the strontium isotope signature analysis of produced water from Upper Devonian/Lower Mississippian gas wells demonstrated that hydraulic fracturing of the Marcellus Shale did not provide fracture pathways that allowed detectable amounts of Marcellus Shale brine to migrate to the Upper Devonian/Lower Mississippian field.

The $^{87}Sr/^{86}Sr$ ratios of the Marcellus Shale brines and the Upper Devonian/Lower Mississippian brines are significantly different. Produced water samples collected from Upper Devonian/Lower Mississippian wells at this site yield $^{87}Sr/^{86}Sr$ values from 0.7199–0.7209, whereas $^{87}Sr/^{86}Sr$ values for produced waters from Marcellus Shale wells range from 0.7113–0.7116. The difference in $^{87}Sr/^{86}Sr$ values, plus the fact that Marcellus Shale brines have 10 times more strontium than Upper Devonian/Lower Mississippian brines, makes strontium isotopes a powerful tool for detecting the possible intermixing of Marcellus Shale brines and Upper Devonian/Lower Mississippian brines. The $^{87}Sr/^{86}Sr$ ratios of produced water from five Upper Devonian/Lower Mississippian wells (two wells did not produce water on a consistent basis) remained stable during hydraulic fracturing and for 5 months afterwards. Mixing models indicate that if 5% of the water produced from the Upper Devonian/Lower Mississippian gas wells was from the Marcellus Shale, it would have produced a detectable shift in $^{87}Sr/^{86}Sr$ values. No shift in $^{87}Sr/^{86}Sr$ values was observed within the timeframe of the study indicating that no detectable volume of Marcellus Shale brine was present in produced water from Upper Devonian/Lower Mississippian gas wells.

3.5 PERFLUOROCARBON TRACERS

Perfluorocarbon tracer analysis of gas from two Upper Devonian/Lower Mississippian Wells did not detect PFC tracers that had been injected into an underlying Marcellus Shale during hydraulic fracturing.

Four PFC tracers were injected with hydraulic fracturing fluids into 10 stages of a 14-stage, horizontal Marcellus Shale well. All four PFC tracers were detected in the gas produced from the injection well, which indicates that the tracers partitioned to the gas phase and were not completely absorbed by the formation. Two of the four PFC tracers were detected in the gas produced from a parallel, offset horizontal Marcellus Shale well. The detected tracers were the two tracers that would be predicted to migrate to the offset well based on the position of perforations in the injection and monitored wells, and the fracture azimuth (obtained from microseismic results). These results suggest that perfluorocarbon tracers are useful gas-phase tracers for shale formations.

Natural gas from two Upper Devonian/Lower Mississippian wells (UD-2 and UD-5; located above the PFC injection well) was monitored for PFC tracers by active and passive methods. Active monitoring consisted of collecting gas samples from UD-2 and UD-5 every 2 to 4 days for a period of 2 months. Seventeen gas samples were collected from each well; no PFC tracers were detected in the gas production from either well (detection limit = 0.001 ppb). An attempt to continuously monitor gas flow from UD-2 and UD-5 for PFC tracers by inserting PFC sorbent tubes into gas flow lines did not provide credible results and was abandoned.

3.6 OVERALL CONCLUSIONS

Microseismic monitoring results indicate that stress imposed on rock formations by hydraulic fracturing did not extend to the Upper Devonian/Lower Mississippian gas field. However, numerous microseismic events were observed above the Tully Limestone, which is thought to be an upper barrier to fracture growth from hydraulic fracturing in the Marcellus Shale when intact.

The geometry and orientation of microseismic event clusters located above the Tully Limestone suggests that energy from hydraulic fracturing was focused along pre-existing joints, low-offset faults, and bedding planes.

Seven wells in an Upper Devonian/Lower Mississippian gas field were monitored for evidence that hydraulic fracturing in the underlying Marcellus Shale had breached 3,800 ft of intervening strata and allowed gas and fluid migration between the two reservoirs. Monitored parameters included: 1) production and pressure history, 2) isotopic composition of gas, 3) Sr isotope ratio in produced water, and 4) presence of PFC tracer. Background conditions were established by sampling gas and produced water 1 month prior to hydraulic fracturing. Monitoring frequency, monitoring duration, and current status of sample analysis are summarized in Table 3 below.

