STRONTIUM ISOTOPES TEST LONG-TERM ZONAL ISOLATION OF INJECTED AND MARCELLUS FORMATION WATER AFTER HYDRAULIC FRACTURING

by

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Strontium Isotopes Test Long-Term Zonal Isolation of Injected and Marcellus Formation Water after Hydraulic Fracturing

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University of Pittsburgh, 2014

The rapidly expanding use of high volume hydraulic fracture stimulation during development of unconventional gas reservoirs such as the Marcellus Shale in northeastern North America has lead to concerns about potential migration or displacement of high TDS (total dissolved solids) fluids from the target formation or overlying units into shallow aquifers. Typical water quality monitoring methods may be unable to differentiate between contamination sources, behave non-conservatively, or require the addition of synthetic chemical tracers. Natural strontium isotope signatures ($^{87}Sr/^{86}Sr$) can be used to distinguish produced waters from the Marcellus Shale from other potential regional contaminants. The research objective of this study, located at the National Energy Technology Laboratory Greene County Site in southwestern Pennsylvania, was to test the assumption that hydraulic fracturing is confined to the target formation, and that injected and formation waters do not migrate to overlying units. Strontium isotope compositions were determined for produced waters taken over a period of approximately four months before and fourteen months after hydraulic fracturing from horizontal wells drilled into the Marcellus Shale and from overlying vertical Upper Devonian/Lower Mississippian (UD/LM) gas-producing wells. Water samples from a nearby spring were also collected to analyze the local ground water geochemistry and test the sensitivity of Sr isotopes as an indicator of brine incursions into fresh water aquifers. The results indicate that there was no significant post-hydraulic fracturing migration of Marcellus-related fluids or displacement of UD/LM brines into shallower units during the study period, and demonstrated that Sr isotopes can detect very small incursions of brine (<0.001%) into groundwater, often at a more sensitive level than shifts in elemental concentrations. The large difference in Sr content between the Marcellus brines and the UD/LM brines allows for detectable isotopic shifts in UD/LM $^{87}Sr/^{86}Sr$ ratios with as little as ~1% incursion of Marcellus fluids. Strontium isotopes have the potential to serve as an excellent long-term monitoring tool.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PREFACE

ACKNOWLEDGMENTS

I thank my committee members Dr. Rosemary Capo, Dr. Brian Stewart, and Dr. Daniel Bain for their advice and support. I thank J. Rodney Diehl, Dennis Stanko and Karl Schroeder (NETL) and Elizabeth Rowan (USGS) for field sampling, and Emily Burt, Andy Wall and Thai Phan for assistance with field and analytical work. This work was supported in part by the U.S. Department of Energy, Office of Fossil Energy, under the Office of Oil and Natural Gas (Energy Policy Act of 2005, Section 999 Complementary Program Research), as performed through the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000.

1.0 INTRODUCTION

Exploration companies in the United States, and increasingly throughout the world, use directional drilling combined with hydraulic fracturing technologies to stimulate and produce hydrocarbons (EIA, 2013). The hydraulic fracturing process is used when hydrocarbons, usually methane, are held in relatively impermeable rock such as shale, and it involves injection of millions of gallons of water containing chemical additives into the well to create fractures in the rock, allowing gas migration to the well. Usually more than half of the injected water stays in the geologic formation, and the remainder is discharged from the well, initially at high rates ("flowback water") that rapidly decline over the first month as total dissolved solids content (TDS) increases. Once gas production begins, the water that continues to flow from the well (at a reduced rate) is generally referred to as "produced water" (Soeder et al., 2014); the transition from flowback to produced water varies with local regulatory definitions.

The Middle Devonian Marcellus Formation in the northeastern United States contains organic-carbon rich mudrocks that serve as both source and reservoir for significant quantities of natural gas (Engelder and Lash, 2008). Late-stage produced water from unconventional Marcellus Shale natural gas wells (i.e., >1 month after start of flowback) tends to be a highly saline sodium-calcium-chloride brine (up to 345,000 ppm TDS; Chapman et al., 2012; Barbot et al., 2013) which, although produced at relatively low rates, presents challenges for environmentally safe disposal (Gregory et al., 2011; Maloney and Yoxtheimer, 2012; Ferrar et al., 2013). Current U.S. Environmental Protection Agency (USEPA) regulations consider TDS as a contaminant at levels above 500 mg/L (U.S. Environmental Protection Agency, 2009). A key issue is the possible contamination of shallow aquifers and surface waters with flowback and produced water (Entrekin et al., 2011; Warner et al., 2012; Brantley et al., 2014). While leakage along drill bore casings and surface spills during disposal are the most likely vectors for produced water release (Soeder et al., 2014), concerns have been raised about possible migration of gas and brine in the subsurface resulting from hydraulic fracturing (Osborn et al., 2011; Myers, 2012; Jackson et al., 2013). One limitation to addressing these concerns has been a general lack of field data documenting the chemistry of formation fluids in adjacent units before and after hydraulic fracturing, due to challenges in site access and in observing small changes in the geochemistry of high-TDS fluids.

Here we present data from the Greene County Site (GCS) in Pennsylvania, a collaboration between the Department of Energy and its industry partners (Hammack et al., 2013), on produced waters from Upper Devonian/Lower Mississippian (UD/LM) gas-producing sandstones and the Marcellus shale. The UD/LM samples were collected both before and after hydraulic fracturing of the underlying Marcellus shale. Strontium (Sr) isotopic compositions ($^{87}Sr/^{86}Sr$ ratios) of the waters were applied as a natural long-term (>1 year) monitoring tool that is sensitive to upward migration of fluids resulting from hydraulic fracturing. Parts of this thesis work are in a manuscript currently in revision for the journal *Environmental Science & Technology*.

1.1 BACKGROUND

1.1.1 The Marcellus Shale: Geology, surrounding units, and hydraulic fracturing

The Marcellus Formation was deposited in portions of West Virginia, Ohio, Pennsylvania, and New York (Figure 1) during Middle Devonian time as the Acadian orogeny impacted the Appalachian Basin to the east. The Marcellus Formation ranges in thickness from 250 m to less than 15 m, and resides 1500 m to 2400 m below the surface in prospective oil and gas regions. In southwestern Pennsylvania the Marcellus is approximately 2,460 m to 2,500 m below the surface (Hammack et al., 2013). Quartz (~35%) and illite (~25%) are the most abundant minerals by volume (Wang and Carr, 2013). The next most abundant minerals are chlorite, pyrite, calcite, dolomite, and plagioclase feldspar. Variable amounts of potassium feldspar, kaolinite, mixed-layer illite-smectite, and apatite are also present.

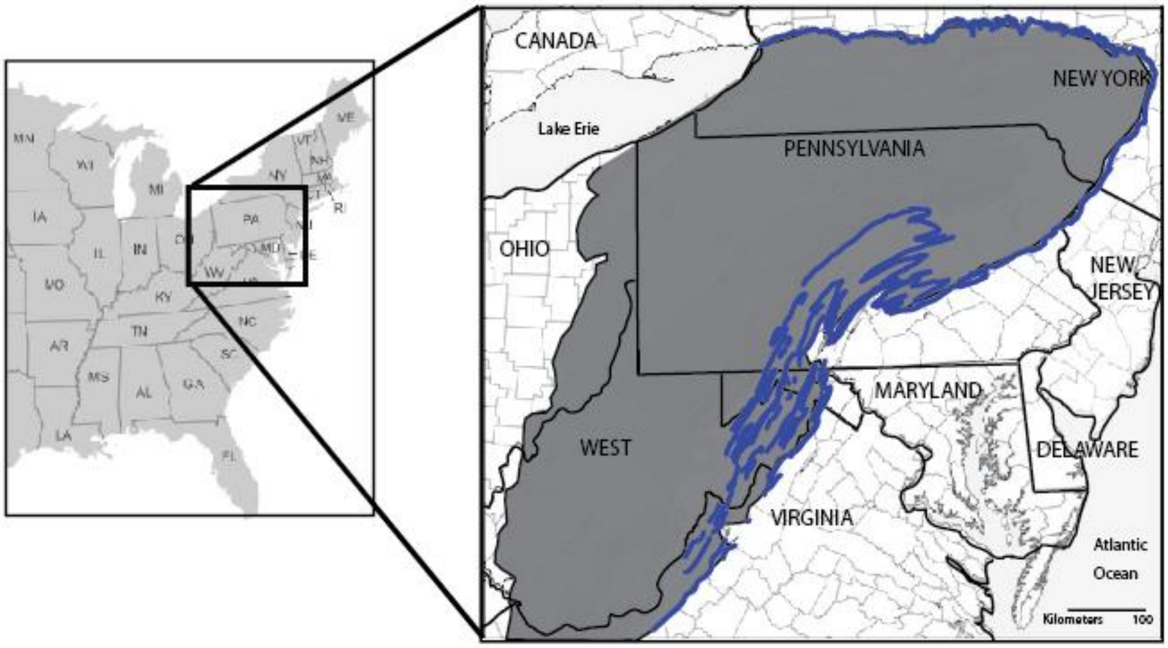

Figure 1. Extent and location of the Marcellus Formation in North America. The gray shaded region indicates the subsurface extent, and the blue indicates Marcellus Shale outcrop. Modified from Penn State Marcellus Center for Outreach and Research (2013).

The Marcellus is the lowermost formation of the Hamilton Group, and overlies the Middle Devonian Onondaga Formation, the Lower Devonian Oriskany Sandstone and Helderberg Limestone Group, and the Upper Silurian Salina Group (Figure 2). The Marcellus is overlain by gray mudrocks of the Mahantango Formation, and the uppermost member of the Hamilton Group, the Tully Limestone. Upper Devonian strata overlying the Tully limestone consist of organic carbon-rich units (the Burket, Geneseo, Middlesex, and Rhinestreet Shales), and deltaic sandstone gas and oil-bearing reservoirs of the Catskill Formation (Venango Group, Bradford Group, and the Elk Group). In some areas, such as the Greene County site described in this study, the Lower Mississippian Shenango Formation also produces natural gas. The shallow aquifer systems at this site are in sandstone and limestone units of the Pennsylvanian-aged Allegheny Formation, Conemaugh Group, and Pittsburgh Formation.

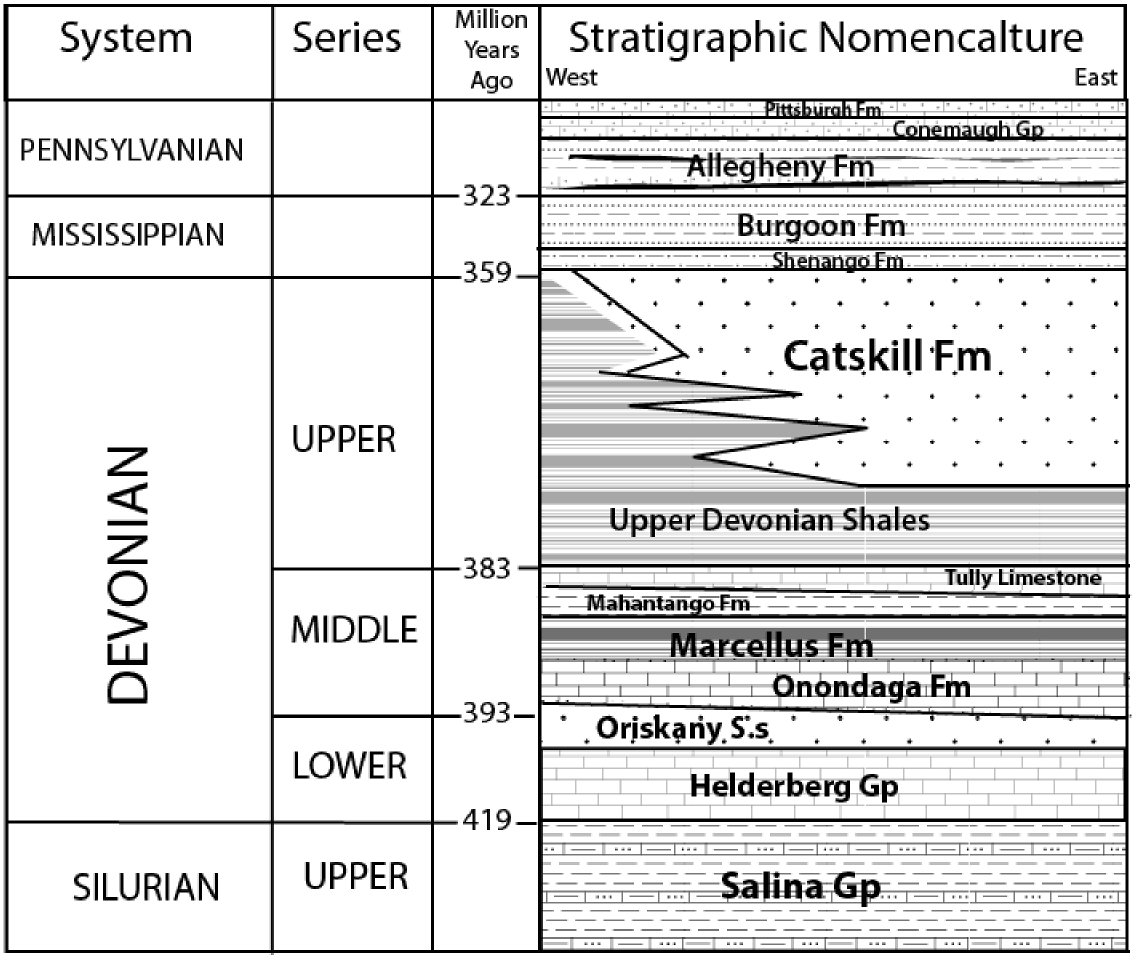

Figure 2. Schematic stratigraphic column of the Marcellus Shale in southwestern Pennsylvania in relation to overlying and underlying units. Modified from Osborn et al. (2012).

Unconventional shale gas reservoirs are low porosity (<10%), low permeability (nanodarcy-scale), and high total organic carbon (TOC) mudrocks. Shale-gas reservoirs are self-sourcing, acting as both source and reservoir for the hydrocarbons. The implementation of technologies such as horizontal drilling and high-volume slickwater hydraulic fracturing has enabled the economic development of these hydrocarbon resources. According to some estimates, the Marcellus could contain as much as 500 trillion cubic feet of recoverable gas (Engelder and Lash, 2008) and 84 trillion cubic feet of additional undiscovered resources (Coleman, 2011). As of 2013, over 7000 horizontal Marcellus wells have been drilled in Pennsylvania (Penn State University Marcellus Center for Outreach and Research, 2013).

High-volume slickwater hydraulic fracturing is the preferred well completion method for shale gas wells in the Appalachian Basin. This completion technique uses high-pressure pumps to inject thousands of gallons of water, mixed with chemicals and proppant (sand particles), into the target formation through perforations in the well. This results in the brittle failure of the target formation, opening millimeter scale fractures generally within a hundred meters of the wellbore (Tiemann and Vann, 2013), but in some cases a few hundred meters away (Hammack et al., 2013). Once the pressure is released, fractures are held open by the proppant, generating high-permeability pathways for water and hydrocarbons to flow into the wellbore.

1.1.2 Potential Environmental Impacts from Hydraulic Fracturing

One concern about shale gas development is that subsurface hydraulic fracturing operations could create fractures that extend beyond the target formation and intersect shallow water aquifers, potentially allowing contaminants in formation water and fracturing fluids to migrate into drinking water supplies (Warner et al., 2012). Hydraulic fracturing fluids consist of

98%-99.5% water and sand, with the remainder consisting of chemical additives to aid in the propagation and sustainment of induced micro fractures, including gelling agents, breaker fluid, surfactants, biocides, corrosion and scale inhibitors, and friction reducers (Fracfocus, 2013). Although present at low concentrations in the hydraulic fracturing fluid (typically <0.50% of the chemical additive solution) the toxicity of these agents, when in high concentrations, can cause detrimental health problems including different forms of cancer, respiratory problems, and liver and kidney diseases (Brantley et al., 2014).

Formation brines from the Marcellus also contain high concentrations of potentially toxic constituents including barium (Ba), bromine (Br), and radium (Ra), (Hayes, 2009; Rowan, 2011; Haluszczak et al., 2013). Barium is typically present in flowback waters in the range of 2000 to 8000 mg/L whereas the Maximum Contamination Level (MCL) for public drinking water as regulated by the U.S. EPA under the Safe Drinking Water Act for Ba is 2 mg/L. Barium can potentially cause gastrointestinal disturbances and muscular weakness (Brantley et al., 2014). The concentration of bromide typically present in Marcellus flowback waters ranges from 2 to 15 mmol/L. During treatment for drinking water, bromide can react with organic matter to form brominated trihalomethanes (THMs) that have been associated with an elevated risk of certain cancers (States et al., 2013; Vidic et al., 2013; Wilson and Van Briesen, 2013). Other concerns are heavy metals and volatile organic compounds (VOCs) (Dresel and Rose, 2010; Haluszczak et al., 2013).

The direct contamination of shallow ground water aquifers from hydraulic fracturing fluid and deep formation brines would require the fractures to propagate several thousand meters beyond the upward boundary of the target formation (up to ~3050 m; Bruner 2011), including through layers of low-permeability shale and limestone, which is considered unlikely. However, pre-existing conduits such as faults or old abandoned wells could pose a threat to the ground water aquifers systems overlying hydraulic fracturing targeted formations. Warner et al. (2012) suggested that Marcellus-derived brines had migrated to the near-surface naturally in north-central Pennsylvania on time scales of 10^4 years, raising the possibility that pathways exist that could be reactivated by hydraulic fracturing. However, it has been noted that the great depths to the Marcellus shale units and high capillary tension within the formation would cause the formation to imbibe the fluids, preventing significant upward movement of injected waters and formation brines (Engelder, 2012; Flewelling and Sharma, 2014). Hammack et al. (2013) presented microseismic data that indicated potential fracturing of both the overlying Tully Formation and underlying Onondaga Limestone during hydraulic fracturing, although no evidence of brine migration was detected.

A far greater risk to groundwater aquifers lies in the integrity of the cement or casing surrounding the wellbore. If the annulus is improperly sealed, natural gas, fracturing fluids and formation water may leak into drinking water aquifers (Vidic et al., 2013; Vengosh et al., 2014). For example, in 2007 a well that had been drilled around 1200 m into the tight sand of the Clinton Formation in Bainbridge, Ohio was not properly sealed with cement, allowing gas from a shale layer above the target tight sand formation to travel through the annulus into an underground source of drinking water (Ohio Department of Natural Resources Division of Mineral Resources Management, 2008).

Thus, the complex nature of Appalachian faulting and jointing, abundance of potentially compromised and unidentified abandoned wells, the discontinuous nature of seal rock integrity, and potential issues with well-bore integrity makes long-term, sensitive monitors of brine migration, and the ability to rapidly distinguish between contaminant sources, a critical part of assuring ground water quality in areas of unconventional hydrocarbon production. The contrasting Sr isotopic compositions of contaminant fluids and shallow groundwaters provide a promising detection and monitoring method.

1.1.3 The Strontium Isotopic System

Strontium isotopes are a powerful tracer for fluids at or near the Earth's surface (Aberg, 1995; Capo et al., 1998; Banner, 2004). Strontium is a divalent alkaline earth element with an ionic radius of 1.18 Å, similar to that of Ca (0.99Å). Because of this, Sr can substitute for Ca in minerals such as plagioclase feldspar, Ca-sulfates, and Ca-carbonates (Capo et al., 1998). Strontium has four naturally occurring isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. The radiogenic isotope ^{87}Sr is produced by the decay of ^{87}Rb (half life = 48.8 b.y.) over geologic time, leading to large differences in the concentration of ^{87}Sr relative to the other (non-radiogenic) isotopes of Sr in rock units of different compositions and geologic histories; this is generally expressed as the ^{87}Sr/^{86}Sr ratio, or as $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$, which is the deviation in parts per 10^4 of the ^{87}Sr/^{86}Sr ratio from that of modern seawater:

$$\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}} = 10^4 \left[\frac{{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{sample}}}{{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{seawater}}} - 1 \right]$$

In general, older Rb-containing rocks will have a higher ^{87}Sr/^{86}Sr than younger rocks, and rocks with an initial high Rb/Sr ratio will also have a high ^{87}Sr/^{86}Sr ratio (e.g., continental crust is generally enriched in Rb compared to oceanic crust). Therefore, rocks with different chemical compositions and geological histories develop distinct ^{87}Sr/^{86}Sr isotopic ratios. Strontium does not fractionate appreciably during physical, chemical, or biological processes such as oxidation, sorption, or evaporation (Capo et al., 1998). Because water that interacts with rocks tends to inherit the $^{87}Sr/^{86}Sr$ ratio of the rock, Sr isotopes can be used as a tracer to constrain flow paths, fluid mixing, and weathering sources for ground and surface waters, provided there are differences among the end member Sr isotopic compositions. The best sensitivity is achieved when there are large differences in Sr concentrations between the end members and less variability of $^{87}Sr/^{86}Sr$ within individual end members. Produced waters from the Marcellus shale have a relatively narrow range of $^{87}Sr/^{86}Sr$ ratios and high Sr concentrations compared to other potential water and contaminant sources, including brines from Upper Devonian oil and gas wells, in the Marcellus natural gas producing region (Chapman et al., 2012; Chapman et al., 2013).

1.1.4 Geochemistry and Isotopic Signature of Marcellus Produced Waters

The geochemistry of late-stage (>one month after the start of flowback) produced waters is believed to essentially reflect formation water (Haluszczak et al., 2013; Capo et al., 2014). Over the first days, TDS levels in the Marcellus flowback water increase to about 200,000 mg/L in constituents including Na, Ca, Ba, Sr, Cl^- and Br^- (Hayes, 2009; Chapman et al., 2012; Barbot et al., 2013; Haluszczak et al., 2013), as well as relatively high radium (Ra) activity (Rowan, 2011; Warner et al., 2013; Skalak et al., 2014). There is some spatial variability, although data are still sparse; Bradford County produced waters have the highest reported concentrations of dissolved constituents and Westmoreland County waters have the lowest (Barbot et al., 2013)

Most of the Marcellus produced waters have a unique and narrow ε_{Sr}^{SW} range between +13.8 and +28.4 (Figure 3). Typical measurement uncertainty is better than ±0.3 ε units. Only the Westmoreland County Marcellus produced waters (orange) deviate from other Marcellus produced waters (+39.8 to +41.6). Even considering these differences, the total range of ε_{Sr}^{SW} values in the Marcellus produced waters is narrow compared with potential interacting water and rock sources or other possible sources of contamination such as Upper Devonian brines and coal mine drainage (Figure 3). This means that Marcellus produced water isotopic compositions are potentially useful as a distinct tracer in fluid migration studies applicable to issues related to hydraulic fracturing of shale-gas reservoirs. The narrow $^{87}Sr/^{86}Sr$ range, combined with the high concentrations of Sr in Marcellus produced water (Hayes, 2009; Chapman et al., 2012; Haluszczak et al., 2013; Capo et al., 2014), results in a sensitive tracer of interactions between Marcellus and Upper Devonian/Lower Mississippian produced waters from conventional wells, and of produced water infiltration into shallow ground waters or surface waters. The following chapter describes our results on the Greene County Site and the sensitivity and longevity of Sr isotopes as a monitoring tool for possible fluid migration.