Table 3: Summary of monitoring frequency, monitoring duration, and current status of sample analysis

Monitoring Type	Sample Frequency	Monitoring Period (months after hydraulic fracturing)	Results in this Report (analyses completed to date)	Comments
Production and Pressure	Weekly	18	1 year after hydraulic fracturing (52 measurements)	Continuing
Natural Gas ($\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$)	Monthly for 5 samples; bimonthly thereafter	18	8 months after hydraulic fracturing (seven samples)	Continuing
Produced water ($^{87}Sr/^{86}Sr$)	Monthly	18	6 months after hydraulic fracturing (five samples)	Continuing
PFC tracers	Every 2 days for 14 days; every 4 days for 20 days; every 6 days thereafter	2	2 months after hydraulic fracturing (17 samples)	Suspended

A comparison of production and pressure records from Upper Devonian/Lower Mississippian wells collected weekly for 1 year after hydraulic fracturing with records collected for a 3-year period before hydraulic fracturing did not reveal pressure or production increases that might indicate migration of gas from the over-pressured Marcellus Shale below. Isotopic analysis of gas and produced water from the Upper Devonian/Lower Mississippian wells did not detect the presence of gas or fluids from the Marcellus Shale. These lines of evidence indicate that there has been no detectable migration of gas and fluids from the Marcellus Shale to the overlying Upper Devonian/Lower Mississippian gas field such as could be provided by open fractures or unplugged wells.

PFC tracers were employed to augment pressure/production and isotope monitoring by detecting the low-volume migration of gas between the hydraulically-fractured formation and the monitored zone in the overlying Upper Devonian/Lower Mississippian gas field. Because PFC tracers are man-made and do not occur naturally, PFC detection in gas produced from Upper Devonian/Lower Mississippian wells would be strong evidence that inter-formational gas

migration has occurred. For 2 months after hydraulic fracturing and tracer injection, the gas produced from two wells (UD-2 and UD-5) in the monitored zone was sampled frequently (every 2–6 days) and analyzed for PFC tracers. No PFC tracers were detected (detection limit = 0.001 ppb) in gas samples collected from UD-2 and UD-5 during the 2-month period after hydraulic fracturing.

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APPENDICES

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APPENDIX A - VERIFICATION OF MICROSEISMIC EVENT LOCATIONS

This report describes microseismic events that were detected and located during the hydraulic fracturing of six horizontal Marcellus Shale gas wells in Greene County, Pennsylvania. Microseismic events were recorded using a single, vertical, wireline array consisting of eight Weatherford SlimWave® tools spaced 100-ft apart. The geophone array was deployed in one of two vertical observation wells (MW-1 and MW-2), depending on which observation well was nearer to the stages being hydraulically fractured. The vertical position of geophones with respect to formation tops is shown for monitoring well 1 (MW-1) and monitoring well 2 (MW-2) in Figures A1 and A2, respectively.

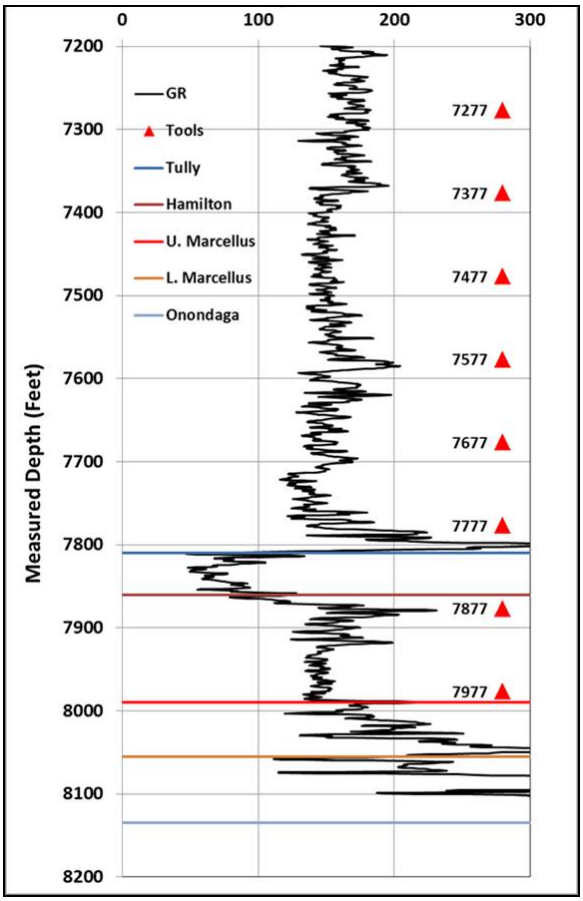

Figure A1: Vertical section showing gamma ray log, formation tops, and geophone positions (red triangles) in MW-1.