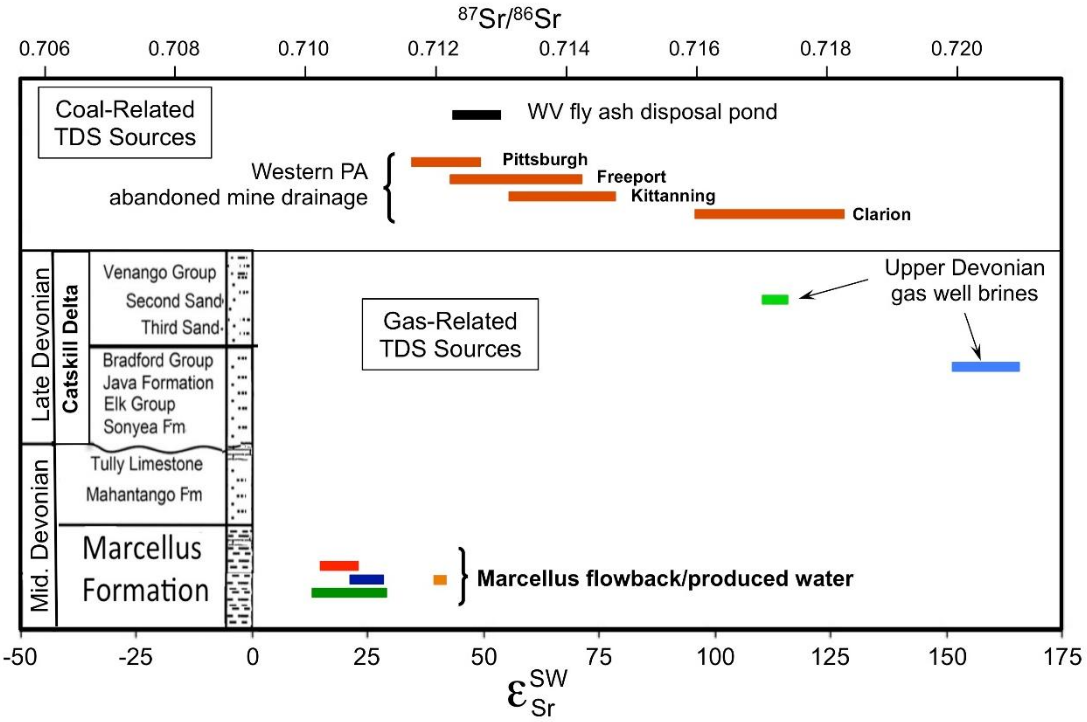

Figure 3. Strontium isotopic variations of Marcellus Formation produced waters compared to western Pennsylvania AMD, Phanerozoic limestone, and brines from the Venango Group, Pennsylvania. The Marcellus produced waters define a relatively tight field compared to other possible sources of Sr in the Marcellus natural gas production region. Stratigraphic location is indicated. The Marcellus produced waters lie within a narrow isotopic range distinct from AMD, Upper Devonian produced waters, and WV fly ash. The blue, red, orange, and green colored produced waters represent samples taken from Washington Co., Greene Co., Westmoreland Co., and Bradford Co., Pennsylvania respectively. Modified from Chapman et al. (2012).

2.0 METHODS

Sample collection at the GCS was arranged through a cooperative agreement between DOE-NETL and the site owner/operator. Flowback water was taken from five Upper Devonian wells, one vertical Marcellus well, and three horizontal legs of a Marcellus well pad **(**Figure 4**)**. The samples were taken periodically from on-site oil and gas separators and storage tanks over a period from January of 2012 through August of 2013. Flowback and production waters from three horizontal legs of a Marcellus well pad were taken from the time hydraulic fracturing began in June 2012 through August 2013. Two of the UD/LM wells (UD-2 and UD-5) lay directly over one of the horizontal Marcellus wells ((MH-E) (Figure 5). When combined with the close proximity of the other surrounding UD/LM wells, this created a nearly ideal setting to monitor possible migration of hydraulic fracturing fluids. Water was also collected from a nearby spring to analyze the local groundwater geochemistry. Initial flowback samples from the horizontal Marcellus wells (as reported in Capo et al. (2014) were collected by the site operators and provided to NETL personnel. After flowback shifted to production, samples were collected by NETL or USGS personnel.

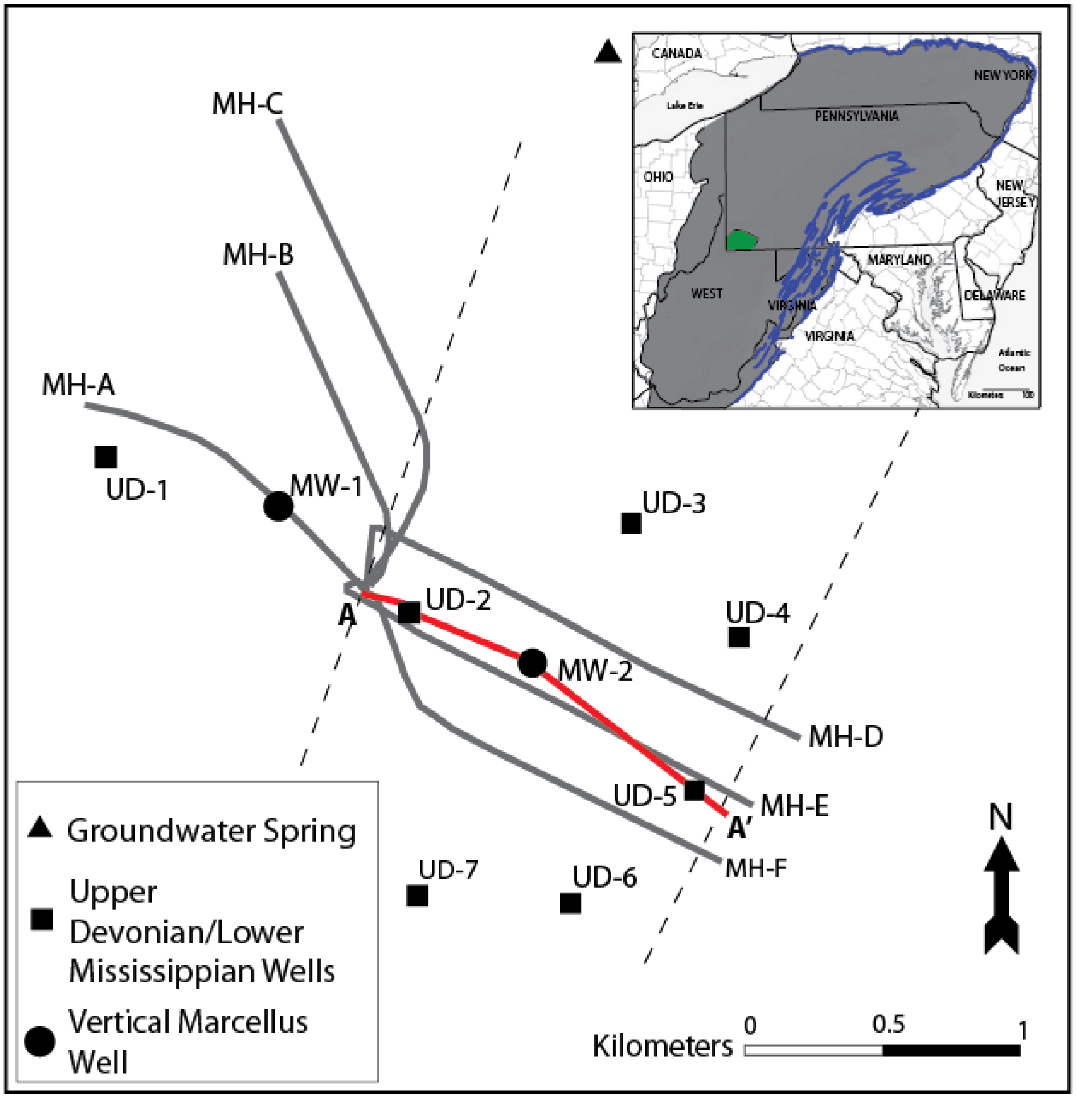

Figure 4. Well site map showing location of horizontal Marcellus wells and vertical Marcellus and Upper Devonian gas wells (modified from Hammack et al., 2013). Inset shows the location of Greene County, PA.

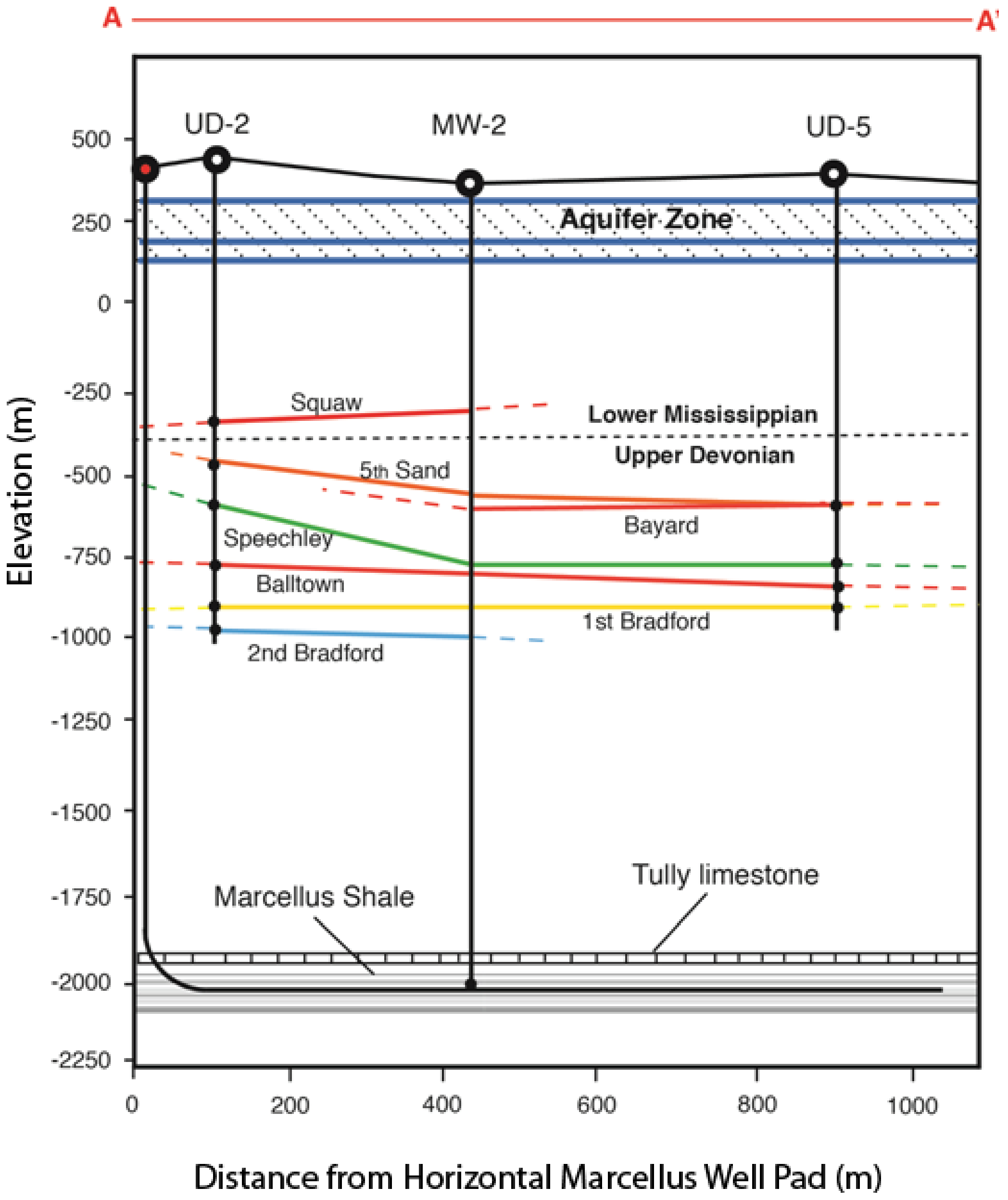

Figure 5. Schematic geologic cross section from the Greene County sites across line A-A' (Fig. 4). Modified from Hammack et al. (2013).

All samples were filtered with a 0.45μm cellulose nitrate filter and preserved with ultra pure nitric acid (acidified to 2%) in the laboratory, preventing precipitation of solids and microbial growth. Later, the samples were acidified to 4% nitric acid to ensure complete dissolution of precipitates. Concentrations of major and minor elements were measured on a Spectroflame Modula Inductively coupled plasma atomic emission spectrometer (ICP-AES) following a modified version of EPA method 6010C (Appendix A). Eichrom® Sr Resin and a vacuum pump chromatograph column were used to isolate the Sr in the samples after the method of Wall et al. (2013). The $^{87}Sr/^{86}Sr$ was then measured on a Neptune Plus multicollector-inductively coupled plasma mass spectrometer (MC-ICPMS). Strontium isotope standard SRM 987 was run repeatedly, and all samples are normalized to an $^{87}Sr/^{86}Sr_{SRM987}$ value of 0.710240. The corresponding value for $^{87}Sr/^{86}Sr_{seawater}$ is 0.709166, based on multiple replicate measurements of seawater and SRM 987.

3.0 RESULTS AND DISCUSSION OF STRONTIUM ISOTOPES

3.1.1 Endmember Characterization

Strontium and calcium concentrations and Sr isotope ratios for all produced and spring waters collected as part of this study are reported in Table 1. Capo et al. (2014) found that produced waters from horizontal Marcellus shale gas wells, including some from this site, continued to evolve toward higher ε_{Sr}^{SW} values up to 3 years after hydraulic fracturing. The GCS vertical Marcellus well MW-1 provides an opportunity to estimate a Marcellus shale produced water endmember value, as this well had been in production for ~6 years at the time the horizontal wells were hydraulically fractured. Figure 6 shows that ε_{Sr}^{SW} continues to rise from a maximum value of +32.1 for the horizontal wells 320 days after hydraulic fracturing (Capo et al., 2014, and Table B1 in Appendix B) to a value of +33.9 in MW-1 six years after hydraulic fracturing in the same unit (Table 1; average value prior to hydraulic fracturing of the horizontal wells). The shift in ε_{Sr}^{SW} subsequent to hydraulic fracturing (discussed in the next section) suggests that there remains a reservoir of formation water that continues to mix with the initial injection water even after 5-6 years of production.

Even so, the increase in $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$ observed from one to six years after hydraulic fracturing is relatively minor, and the values obtained from well MW-1 represent the likely Marcellus formation water endmember for evaluation of fluid migration from hydraulic fracturing at this site.

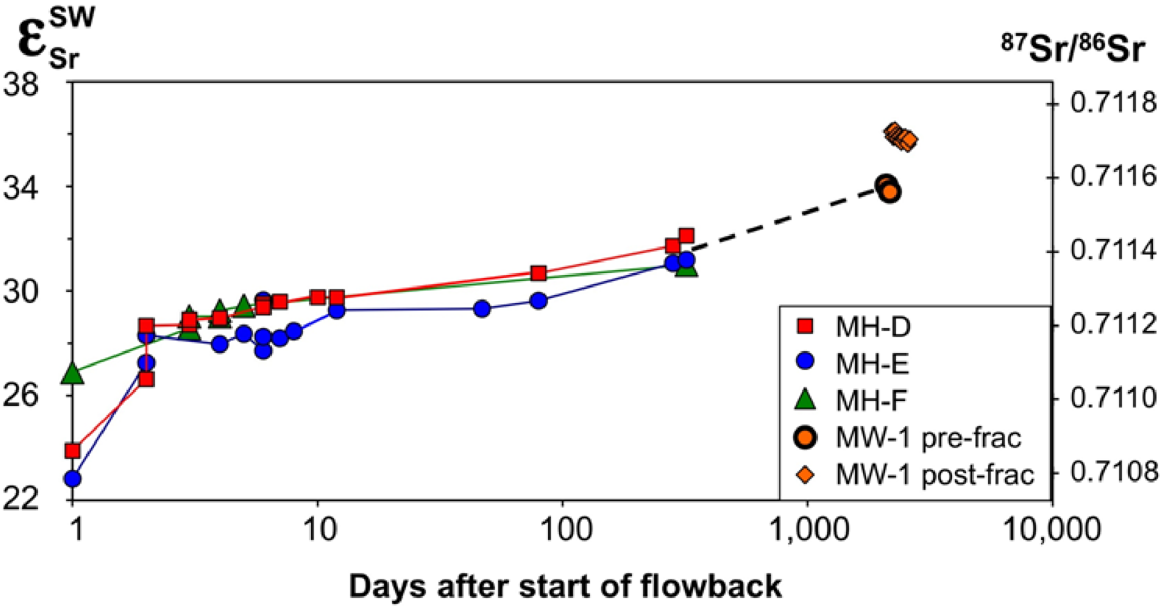

Figure 6. Evolution of the Sr isotope composition over time from beginning of flowback for vertical and horizontal Marcellus wells from the Greene County site. Horizontal well data (MH-D, E, F) are primarily from Capo et al. (2014). Sample MW-1 is from a vertical Marcellus well that was hydraulically fractured and began production in 2006, six years prior to hydraulic fracturing of the horizontal wells. Data from MW-1 are reported in Table 1.

Table 1. Sample information elemental concentrations, and Sr isotope compositions from the Greene County Test Site

Sample Name	Date Collected	Sample Type	Ca mg L^{-1}	Sr mg L^{-1}	^{87}Sr/^{86}Sr[a,b]			ε_{Sr}[c]		
Well UD-2: Upper Devonian/Lower Mississippian										
UD2-120125-T	1/25/12	Tank	13,600	251	0.719902	±	0.000015	151.39	±	0.21
UD2-120310-S	3/10/12	Separator	14,400	258	0.719976	±	0.000013	152.43	±	0.19
(replicate)					0.720006	±	0.000015	152.86	±	0.21
UD2-120518-S	5/18/12	Separator	12,900	225	0.720076	±	0.000016	153.84	±	0.22
UD2-120628-S	6/28/12	Separator	14,000	248	0.720057	±	0.000007	153.57	±	0.10
UD2-120628-T	6/28/12	Tank	13,000	234	0.719941	±	0.000007	151.94	±	0.10
(replicate)					0.719954	±	0.000007	152.12	±	0.10
UD2-120726-S	7/26/12	Separator	14,900	281	0.719873	±	0.000009	150.98	±	0.13
UD2-120726-T	7/26/12	Tank	14,000	257	0.719937	±	0.000007	151.88	±	0.10
UD2-120829-S	8/29/12	Separator	15,000	265	0.719955	±	0.000008	152.14	±	0.11
UD2-120829-T	8/29/12	Tank	13,100	237	0.719934	±	0.000006	151.84	±	0.09
UD2-120928-S	9/28/12	Separator	13,000	236	0.719933	±	0.000006	151.83	±	0.09
UD2-120928-T	9/28/12	Tank	12,400	223	0.719914	±	0.000007	151.56	±	0.10
UD2-121025-S	10/25/12	Separator	14,300	256	0.719932	±	0.000006	151.81	±	0.09
(replicate)					0.719937	±	0.000009	151.88	±	0.12
UD2-121025-T	10/25/12	Tank	13,300	236	0.719930	±	0.000008	151.78	±	0.11
UD2-121213-S	12/13/12	Separator	13,800	240	0.720018	±	0.000010	153.02	±	0.15
UD2-130123-T	1/23/13	Tank	13,200	240	0.719945	±	0.000010	152.00	±	0.14
(replicate)					0.719941	±	0.000009	151.94	±	0.13
UD2-130219-T	2/19/13	Tank	9,700	232	0.719886	±	0.000011	151.16	±	0.16
UD2-130325-T	3/25/13	Tank	13,200	237	0.719902	±	0.000011	151.39	±	0.15
UD2-130426-S	4/26/13	Separator	12,700	230	0.719909	±	0.000010	151.49	±	0.14
UD2-130626-S	6/26/13	Separator	13,800	245	0.720026	±	0.000010	153.14	±	0.14
UD2-130807-S	8/7/13	Separator	12,500	226	0.720084	±	0.000011	153.96	±	0.16
Well UD-4: Upper Devonian/Lower Mississippian										
UD4-120310-T	3/10/12	Tank	13,600	216	0.720295	±	0.000011	156.93	±	0.16
UD4-120518-T	5/18/12	Tank	13,700	217	0.720267	±	0.000012	156.54	±	0.17
(replicate)					0.720304	±	0.000009	157.06	±	0.13
UD4-120628-T	6/28/12	Tank	13,900	218	0.720281	±	0.000006	156.73	±	0.09
UD4-120726-T	7/26/12	Tank	14,000	222	0.720284	±	0.000007	156.78	±	0.10
UD4-120829-T	8/29/12	Tank	14,000	222	0.720265	±	0.000006	156.51	±	0.08
UD4-120928-T	9/28/12	Tank	13,900	218	0.720264	±	0.000006	156.49	±	0.09
UD4-121025-T	10/25/12	Tank	14,000	221	0.720281	±	0.000007	156.73	±	0.10
(replicate)					0.720282	±	0.000011	156.75	±	0.16
UD4-121213-T	12/13/12	Tank	13,900	219	0.720275	±	0.000010	156.65	±	0.14
UD4-130123-T	1/23/13	Tank	13,900	219	0.720283	±	0.000011	156.76	±	0.15
UD4-130219-T	2/19/13	Tank	13,900	221	0.720278	±	0.000010	156.69	±	0.15
UD4-130325-T	3/25/13	Tank	14,400	213	0.720283	±	0.000012	156.76	±	0.16
UD4-130426-T	4/26/13	Tank	14,400	204	0.720280	±	0.000011	156.72	±	0.16
UD4-130807-T	8/7/13	Tank	14,200	201	0.720256	±	0.000012	156.38	±	0.16
					0.720249	±	0.000010	156.28	±	0.14
Well UD-5: Upper Devonian/Lower Mississippian										
UD5-120125-S	1/25/12	Separator			0.720875	±	0.000012	165.11	±	0.17
UD5-120125-T	1/25/12	Tank	13,100	160	0.720954	±	0.000009	166.22	±	0.13
UD5-120310-S	3/10/12	Separator	13,200	162	0.720949	±	0.000011	166.15	±	0.15
(replicate)					0.720981	±	0.000013	166.60	±	0.18

Table 1 (continued).