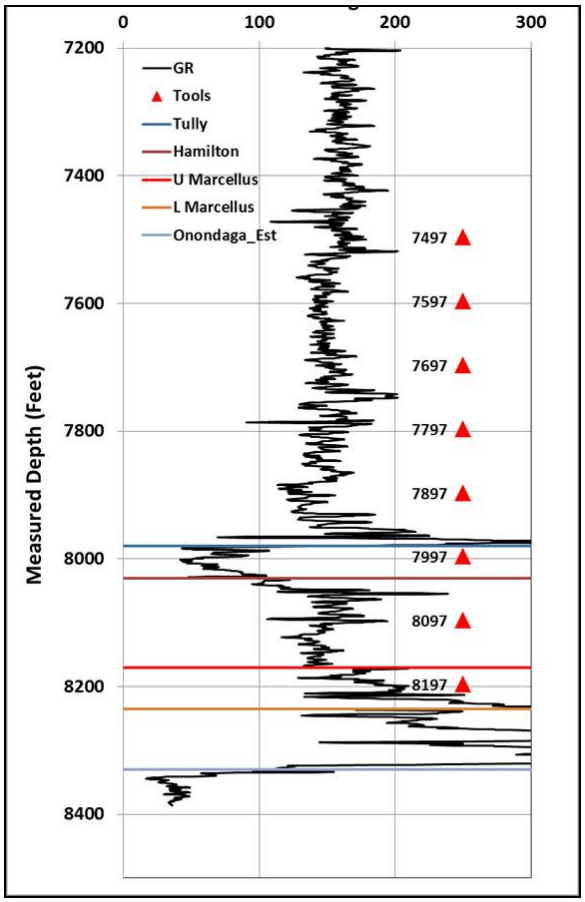

Figure A2: Vertical section showing gamma ray log, formation tops, and geophone positions (red triangles) in MW-2.

For Wells A, B, and C, the micoseismic monitoring array consisted of eight, 30-Hz 3C geophones (SMC-1850). Specifications, dimensions, and frequency response of SMC-1850 geophones are available at http://www.geospace.com/smc-1850/. For Wells D, E, and F, the monitoring array consisted of eight, 28-Hz 3C geophones (GS-14-L9). Specifications, dimensions, and frequency response for GS-14-L9 geophones are available at http://www.geospace.com/gs-14-industrial-geophone/. Data were recorded using a sampling rate of 0.25 ms (4000 Hz). The reported bandwidth for both geophones is 1600 Hz.

A.1 INITIAL VELOCITY MODEL

The initial velocity model was constructed using sonic velocity logs from a vertical Marcellus Shale gas well (Figure A3) near the study area. The velocity model was then correlated to MW-1 and MW-2 using gamma ray logs to assign formation tops. The initial velocity model for MW-2 is shown in Figure A4. The recording of perforation shots at known location and depth were used to update the velocity model periodically during the treatment of each well.

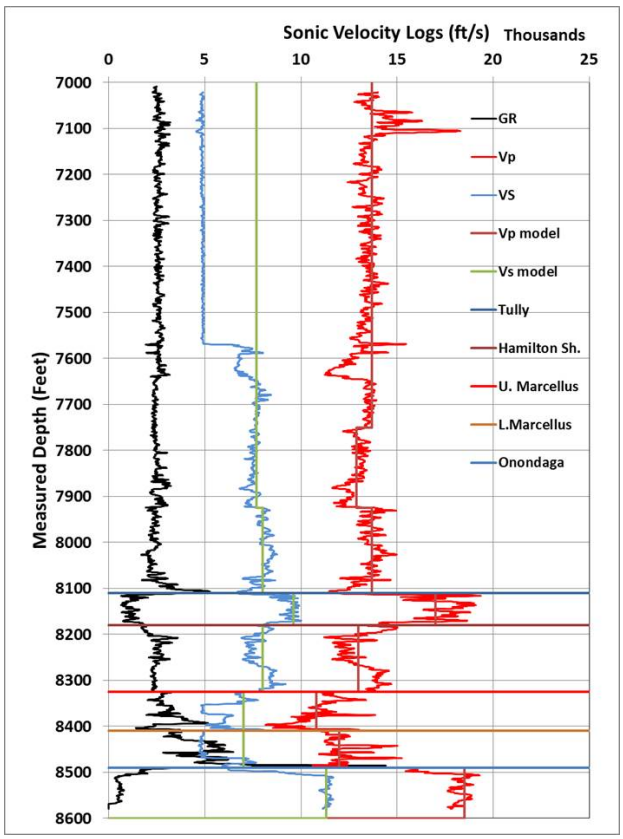

Figure A3: Vertical section showing gamma ray (GR) log, Vp log and model, Vs log and model, and formation tops for a nearby vertical Marcellus Shale gas well.