UD5-120310-T	3/10/12	Tank	13,800	167	0.720921	±	0.000013	165.76	±	0.18
(replicate)					0.720909	±	0.000013	165.59	±	0.19
UD5-120518-S	5/18/12	Separator	13,600	192	0.720853	±	0.000013	164.80	±	0.19
UD5-120518-T	5/18/12	Tank	13,400	190	0.720916	±	0.000014	165.69	±	0.19
UD5-120628-S	6/28/12	Separator	14,500	197	0.721120	±	0.000006	168.56	±	0.09
UD5-120628-T	6/28/12	Tank	13,100	193	0.720944	±	0.000006	166.08	±	0.09
UD5-120726-S	7/26/12	Separator	16,300	236	0.720934	±	0.000008	165.94	±	0.11
UD5-120829-S	8/29/12	Separator	14,600	208	0.720950	±	0.000006	166.17	±	0.09
UD5-120928-S	9/28/12	Separator	15,400	217	0.720955	±	0.000007	166.24	±	0.10
UD5-120928-T	9/28/12	Tank	13,500	194	0.720945	±	0.000006	166.10	±	0.09
UD5-121025-T	10/25/12	Tank	13,800	194	0.720951	±	0.000008	166.18	±	0.11
UD5-121213-T	12/13/12	Tank	16,400	230	0.720948	±	0.000012	166.14	±	0.17
UD5-130123-T	1/23/13	Tank	12,000	167	0.720953	±	0.000010	166.21	±	0.14
UD5-130219-T	2/19/13	Tank	13,700	198	0.720944	±	0.000014	166.08	±	0.19
UD5-130325-S	3/25/13	Separator	13,400	186	0.720960	±	0.000015	166.31	±	0.22
UD5-130325-T	3/25/13	Tank	13,600	190	0.720954	±	0.000009	166.22	±	0.13
UD5-130426-T	4/26/13	Tank	14,000	196	0.720959	±	0.000013	166.29	±	0.18
UD5-130626-T	6/26/13	Tank	14,200	198	0.720865	±	0.000011	164.97	±	0.15
UD5-130807-S	8/7/13	Separator	17,000	245	0.720820	±	0.000011	164.33	±	0.16
Well UD-6: Upper Devonian/Lower Mississippian										
UD6-120310-S	3/10/12	Separator	15,100	266	0.720033	±	0.000014	153.24	±	0.19
UD6-120518-S	5/18/12	Separator	14,200	255	0.719918	±	0.000014	151.61	±	0.20
(replicate)					0.719944	±	0.000015	151.98	±	0.21
(replicate)					0.719951	±	0.000020	152.08	±	0.28
(replicate)					0.719969	±	0.000016	152.33	±	0.23
(replicate)					0.719966	±	0.000018	152.29	±	0.25
(replicate)					0.719977	±	0.000015	152.45	±	0.22
UD6-120628-S	6/28/12	Separator	14,200	246	0.720032	±	0.000006	153.22	±	0.08
UD6-120628-T	6/28/12	Tank	14,800	253	0.720102	±	0.000007	154.21	±	0.10
UD6-120726-S	7/26/12	Separator	15,300	280	0.719770	±	0.000006	149.53	±	0.08
UD6-120726-T	7/26/12	Tank	14,800	253	0.720097	±	0.000007	154.14	±	0.10
UD6-120829-T	8/29/12	Tank	14,900	255	0.720092	±	0.000008	154.07	±	0.11
UD6-120928-T	9/28/12	Tank	13,800	240	0.720091	±	0.000008	154.05	±	0.11
UD6-121025-T	10/25/12	Tank	14,500	248	0.720102	±	0.000009	154.21	±	0.12
(replicate)					0.720097	±	0.000010	154.14	±	0.14
UD6-121213-T	12/13/12	Tank	14,600	249	0.720081	±	0.000010	153.91	±	0.14
UD6-130123-T	1/23/13	Tank	14,400	243	0.720092	±	0.000010	154.07	±	0.15
UD6-130219-T	2/19/13	Tank	14,300	245	0.720089	±	0.000009	154.03	±	0.12
(replicate)					0.720097	±	0.000011	154.14	±	0.15
UD6-130325-T	3/25/13	Tank	14,300	244	0.720074	±	0.000009	153.81	±	0.13
UD6-130426-T	4/26/13	Tank	14,300	244	0.720083	±	0.000010	153.94	±	0.14
UD6-130626-T	6/26/13	Tank	14,400	242	0.720096	±	0.000009	154.12	±	0.13
UD6-130807-T	8/7/13	Tank	14,400	241	0.720087	±	0.000008	154.00	±	0.11
Well UD-7: Upper Devonian/Lower Mississippian										
UD7-120310-T	3/10/12	Tank	14,300	204	0.720222	±	0.000014	155.90	±	0.19
UD7-120518-T	5/18/12	Tank	14,200	198	0.720235	±	0.000012	156.08	±	0.17
(replicate)					0.720285	±	0.000011	156.79	±	0.16
UD7-120628-T	6/28/12	Tank	14,400	202	0.720280	±	0.000005	156.72	±	0.07
UD7-120726-T	7/26/12	Tank	14,600	206	0.720270	±	0.000006	156.58	±	0.09
(replicate)					0.720270	±	0.000007	156.58	±	0.10
UD7-120829-T	8/29/12	Tank	14,500	210	0.720285	±	0.000004	156.79	±	0.06
(replicate)					0.720283	±	0.000005	156.76	±	0.06
UD7-120928-T	9/28/12	Tank	14,200	183	0.720275	±	0.000006	156.65	±	0.09

Table 1 (continued).

UD7-121025-T	10/25/12	Tank	14,700	209	0.720286	±	0.000006	156.80	±	0.08
(replicate)					0.720294	±	0.000010	156.92	±	0.14
UD7-121213-T	12/13/12	Tank	14,400	208	0.720281	±	0.000013	156.73	±	0.18
UD7-130123-T	1/23/13	Tank	14,500	206	0.720255	±	0.000009	156.37	±	0.13
UD7-130219-T	2/19/13	Tank	14,500	209	0.720255	±	0.000010	156.37	±	0.14
UD7-130325-T	3/25/13	Tank	15,000	212	0.720254	±	0.000012	156.35	±	0.17
(replicate)					0.720238	±	0.000010	156.13	±	0.14
UD7-130426-T	4/26/13	Tank	14,500	206	0.720252	±	0.000009	156.32	±	0.13
UD7-130626-T	6/26/13	Tank	14,700	203	0.720252	±	0.000011	156.32	±	0.16
UD7-130807-T	8/7/13	Tank	14,800	205	0.720263	±	0.000013	156.48	±	0.19
Well MW-1: Middle Devonian, vertical, hydraulically fractured in 2006										
MW1-120310-T	3/10/2012	Tank	13,900	1,700	0.711580	±	0.000006	34.04	±	0.09
MW1-120518-T	5/18/2012	Tank	10,400	1,280	0.711541	±	0.000016	33.49	±	0.22
(replicate)					0.711570	±	0.000013	33.90	±	0.18
(replicate)					0.711576	±	0.000006	33.98	±	0.08
MW1-120628-T	6/28/2012	Tank	11,800	1,510	0.711726	±	0.000006	36.10	±	0.09
MW1-120726-T	7/26/2012	Tank	15,000	1,840	0.711710	±	0.000008	35.87	±	0.11
(replicate)					0.711712	±	0.000007	35.90	±	0.10
MW1-120829-T	8/29/2012	Tank	11,000	1,280	0.711729	±	0.000007	36.14	±	0.09
MW1-120928-T	9/28/2012	Tank	10,800	1,380	0.711712	±	0.000006	35.90	±	0.09
(replicate)					0.711720	±	0.000005	36.01	±	0.08
MW1-121025-T	10/25/2012	Tank	11,000	1,370	0.711710	±	0.000006	35.87	±	0.08
(replicate)					0.711705	±	0.000007	35.80	±	0.09
MW1-121213-T	12/13/2012	Tank	13,500	1,780	0.711711	±	0.000007	35.89	±	0.10
MW1-130123-T	1/23/2013	Tank	13,300	1,790	0.711698	±	0.000007	35.70	±	0.10
MW1-130219-T	2/19/2013	Tank	13,500	1,890	0.711709	±	0.000006	35.86	±	0.08
MW1-130325-T	3/25/2013	Tank	13,500	1,850	0.711703	±	0.000007	35.77	±	0.10
MW1-130426-T	4/26/2013	Tank	15,900	1,880	0.711710	±	0.000007	35.87	±	0.10
MW1-130626-T	6/26/2013	Tank	14,500	2,000	0.711692	±	0.000008	35.62	±	0.11
MW1-130807-T	8/7/2013	Tank	13,900	2,130	0.711705	±	0.000007	35.80	±	0.10
Spring water: Shallow groundwater										
SPW-120518	5/18/12	Spring	50.6	0.161	0.713329	±	0.000026	58.70	±	0.37
(replicate)					0.713349	±	0.000010	58.98	±	0.15
SPW-120628	6/28/12	Spring	58.4	0.176	0.713353	±	0.000006	59.04	±	0.08
SPW-120726	7/26/12	Spring	61.0	0.190	0.713384	±	0.000007	59.48	±	0.10
SPW-120829	8/29/12	Spring	60.3	0.191	0.713361	±	0.000005	59.15	±	0.06
SPW-120928	9/28/12	Spring	64.6	0.196	0.713347	±	0.000008	58.96	±	0.11
SPW-121025	10/25/12	Spring	65.9	0.203	0.713357	±	0.000008	59.10	±	0.11
(replicate)					0.713352	±	0.000009	59.03	±	0.13
SPW-121213	12/13/12	Spring	53.7	0.162	0.713384	±	0.000008	59.48	±	0.11
SPW-130123	1/23/13	Spring	50.4	0.153	0.713434	±	0.000010	60.18	±	0.15
SPW-130219	2/19/13	Spring	51.7	0.153	0.713422	±	0.000013	60.01	±	0.18
SPW-130325	3/25/13	Spring	53.7	0.154	0.713353	±	0.000010	59.04	±	0.14
SPW-130426	4/26/13	Spring	57.7	0.175	0.713332	±	0.000011	58.75	±	0.16
SPW-130626	6/26/13	Spring	60.3	0.191	0.713363	±	0.000012	59.18	±	0.17
SPW-130807	8/7/13	Spring	64.0	0.193	0.713442	±	0.000009	60.30	±	0.13

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[a] Normalized to SRM 987 Sr standard = 0.710240; 2s uncertainty based on in-run statistics.

[b] Reported replicates represent separate aliquots processed through columns and analyzed for $^{87}Sr/^{86}Sr$.

[c] ε_{Sr} defined as $(^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater} - 1)10^4$ where $^{87}Sr/^{86}Sr_{seawater} = 0.709166$.

Produced waters from the conventional UD/LM gas wells collected prior to hydraulic fracturing ("pre-frac") of the horizontal Marcellus wells have ε_{Sr}^{SW} values from +151.4 to +166.6 ($^{87}Sr/^{86}Sr$ = 0.71990-0.72098), a total spread of about 15 ε units (Table 1). These values are in the range of those reported for other Upper Devonian produced waters in Pennsylvania (Osborn et al., 2012; Warner et al., 2012; Chapman et al., 2013), which have ε_{Sr}^{SW} values of +93 to +181. Produced water from each of the UD/LM gas-producing units tends to be isotopically and chemically distinct, even within the limited geographic and stratigraphic range of the GCS. Figure 7 shows the pre-frac Sr isotope ratios are plotted against molar Sr/Ca ratios. While there is some overlap (particularly with produced water from wells UD-2 and UD-6), each defines a relatively distinct field. However, the UD/LM values can be considered rather tightly clustered when compared to produced water from vertical Marcellus well MW-1 (Figure 7 inset), as noted previously by Chapman et al. (2013). A mixing curve between the average for MW-1 and the most radiogenic Upper Devonian well (UD-5) demonstrates the sensitivity of Sr isotopes to incursions of Marcellus fluid into shallow conventional gas reservoirs (Figure 7). An addition of just over 1% of Marcellus fluid to the UD/LM reservoirs could explain the total range in ε_{Sr}^{SW} values. However, most of the UD/LM samples fall off the Marcellus mixing curve, and in fact all but UD-7 define a strong linear correlation (R^2 = 0.94; dashed line in Fig. 7). This suggests that most of the pre-frac geochemical variation reflects within-well mixing of produced water among the different UD/LM reservoirs tapped by each well. In either case, the large isotopic difference between all UD/LM produced waters and those of the Marcellus indicate that any of the Sr isotope ratios measured in UD/LM produced waters at the GCS would be sensitive to incursions of Marcellus brine that could take place over days to years following hydraulic fracturing.