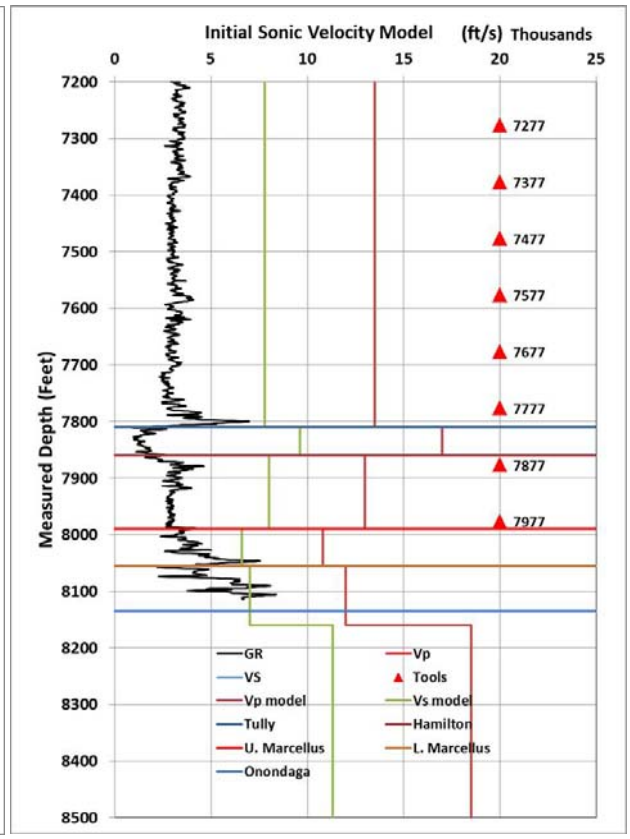

Figure A4: Vertical section showing gamma ray (GR) log, Vs model, Vp model, formation tops, and geophone locations for MW-2.

A.2 GEOPHONE ORIENTATION

When a geophone array is deployed in a vertical well via wireline cable, each 3C sensor is randomly oriented and constitutes a 3-axis, local coordinate system. Perforation shots from a known location and depth were recorded and used to mathematically rotate each sensor into a global coordinate system. Table A1 shows the unit vector components and azimuth used to rotate each 3C sensor (tool), while the geophone array was deployed in MW-1 during the hydraulic fracturing of Wells A, B, and C.

Table A1: Vector and azimuth corrections applied to geophones while monitoring the hydraulic fracturing of horizontal Marcellus Shale Wells A, B, and C.

Tool	Geophone	Unit Vector Components			X-component
		Northing	Easting	Depth	Azimuth
1	X	-0.515	-0.857	0.002	239.00
1	Y	0.857	-0.515	0.010	329.00
1	Z	0.000	0.000	-1.000	0.00
2	X	-0.999	-0.035	-0.008	182.00
2	Y	0.035	-0.999	0.007	272.00
2	Z	0.000	0.000	-1.000	0.00
3	X	-0.616	-0.788	-0.005	232.00
3	Y	0.788	-0.616	0.018	321.99
3	Z	0.000	0.000	-1.000	0.00
4	X	-0.891	-0.454	-0.012	207.00
4	Y	0.454	-0.891	0.015	296.99
4	Z	0.000	0.000	-1.000	0.00
5	X	0.438	0.899	0.006	64.00
5	Y	-0.899	0.438	-0.014	154.00
5	Z	0.000	0.000	-1.000	0.00
6	X	0.799	0.602	0.010	37.00
6	Y	-0.602	0.799	0.002	127.00
6	Z	0.000	0.000	-1.000	0.00
7	X	-0.966	-0.259	-0.009	195.00
7	Y	0.259	-0.966	-0.006	285.00
7	Z	0.000	0.000	-1.000	0.00
8	X	0.951	0.309	0.010	18.00
8	Y	-0.309	0.951	0.016	108.01
8	Z	0.000	0.000	-1.000	0.00

A.3 PERFORATION SHOT LOCATION

Perforation shots are seismic sources with accurately known locations. During microseismic monitoring of hydraulic fracturing, perforation shots are a convenient means to: 1) orient geophones, 2) confirm or update velocity model, and 3) assess the accuracy of event location. Forty perforation shots were located during the hydraulic fracturing of Wells A, B, C, D, E, and F. The distance and depth errors of perforation shot location are summarized by well in Table A2. The distance and depth errors associated with the location of all 40 perforation shots are provided in Table A3. Only one stage in Well C was treated; no perforation shots were located in this well.

Table A2: Summary of distance and depth errors for perforation shot locations by well

Well	Number of Shots	Average Distance Error (ft)	Maximum Distance Error (ft)	Minimum Distance Error (ft)	Average Depth Error (ft)	Maximum Depth Error (ft)	Minimum Depth Error (ft)
A	6	116.96	152.31	78.75	77.14	127.88	49.46
B	6	128.29	164.03	71.87	47.27	66.89	1.31
C	0	ND	ND	ND	ND	ND	ND
D	17	100.66	179.91	43.31	52.28	107.01	3.12
E	5	76.37	100.86	51.20	27.29	37.48	12.52
F	6	136.30	173.01	115.59	77.28	112.24	28.92

Table A3: Distance and depth errors for all perforation shot locations

Well/Stage	Shot	Distance between actual shot and located shot (ft)	Depth difference between actual shot and located shot (ft)
A/3	1	99.73	49.46
A/3	2	151.04	75.28
A/3	3	152.31	127.88
A/7	1	78.75	71.88
A/7	2	117.55	66.28
A/7	3	102.39	72.07
B/2	1	164.03	54.48
B/2	2	162.42	66.89
B/2	3	139.12	39.63
B/4	1	115.27	65.55
B/4	2	71.87	1.31
B/4	3	117.05	55.77
D/11	1	142.33	107.01
D/11	2	141.11	34.40
D/11	3	120.71	49.62
D/11	4	179.91	63.40
D/11	5	150.22	5.78
D/13	1	129.46	92.74
D/13	2	114.43	68.37
D/13	3	112.58	88.72
D/13	4	50.95	28.16
D/13	5	43.31	42.89
D/13	6	71.85	3.12
D/14	1	49.15	46.14
D/14	2	71.38	71.19
D/14	3	79.80	69.12
D/14	4	87.00	46.24
D/14	5	44.34	14.28
D/14	6	122.70	40.56
E/14	1	76.91	12.52
E/14	2	71.76	19.88
E/14	3	81.12	37.48
E/14	4	100.86	29.57
E/14	5	51.20	37.02
F/8	1	126.62	112.24
F/8	2	115.59	107.21
F/8	3	121.60	28.92
F/10	1	173.01	82.16
F/10	2	154.53	63.09
F/10	3	126.43	70.08

A.4 SIGNAL-TO-NOISE RATIO (SNR) FOR LOCATED EVENTS

The signal-to-noise ratio (SNR) histograms for events located during the treatment of Wells A, B, and C (Stage 1 only) and Wells D, E, and F are shown in Figures A5 and A6, respectively. Most events have SNR greater than 2; events with SNR less than 2 (high-uncertainty events) were removed prior to data interpretation. In Wells A and E, the proximity of the monitoring well to the treatment well resulted in a higher noise background.

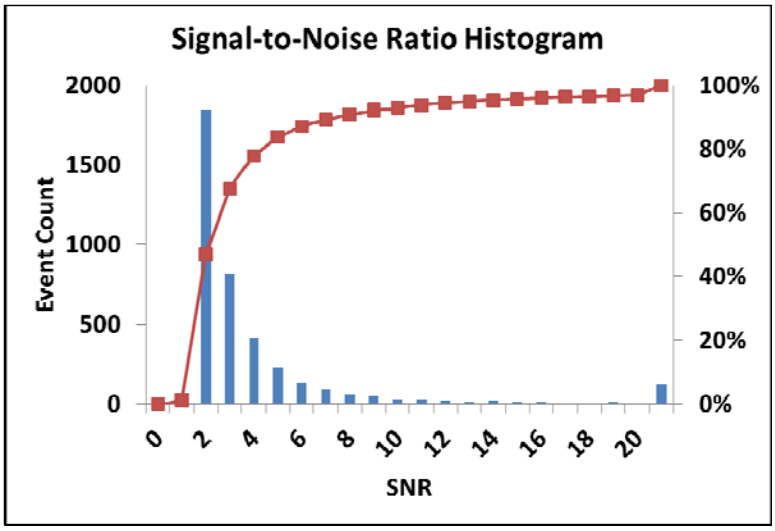

Figure A5: Signal-to-noise ratio histogram for microseismic events located during the treatment of Wells A, B, and C (Stage 1 only).

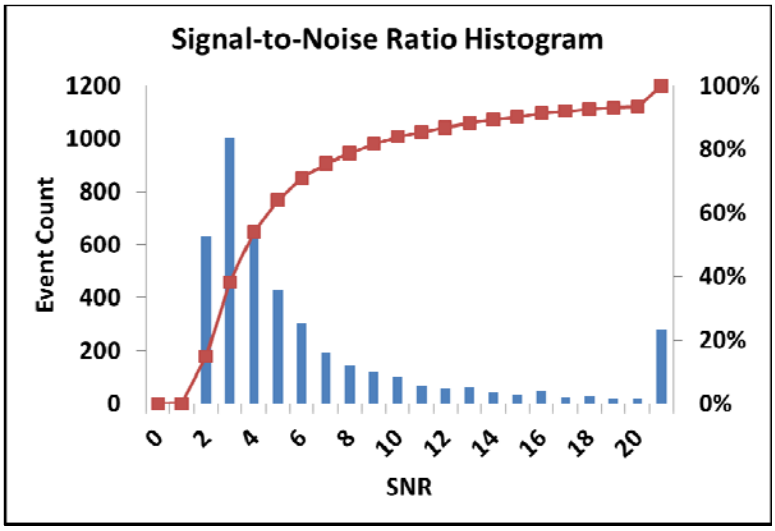

Figure A6: Signal-to-noise ratio histogram for microseismic events located during the treatment of Wells D, E, and F.