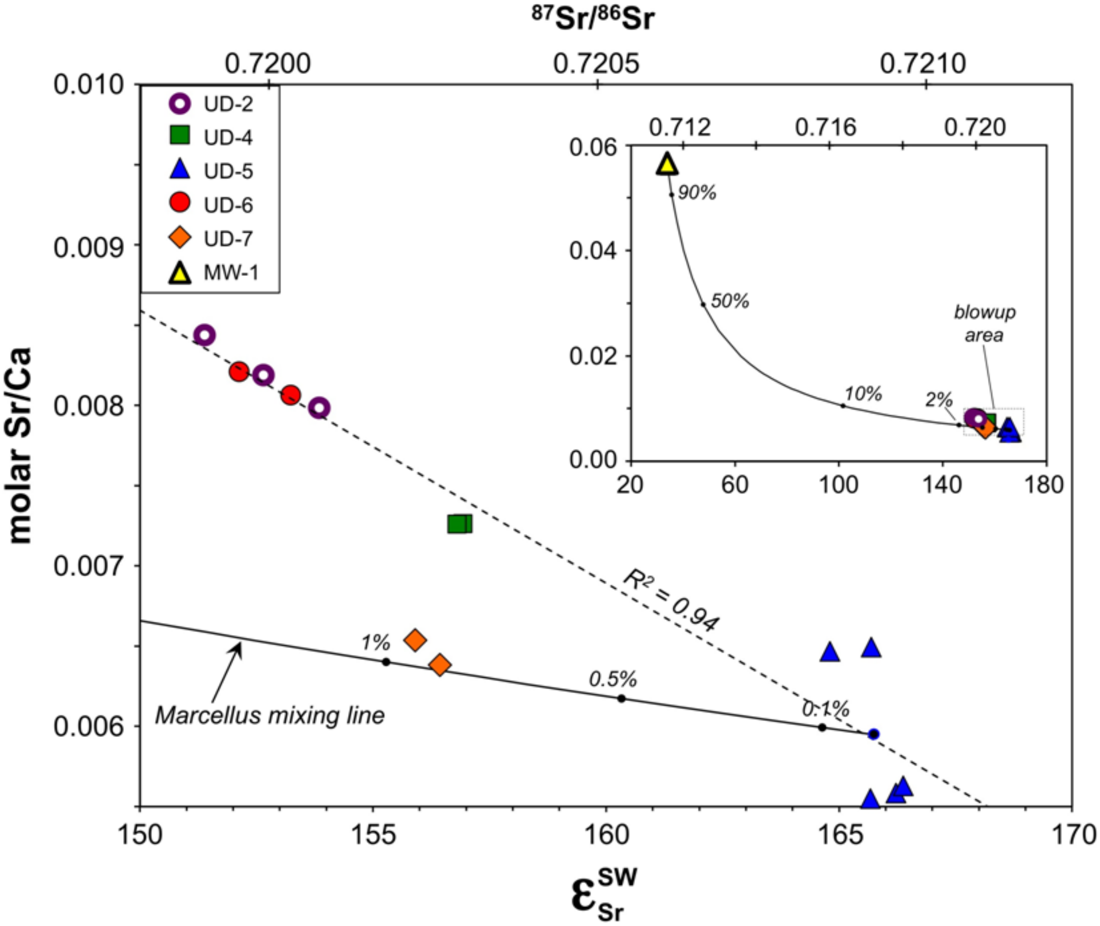


Figure 7. Plot of molar Sr/Ca ratios against Sr isotope composition for pre-frac Upper Devonian/Lower Mississippian and vertical well MW-1 Marcellus produced waters. The inset shows a hypothetical mixing curve between Marcellus brines and UD/LM produced waters, with the numbers on the curve indicating the amount of Marcellus brine in the mixture. The main plot focuses in on the variation in the UD/LM samples (bottom right corner of inset), with the same mixing curve indicated as a solid line. The dashed line shows the linear correlation of all UD/LM pre-frac samples except for UD-7; this correlation is thought to represent within-well mixing of produced waters from multiple units.

3.1.2 Effects of Hydraulic Fracturing on Overlying Units

Elemental concentrations and Sr isotope compositions of produced waters collected after hydraulic fracturing of the underlying Marcellus (all collection dates 6/28/12 and later) are reported in Table 1. In general, samples collected from storage tanks showed less variation than those from the gas-liquid separator, because the tank samples represent averaging over a longer period. Nonetheless, there is generally good agreement between tank and separator ε_{Sr}^{SW} values. Both pre- and post-frac samples from UD/LM wells are plotted in Figure 8. The shaded regions represent the 95% confidence interval (2σ) for variations within for the pre- and post-frac sample groups. For three wells (UD-4, UD-6 and UD-7), only two pre-frac data were available; the confidence interval was calculated the same way as the others, with the recognition that additional samples, had they been available, would likely have changed the size of the uncertainty envelope. Pre- and post-hydraulic fracturing analyses of UD/LM produced waters from units overlying the horizontal Marcellus wells show no significant difference; heteroscedastic t-tests yield p-values from 0.12 to 0.54 (two tailed), indicating that there was no statistically significant change to the $^{87}Sr/^{86}Sr$ ratios following hydraulic fracturing (Table B2 in Appendix B). The lowest p-value occurs in pre- and post-frac samples from well UD-4, which also shows the smallest amount of variation in ε_{Sr}^{SW} over time. For the isotopic shifts to be considered significant enough to suggest an incursion of Marcellus-derived fluid, the mean ε_{Sr} values would need to decrease by 1-3 ε units after hydraulic fracturing, depending on the constancy of the pre-hydraulic fracturing measurements. For these Upper Devonian reservoirs, this corresponds to an addition of only 0.1-0.3% Marcellus produced water. This suggests that the UD/LM reservoirs were not measurably affected by upward-migrating Marcellus-derived brines subsequent to hydraulic fracturing over the ~15 month duration of the present study. The lack of evidence of such a shift suggests that the UD/LM reservoirs were not measurably affected by upward-migrating Marcellus-derived brines subsequent to hydraulic fracturing over the ~15 month duration of the present study.

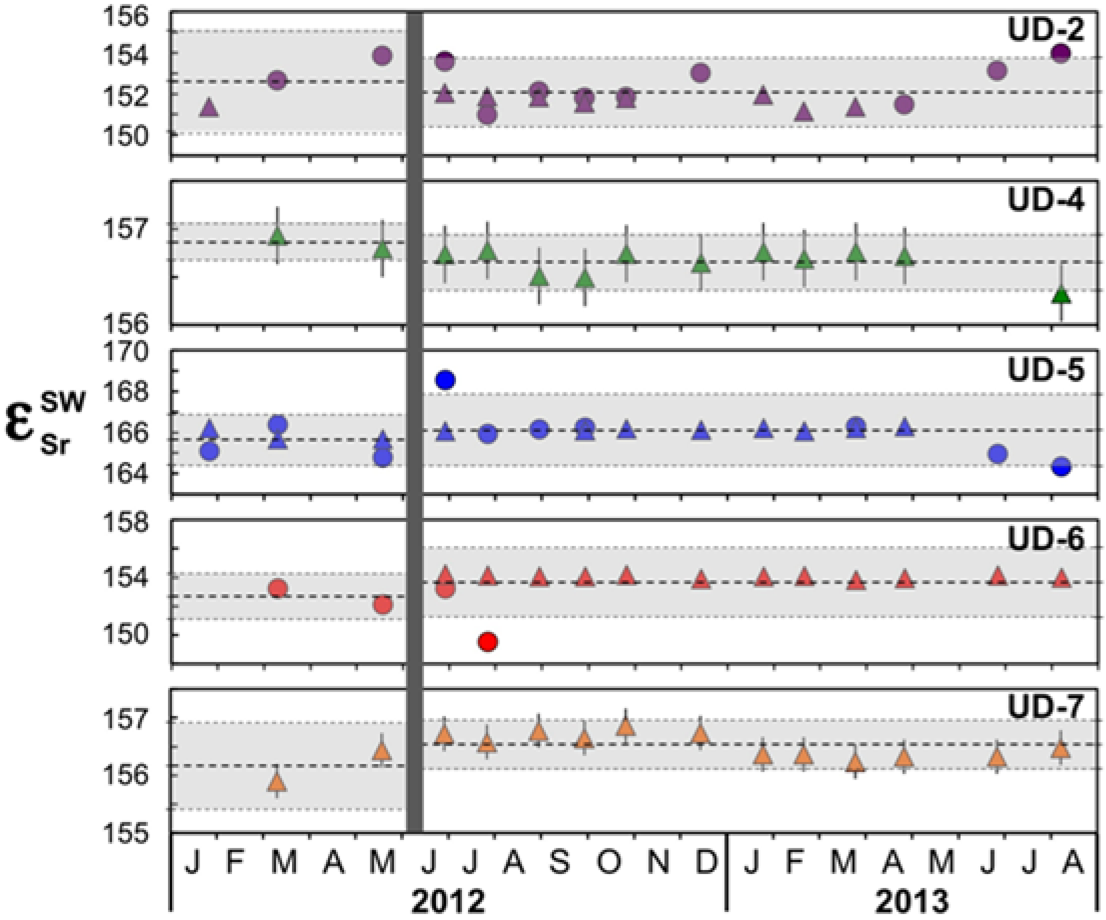


Figure 8. Strontium isotope composition of Upper Devonian/Lower Mississippian produced waters before and after hydraulic fracturing of the horizontal Marcellus wells (MH-D, E, F), with the time of hydraulic fracturing indicated by the vertical gray bar. Circles represent samples from separators, triangles samples from storage tanks. The shaded region represents the 2 σ variation (96% confidence interval) of pre-frac and post-frac samples.

Spring water chemistry in the area was also measured to evaluate possible natural or induced migration of Marcellus brine to higher stratigraphic levels, or hydraulic fracture-induced forcing of UD/LM brines into the aquifer. The isotopic composition of the spring water lies between values for the Marcellus brines and the UD/LM brines, with an average ε_{Sr}^{SW} value of +59.3 ($^{87}Sr/^{86}Sr = 0.71337$). Spring water ε_{Sr}^{SW} values shift systematically slightly above and below the mean on a semi-annual basis (Fig. 9). Because the spring water has relatively low Sr concentrations (generally <0.2 mg L^{-1}) relative to the produced waters at the site, its $^{87}Sr/^{86}Sr$ ratio is very sensitive to small incursions of produced water. Admixing only 0.003% Marcellus brine to the shallow groundwater would shift the isotope ratio of the groundwater downward by >5 ε units, and a 0.05% addition would shift it by 20 ε units, compared to a total observed annual variation of ±0.8 ε units. Similarly, a 0.01% addition of UD/LM brine would shift the groundwater value upward by nearly 10 ε units, and an addition of 0.05% would shift it by over 30 ε units. The spring at the GCS is most likely too far from the hydraulic fracturing zone to be an effective short-term monitoring site, but the natural variation in spring water isotope values (±0.8 ε units) provides a basis for evaluating possible contamination in other situations. In the ideal case, shallow groundwater would be sampled above or near the hydraulically fractured zone with 2-3 seasons of pre-frac baseline data to account for background variations.