APPENDIX B - PROCEDURES FOR THE COLLECTION AND ANALYSIS OF GAS SAMPLES FOR CARBON ISOTOPE DETERMINATIONS

Sample Collection: Gas samples are collected in 300 ml stainless steel high-pressure cylinders with stainless steel 3,500 psig valves. The wellhead is vented for approximately 10 seconds to remove accumulated moisture and then the cylinders are attached directly to the ¼ in. NPT sampling port of the wellhead with Teflon tape. The pressure is measured directly at the wellhead and has ranged from approximately 30 psi to approximately 200 psi over the course of sampling (March 2012–June 2013). Differences in cylinder pressure have not been observed to affect isotope signatures. The cylinders are flushed through with gas from the wellhead for five minutes to remove residual atmosphere in the cylinder before the outer valve is shut and the cylinder equilibrated at wellhead pressure. The cylinder valve closest to the wellhead is then shut and the gas vented by opening the outer cylinder valve. The outer valve is then closed before complete positive pressure is lost in order to prevent atmosphere intrusion. This purge procedure is repeated five more times to ensure that the gas collected is representative before all valves are closed sequentially from the outer valve to the valve closest to the sampling port. At some sites duplicate gas samples are collected in one-time use gas sampling "Isotubes" supplied by ISOTECH. The Isotubes are attached to the sampling port of the wellhead using a 3,000 psig rated well-head sampler. The well-head sampler has pressure regulator and 3-way valve to reduce pressure and vent gas before final sample collection. The gas cylinders are transported to the West Virginia University (WVU) Stable Isotope lab and then shipped to ISOTECH labs for natural gas characterization and isotope analysis.

Sample Analysis: The $\delta^{13}C_{CH4}$ analysis of methane was performed on Delta S and Delta Plus XL dual-inlet Isotope Ratio Mass Spectrometer (IRMS) at ISOTECH labs. The internal check standards for methane isotopes cover a wide range of natural gas samples contained in high volumes at ISOTECH. Precision for methane isotopes at ISOTECH are $\delta^{13}C_{CH4}$-offline ± 0.1‰, $\delta^{13}C_{CH4}$-online ± 0.4‰ vs. V-PDB. The duplicate samples collected in Isotubes from the same well at the same time had similar isotopic signature to gas collected in the high-pressure steel cylinders with standard deviations ranging from 0–0.04 ‰ vs. V-PDB indicating good quality control of our sample collection procedure.

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APPENDIX C - PROCEDURES FOR THE COLLECTION OF PRODUCED WATER SAMPLES

The scientific study of Marcellus Shale fluids related to well completion and gas production requires: 1) the collection of samples in the field, 2) the transport of samples to NETL, 3) the processing of samples within NETL laboratories, and 4) the ultimate disposal of all waste materials.

C.1 FIELD COLLECTION OF WATER SAMPLES

Produced water samples were collected with the assistance of a company well tender who performed any necessary operations on the well equipment. Samples were obtained from the water holding tanks (storage tanks) from the outlet at the bottom of the tank typically used when the tanks are emptied. When possible, samples were also obtained from the liquid/gas separator by tripping the outlet of the accumulator and intercepting the flow as it discharges into the storage tank. In both cases the effluent was initially captured in a plastic 2.5 gallon bucket and subsequently transferred to sample containers for sub-sampling and transport back to NETL.

The initial 250 mL sample is sub-sampled in the field to generate a raw, a filtered un-acidified, and a filtered and acidified 50 mL sample for submission to the Pittsburgh Analytical Laboratory. The raw sample is untreated and occupies most of the 50 mL container in order to minimize the headspace and further exposure to air. Filtering is performed using a 50 mL syringe and 0.45 micron cellulose filters. The un-acidified sample occupies most of the 50 mL container in order to minimize the headspace and further exposure to air. Acidification is performed by adding 1 mL of ultrapure grade nitric acid to approximately 48 mL of water in a 50 mL container. Water samples were stored in a refrigerator designated for this purpose under secondary containment prior to further sampling.