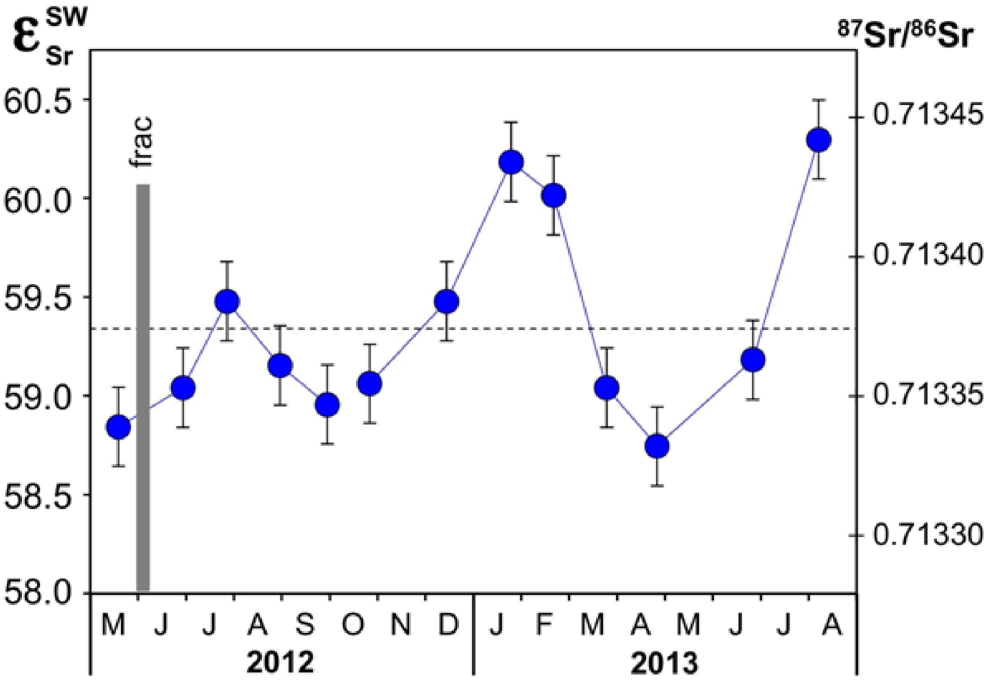


Figure 9. Variation in spring water Sr isotope ratio over the period of the study. The shaded vertical bar represents the period of hydraulic fracturing of horizontal Marcellus wells MH-D, E and F**.**

The one well that showed a potentially significant change in ε_{Sr}^{SW} subsequent to hydraulic fracturing is the vertical Marcellus well MW-1 that taps into the hydraulically fractured unit. Two pre-frac measurements yielded values of +33.5 and +34.0, while the post-frac values jumped to an average of +35.9 (ranging from +35.6 to +36.1; Fig. 9). The relatively low p-value calculated (0.043; Table B2) suggests that the shift could be significant. This is not unexpected; we posit that hydraulic fracturing in the same unit opened up new pathways for formation water within or below the shale to enter the vertical well. The relative constancy of the post-frac values suggest that these values represent formation waters which the well would have produced several years into the future.

3.1.3 Sensitivity of Strontium Isotopes to Subsurface Brine Migration

Monitoring of ground and surface water for contamination from drilling and hydraulic fracturing requires sensitive tracers that can provide an early warning of unexpected fluid migration. Given the multiple potential sources of high TDS brine, knowledge of the source of exogenous fluid is also critical. The differences in chemistry between produced waters and fresh waters allow for potential early detection of produced water incursions, where elements with the highest produced water:fresh water concentration ratios are more likely to be detected first. Elements that fit this description include Ba, Sr, Br, Cl, Na, Ca, and Ra (activity). The high concentrations of Sr in produced waters, when combined with a difference in isotope ratio from the fresh water, make Sr isotopes a very sensitive natural tracer that can also identify provenance (Chapman et al., 2012; Chapman et al., 2013).

To evaluate the use of elemental and isotopic tracers for monitoring produced water migration, we compiled available elemental data from Upper Devonian conventional wells (; Dresel and Rose, 2010; Osborn and McIntosh, 2010; Osborn et al., 2012) and Marcellus produced water (Hayes, 2009; Rowan, 2011; Chapman et al., 2012; Warner et al., 2012; Haluszczak et al., 2013; Capo et al., 2014), and compared it in a series of mixing models to potable groundwater, based on Susquehanna County "Type A" groundwater of Warner et al. (2012). Elemental data used in the mixing models are summarized in Table B3 (Appendix B). The Sr isotope endmember for the modeled Upper Devonian brine (+140) falls in the middle of measured $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$ values for Upper Devonian brines from this and other studies (Chapman et al., 2013; Osborn and McIntosh, 2010) and the Marcellus produced water endmember (+30) is in the mid-range of measured values (Chapman et al., 2012; Warner et al., 2012; Capo et al., 2014). The groundwater $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$ value reflects that of the spring at the GCS (+60); this could vary considerably from site to site, which emphasizes the importance of obtaining baseline data prior to possible environmental impacts of gas exploration.

The change in elemental concentrations (relative to the groundwater baseline) and Sr isotope composition as a function of produced water added are shown in Figure 10. Of the element concentrations shown, Ba, Br, Cl and Sr tend to be most sensitive for both Upper Devonian and Marcellus produced waters. The activity of Ra (combined ^{226}Ra + ^{228}Ra) can be a sensitive indicator of admixing Marcellus brines. As indicated by the curve for $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$ (the absolute shift in ε units), the Sr isotope composition is also sensitive to incursions of produced waters; when Upper Devonian waters are added, it drives the groundwater values upward, and when Marcellus waters are added, the ratio of the mixture shifts downward. Relative sensitivity can be demonstrated by comparing the element that shows the most rapid change for each water type with the shift in ε_{Sr}^{SW} values. For Marcellus produced water, Ba is potentially most sensitive; it reaches a value of 1.5 times the groundwater baseline when 0.003% Marcellus water has been added. At this same mixture level, the ε_{Sr}^{SW} would have shifted downward by 6 ε units, which is easily detectable and well outside of groundwater fluctuation observed in the GCS. In Upper Devonian waters, Br tends to be most sensitive; it also reaches a level of 1.5 time baseline at 0.003% produced water added, which corresponds to a shift in ε_{Sr}^{SW} of +5.

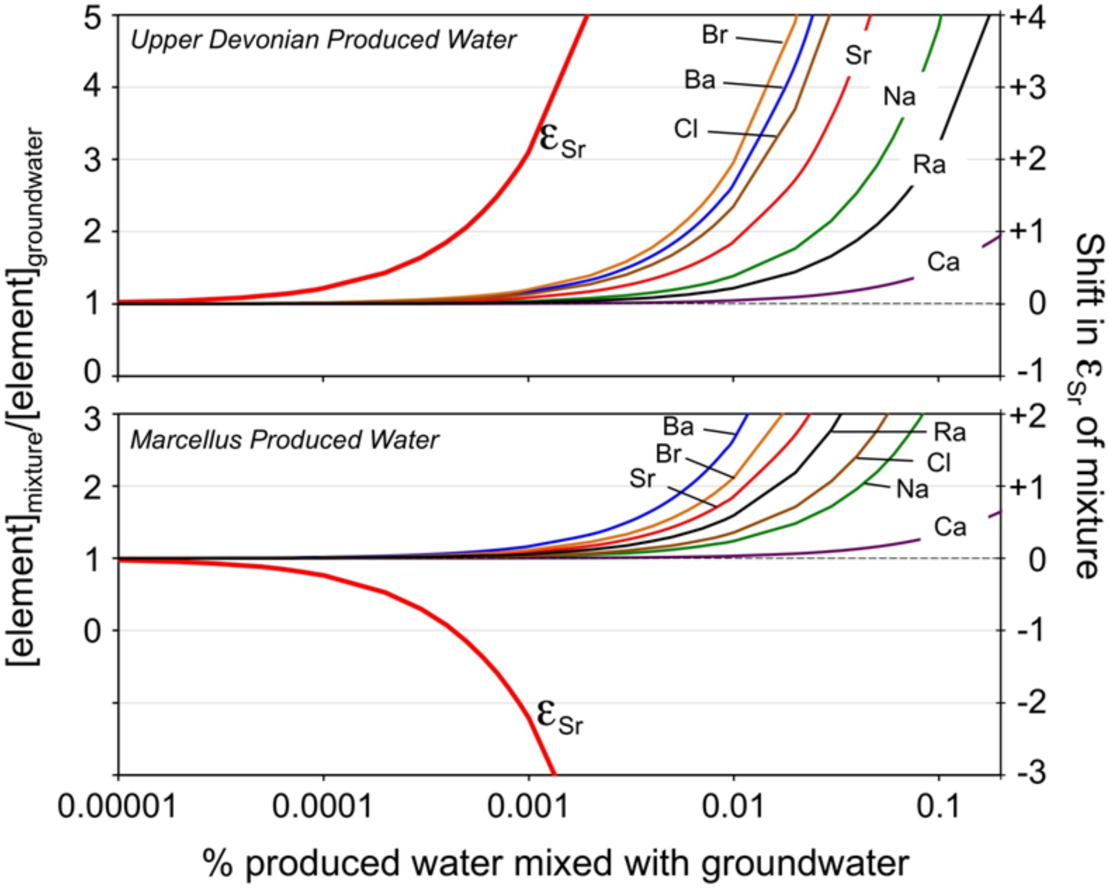


Figure 10. Modeled changes in selected chemical species and Sr isotope composition (ε_{Sr}) of fresh groundwater relative to baseline values as a function of the percent infiltration of Upper Devonian (top) or Marcellus (bottom) produced water.

Conversely, by the time the $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$ has shifted by -3 in the Marcellus case, the maximum increase in any element is 1.2 times baseline (Ba), and a +3 shift in the Upper Devonian case corresponds to a maximum increase of 1.3 times baseline (Br). The absolute concentrations of these elements in produced waters can vary significantly (Barbot, et al., 2013), and in some cases the most sensitive elements could behave non-conservatively. For example, Ba is likely to precipitate as barite if it encounters sulfate-rich waters such as acid mine drainage (Kondash et al., 2014), which may also pull Ra out of the system. In contrast, the Sr isotope ratio of Marcellus produced water falls within a narrow range (Chapman et al., 2012), and Sr behaves conservatively under most subsurface conditions. The relatively constant $\varepsilon_{\mathrm{Sr}}^{\mathrm{SW}}$ values in the Marcellus produced waters over long time periods (≥6 yrs.) indicate that Sr isotopes can be monitored for many years subsequent to hydraulic fracturing to identify signs of fluid migration.

4.0 CONCLUSION

The strontium isotope composition is a sensitive indicator of ground and surface water contamination by produced water, whether by surface spills, well leakage, or hydraulic fracturing-induced migration. Moreover, the direction of the shift in ε_{Sr}^{SW} can provide direct information about the source of migrating fluids (i.e., Upper Devonian/Lower Mississippian vs. Marcellus). Because Sr is present at high levels in the formation waters, it serves as a natural indicator of contamination, without need for added chemical tracers (Hammack et al., 2013). Given the development of methods for rapid analysis and the small samples required for analysis (Wall et al., 2013), Sr isotopes are an excellent natural long-term monitoring tool that can be used indefinitely as a sensitive indicator of brine incursion and its source. In addition, because of the long history of conventional oil and gas development in the Appalachian Basin, thousands of wells already exist in the Marcellus-producing region (approximately 350,000 as of 2000; PADEP, 2000), some of which could be used as an early warning of subsurface produced water migration. By taking baseline measurements in water wells, monitoring wells, and the many nearby shallower producing wells, Sr isotopes can be used to determine flow path and to identify the nature of fluid migration.