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APPENDIX D - ANALYTICAL PROCEDURE FOR DETERMINING STRONTIUM ISOTOPES IN PRODUCED WATER

Samples were prepared for Sr isotope analysis following high-throughput methods detailed in Wall et al. (2013). All sample handing was conducted in a Class 100 vertical laminar flow hood at the University of Pittsburgh. In each sample, Sr was separated from matrix elements to eliminate isobaric interferences and other matrix effects to allow for precise and accurate isotopic measurements. Strontium isotope ratios ($^{87}Sr/^{86}Sr$) were analyzed on a Thermo Scientific Neptune Plus double-focusing multi-collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS, Thermo Scientific, Bremen, Germany). After correcting for instrumental mass bias using standard methods such as exponential law and interference corrections, ratios were normalized to the isotopic reference standard SRM 987 = 0.71024. QA/QC procedures for Sr isotope data are carried out for all samples by monitoring the following parameters: the magnitude of interference corrections, the variation of SRM 987 measured during the analytical session, and adequate signal strength and peak to background values.

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APPENDIX E - PROCEDURE FOR INJECTING, SAMPLING, AND ANALYZING PERFLUOROCARBON (PFC) TRACERS

E.1 PFC TRACER INJECTION WITH HYDRAULIC FRACTURING FLUIDS

PFC tracers were injected with hydraulic fracturing fluids into 10 stages (Stages 5–14) of the 14-stage, horizontal Marcellus Shale gas Well E (Figure 5). Four PFC tracers were used: perfluoromethylcyclohexane (PMCH) was injected into Stages 5, 6, and 7; perfluorotrimethylcyclohexane (PTCH) was injected into Stages 8, 9, and 10; perfluorodimethylcyclobutane (PDCB) was injected into Stages 11, 12, and 13; and perfluoro-i-propylcyclohexane (iPPCH) was injected into Stage 14. For each stage, 473 mL (0.125 gal) of PFC tracer was introduced into hydraulic fracturing fluids between the blender and high pressure pumps. The tracer injection was timed to coincide with the pumping of the pad (post-acid and pre-proppant), which would allow the tracer to be carried away from the perforations to the most distant parts of created fractures. Within the reservoir, the PFC tracer was expected to form a non-aqueous, buoyant phase that would migrate to the uppermost extremities of created and existing fractures. The chemical composition of hydraulic fracturing fluids used for the treatment of horizontal Marcellus Shale gas Well E is provided in Table E1. Table E2 provides important treatment parameters for Stages 5–14 of horizontal Marcellus Shale gas Well E.

Table E1. Industry reported information from FracFocus on the composition of hydraulic fracturing chemicals used in the treatment of horizontal Marcellus Shale gas Well E (accessed on October 9, 2013).

Trade Name	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (by mass)	Maximum Ingredient Concentration in HF Fluid (by mass)
Water	Base fluid	Fresh and recycled water		100.000	90.68179
Scale Hib A	Scale inhibitor	Ethylene glycol	107-21-1	30.000	0.01306
I-7L	Iron control for acid	Ethylene glycol	107-21-1	30.000	0.00518
Unislick ST-50	Friction reducer	Hydrotreated light distillate	64742-47-8	30.000	0.02183
WGA-3, CMHPG	Dry gellant	Guar gum	9000-30-0	100.000	0.02633
Unihib G	Corrosion inhibitor for acid	2-Ethyl hexanol	104-76-7	75.000	0.00042
Unihib G	Corrosion inhibitor for acid	Short chained glycol ether	N/A	25.000	0.00014
LEB 10X	Breaker	Ethylene glycol	107-21-1	60.000	0.00041
EC6116A	Biocide	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	30.000	0.00901
EC6116A	Biocide	Dibromoacetonitrile	3252-43-5	5.000	0.00150
EC6116A	Biocide	Polyethylene glycol	25322-68-3	60.000	0.01802
15% Hydrochloric acid	Acid	Hydrochloric acid	7647-01-0	15.000	0.13479
Proppant-40/70	Proppant	Crystalline silica quartz	14808-60-7	100.000	7.27598
Proppant-100 mesh	Proppant	Crystalline silica quartz	14808-60-7	100.000	1.81155

Table E2: Treatment information for Stages 5–14 of horizontal Marcellus Shale Well E where PFC tracers were injected.

Stage	Tracer	Interval MD, ft	Clean Treatment Volume (gal)	Pad Volume (gal)	Average Rate (bpm)	Average Pressure (psi)
5	Perfluoromethylcyclohexane	11,650-11,873	317,801	45,982	79.3	8,450
6	Perfluoromethylcyclohexane	11,319-11,542	311,916	40,724	83	8,397
7	Perfluoromethylcyclohexane	10,988-11,211	324,260	48,953	88.6	8,227
8	Perfluorotrimethylcyclohexane	10,657-10,880	320,984	48,682	91.2	8,366
9	Perfluorotrimethylcyclohexane	10,326-10,549	315,070	31,680	93.3	8,311
10	Perfluorotrimethylcyclohexane	9,995-10,218	319,979	48,788	95.5	8,448
11	Perfluorodimethylcyclobutane	9,664-9,887	179,136	46,799	39.2	8,471
12	Perfluorodimethylcyclobutane	9,333-9,556	162,923	29,704	49.6	8,458
13	Perfluorodimethylcyclobutane	8,968-9,225	396,673	92,022	65.9	8,385
14	Perfluoro-i-propylcyclohexane	8,671-8,894	322,622	49,361	82.7	7,886

E.2 SAMPLING FOR PFC TRACERS

PFC tracers were collected in 3-in. long, glass tubes that contained a small amount of Ambersorb collection material (Gerstel® tubes; Figure E1). These tubes were placed in the production gas stream of Upper Devonian/Lower Mississippian Wells UD-2 and UD-5. Tracer sampling tubes were collected from UD-2, UD-5, and MW-2 on an approximately weekly basis for the first 6 months following PFC tracer injection, then on a monthly basis for the remainder of the first year. The sorbent tubes were labeled, logged and sent back to the NETL Pittsburgh PFC tracer laboratory for analysis.

Figure E1: Gerstel™ glass air sampling tubes containing the carbonaceous polymer Ambersorb® adsorbent material.

Figure E2: Gerstel® tubes were inserted through a valve into the gas production lines for Upper Devonian/Lower Mississippian Well UD-2 and UD-5

At the Upper Devonian Wells UD-2 and UD-5, the industry partner modified existing piping to allow a sorbent tube to be placed in the production gas stream. To exchange sorbent tubes, the sorbent tube is lifted up on a ¼ in. slide rod through a compression fitting until the sorbent tube is above a ball valve which isolates the main flow of gas (Figure E2). The ball valve is then closed. The high production pressure is allowed to bleed off from this isolation chamber and the chamber is opened by removing a ½ in. FPT to ¼ in. compression fitting to allow the quick exchange to a fresh unexposed sorbent tube. To reinsert a fresh sorbent tube into the gas stream, the reverse procedure in used. The fresh sorbent tube on the end of the slide rod is sealed into the isolation chamber. Then the ball valve is opened and the sorbent tube is slid into place in the gas stream and the slide rod's position is secured by tightening the ¼ in. compression fitting nut.

E.3 PROTOCOL TO PREVENT PFC CROSS CONTAMINATION

The detection limit for PFC tracers, approaching the part-per-quadrillion level, requires a strict protocol to prevent cross-contamination of sorbent tubes. No NETL researchers handled PFC tracers or were in the vicinity of treatment wells during PFC injection or the subsequent sampling of gas produced from horizontal Marcellus Shale Wells E and F. PFC tracer injection and gas sampling activities on the wellpad were conducted by a contractor (ProTechnics, Inc.) There was no direct contact between the ProTechnics employees and NETL researchers. This reduces the possibility that PFC tracers will be inadvertently transferred to sorbent tubes used in the monitoring operations via personal contact or clothing.

After hydraulic fracturing was completed, hydraulic fracturing fluids including PFC tracers were flowed back into frac tanks on the wellpad or into nearby surface impoundments. This was expected to release a significant plume of PFC tracers to the atmosphere. Because sorbent tubes are open to the atmosphere for some number of seconds during sorbent tube exchange, a step is taken to account for possible atmospheric contamination. While a sorbent tube is being inserted or removed from the sampling apparatus at the well, a second sorbent tube ("control") is exposed to the immediate atmosphere around the sampled well for the same amount of time that the analyte or "measured" tube is exposed to the atmosphere. Tracers collected on this "control" tube are then analyzed for and plotted together with the "measured" value on time series graphs. The "control" sample tubes also provide a measurement of the background levels of PFC tracer at the site, which can persist for weeks.

E.4 ANALYSIS OF PFC TRACER SAMPLES

The inert PFC tracer gases were analyzed using an Agilent 6890N gas chromatograph (GC) with cryogenic cooling, coupled to an Agilent 5975 mass selective detector (MSD), and using chemical ionization (CI) in the selected ion mode (SIM). A Varian CP-SIL 5 CB Fused Silica column (100M x 0.32mm, 5.0 µM) was used in the GC.

Gerstel™ glass air sampling tubes containing the carbonaceous polymer Ambersorb® adsorbent material were conditioned by heating at 400°C for one hour with ultra-high purity helium flowing through. After exposure in the field, the tubes were dried for at least two hours by purging with ultra-high purity helium. The samples were then placed on the Gerstel™ Multi-Purpose Sampler (MPS 2) for analysis.

Scott Specialty gas cylinders containing known concentrations of mixtures of various PFCs at an approximate concentration of 0.055 ppb for each PFC, were used to calibrate the GC/MS system. Different calibration gas volumes were adsorbed and then desorbed from conditioned sample tubes to generate a five-point calibration curve. Results were calculated in femtoliters PFC/liter of air volume. The lower reporting limit for the PFCs was 2 fl/L.

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