5.0 REFERENCES

Aberg, G., 1995, The use of Natural Strontium Isotoes as Tracers in Environmental Studies: Water Air and Soil Pollution, v. 79, p. 309-322.

Banner, J.L., 2004, Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy: Earth-Science Reviews, v. 65, p. 141-194.

Barbot, E., Vidic, N.S., Gregory, K.B., and Vidic, R.D., 2013, Spatial and Temporal Correlation of Water Quality Parameters of Produced Waters from Devonian-Age Shale following Hydraulic Fracturing: Environmental Science & Technology, v. 47, p. 2562-2569.

Brantley, S.L., Yoxtheimer, D., Arjmand, S., Grieve, P., Vidic, R., Pollak, J., Llewellyn, G.T., Abad, J., and Simon, C., 2014, Water resource impacts during unconventional shale gas development: The Pennsylvania experience: International Journal of Coal Geology, v. 126, p. 140-156.

Bruner, K.A.S., R, 2011, A Comparative Study of the Mississippian Barnett Shale, Fort Worth Basin, and Devonian Marcellus Shale, Appalachian Basin, NETL (National Energy Technology Laboratory) Report, U.S. Department of Energy, DOE/NETL-2011/1478.

Capo, R.C., Stewart, B.W., and Chadwick, O.A., 1998, Strontium isotopes as tracers of ecosystem processes: theory and methods: Geoderma, v. 82, p. 197-225.

Capo, R.C., Stewart, B.W., Rowan, E.L., Kolesar Kohl, C.A., Wall, A.J., Chapman, E.C., Hammack, R.W., and Schroeder, K.T., 2014, The strontium isotopic evolution of Marcellus Formation produced waters, southwestern Pennsylvania: International Journal of Coal Geology, v. 126, p. 57-63.

Chapman, E.C., Capo, R.C., Stewart, B.W., Hedin, R.S., Weaver, T.J., and Edenborn, H.M., 2013, Strontium isotope quantification of siderite, brine and acid mine drainage contributions to abandoned gas well discharges in the Appalachian Plateau: Applied Geochemistry, v. 31, p. 109-118.

Chapman, E.C., Capo, R.C., Stewart, B.W., Kirby, C.S., Hammack, R.W., Schroeder, K.T., and Edenborn, H.M., 2012, Geochemical and Strontium Isotope Characterization of Produced Waters from Marcellus Shale Natural Gas Extraction: Environmental Science & Technology, v. 46, p. 3545-3553.

Coleman, J.L., Milici, R.C., Cook, T.A., Charpentier, R.R., Kirschbaum, Mark, Klett, T.R., Pollastro, R.M., and Schenk, C.J, 2011, Assessment of undiscovered oil and gas resources of the Devonian Marcellus Shale of the Appalachian Basin Province: U.S.Geological Survey, http://pubs.usgs.gov/fs/2011/3092/pdf/fs2011-3092.pdf

Dresel, P.E., and Rose, A.W., 2010, Chemistry and Origin of Oil and Gas Well Brines in Western Pennsylvania: Harrisburg, PA, Pennsylvania Geological Survey Open-File Report OFOG 10-01.0, 48 p.

Engelder, T., 2012, Capillary tension and imbibition sequester frack fluid in Marcellus gas shale: Proceedings of the National Academy of Sciences of the United States of America, v. 109, p. E3625-E3625.

Engelder, T., and Lash, G.G., 2008, Marcellus shale play's vast resource potential creating stir in Appalachia, The American Oil and Gas Reporter.

Entrekin, S., Evans-White, M., Johnson, B., and Hagenbuch, E., 2011, Rapid expansion of natural gas development poses a threat to surface waters: Frontiers in Ecology and the Environment, v. 9, p. 503-511.

Ferrar, K.J., Michanowicz, D.R., Christen, C.L., Mulcahy, N., Malone, S.L., and Sharma, R.K., 2013, Assessment of Effluent Contaminants from Three Facilities Discharging Marcellus Shale Wastewater to Surface Waters in Pennsylvania: Environmental Science & Technology, v. 47, p. 3472-3481.

Flewelling, S.A., and Sharma, M., 2014, Constraints on Upward Migration of Hydraulic Fracturing Fluid and Brine: Ground Water, v. 52, p. 9-19.

Fracfocus, 2013, Chemical Use in Hydraulic Fracturing, http://fracfocus.org/water-protection/drilling-usage

Gregory, K.B., Vidic, R.D., and Dzombak, D.A., 2011, Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing: Elements, v. 7, p. 181-186.

Haluszczak, L.O., Rose, A.W., and Kump, L.R., 2013, Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA: Applied Geochemistry, v. 28, p. 55-61.

Hammack, R., Sharma, S., Capo, R., Zorn, E., Siriwardane, H., and Harbert, W., 2013, An Evaluation of Zonal Isolation After Hydraulic Fracturing; Results From Horizontal Marcellus Shale Gas Wells at NETL's Greene County Test Site in Southwestern Pennsylvania, Society of Petroleum Engineers.

Hayes, T., 2009, Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas, Marcellus Shale Coalition: Des Plaines, IL, Gas Technology Institute.

Jackson, R.B., Vengosh, A., Darrah, T.H., Warner, N.R., Down, A., Poreda, R.J., Osborn, S.G., Zhao, K., and Karr, J.D., 2013, Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction: Proceedings of the National Academy of Sciences, v. 110, p. 11250-11255.

Kondash, A.J., Warner, N.R., Lahav, O., and Vengosh, A., 2014, Radium and Barium Removal through Blending Hydraulic Fracturing Fluids with Acid Mine Drainage: Environmental Science & Technology, v. 48, p. 1334-1342.

Maloney, K.O., and Yoxtheimer, D.A., 2012, Research Article: Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania: Environmental Practice, v. 14, p. 278-287.

Myers, T., 2012, Potential Contaminant Pathways from Hydraulically Fractured Shale to Aquifers: Ground Water, v. 50, p. 872-882.

Ohio Department of Natural Resources Division of Mineral Resources Management, 2008, Report on the Investigation of the Natural Gas Invasion of Aquifers in Bainbridge Township of Geauga County, Ohio: Chargin Falls, Ohio.

Osborn, S.G., and McIntosh, J.C., 2010, Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin: Applied Geochemistry, v. 25, p. 456-471.

Osborn, S.G., McIntosh, J.C., Hanor, J.S., and Biddulph, D., 2012, Iodine-129, Sr-87/Sr-86, and Trace Elemental Geochemistry of Nothern Appalachian Basin Brines: Evidence for Basinal-Scale Fluid Migration and Clay Mineral Diagenesis: American Journal of Science, v. 312, p. 263-287.

Osborn, S.G., Vengosh, A., Warner, N.R., and Jackson, R.B., 2011, Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing: Proceedings of the National Academy of Sciences of the United States of America, v. 108, p. 8172-8176.

Penn State University Marcellus Center for Outreach and Research, 2013, http://www.marcellus.psu.edu/index.php

Rowan, E.L., Engle, M.A., Kirby, C.S., and Kraemer, T.F., 2011, Radium content of oil- and gas-field produced waters in the northern Appalachian Basin (USA)-Summary and discussion of data, Scientific Investigations Report, U.S. Geological Survey 2011-5135, 31 p.

Skalak, K.J., Engle, M.A., Rowan, E.L., Jolly, G.D., Conko, K.M., Benthem, A.J., and Kraemer, T.F., 2014, Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments: International Journal of Coal Geology, v. 126, p. 162-170.

Soeder, D.J., Sharma, S., Pekney, N., Hopkinson, L., Dilmore, R., Kutchko, B., Stewart, B., Carter, K., Hakala, A., and Capo, R., 2014, An approach for assessing engineering risk from shale gas wells in the United States: International Journal of Coal Geology, v. 126, p. 4-19.

States, S., Cyprych, G., Stoner, M., Wydra, F., Kuchta, J., Monnell, J., and Casson, L., 2013, Marcellus Shale drilling and brominated THMs in Pittsburgh, Pa., drinking water: Journal American Water Works Association, v. 105, p. 53-54.

Tiemann, M., and Vann, A., 2013, Hydraulic Fracturing and Safe Drinking Water Act Regulatory Issues, Congressional Research Service, Report no. R41760

U.S. Environmental Protection Agency, 2009, National Primary Drinking Water Regulations *in* U.S.E.P.A, ed., Volume 816-F-09-004: Washington, DC.

Vengosh, A., Jackson, R.B., Warner, N., Darrah, T.H., and Kondash, A., 2014, A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States: Environmental Science & Technology, DOI: 10.1021/es405118y

Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxtheimer, D., and Abad, J.D., 2013, Impact of Shale Gas Development on Regional Water Quality: Science, v. 340. no. 6134

Wall, A.J., Capo, R.C., Stewart, B.W., Phan, T.T., Jain, J.C., Hakala, J.A., and Guthrie, G.D., 2013, High throughput method for Sr extraction from variable matrix waters and ^{87}Sr/^{86}Sr isotope analysis by MC-ICP-MS: Journal of Analytical Atomic Spectrometry, v. 28, p. 1338-1344.

Wang, G., and Carr, T.R., 2013, Organic-rich Marcellus Shale lithofacies modeling and distribution pattern analysis in the Appalachian Basin: AAPG bulletin, v. 97, p. 2173-2205.

Warner, N.R., Christie, C.A., Jackson, R.B., and Vengosh, A., 2013, Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania: Environmental Science & Technology, v. 47, p. 11849-11857.

Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., and Vengosh, A., 2012, Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania: Proceedings of the National Academy of Sciences of the United States of America, v. 109, p. 11961-11966.

Wilson, J.M., and Van Briesen, J.M., 2013, Source water changes and energy extraction activities in the Monongahela River, 2009–2012: Environmental Science & Technology, v. 47, p. 12575-12582.

APPENDIX A

A.1 METHODS

A.1.1 Filtration and Acidification

All bottles and filters used in processing the samples from this study were pre-cleaned with nitric acid (HNO_3) and rinsed with ultrapure water. All samples were originally filtered to <0.45µm in the laboratory and subsequently preserved with ultrapure HNO_3 to a 2% acidification level to prevent precipitation of solids and microbial growth. Initial elemental analysis and Sr isotope chemistry was carried out on these samples. When additional elemental analyses were required (in some cases after >2 years of storage), the samples were acidified to a 4% level by weight. Many of the samples had been stored in a refrigerator for over two years, therefore to ensure complete dissolution of precipitates.

A.1.2 Elemental Analysis

After filtration and acidification all produced water samples were diluted to 1:100 or 1:1000 (UD/LM samples and Marcellus shale samples respectively) with 4% HNO_3.

Concentrations of Sr and Ca were measured on a Spectroflame Modula ICP-AES following a modified version of EPA method 6010C. Samples, calibration solutions, and calibration verification solutions were spiked with ~1 ppm Sc internal standard (by weight) to monitor instrument drift and matrix effects during elemental analysis. Acceptable Sr and Ca calibration curves had a correlation coefficient greater than or equal to 0.999. Further QA/QC analysis was carried out using matrix-matched calibration verifications: an initial calibration verification (ICV), continuing calibration verification (CCV), continuing calibration blank, and a certified standard solution (NIST 1640a). The ICV, CCV, and NIST 1640a Sr and Ca concentrations were measured to be within ± 10% of reported values before measurement of any samples. Throughout the analytical run, the CCB and CCV were measured after every ten produced water samples. Sr and Ca concentrations in the CCB were measured to be well below detection limits to ensure complete rinsing of any constituents within the ICP-AES tubing and nebulizer. Sample data were only accepted if (1) the CCV produced Sr and Ca concentrations within ± 10%, and (2) the Sr and Ca concentrations reported for the CCB were above detection limits.

All samples were originally filtered to <0.45μm in the laboratory and subsequently preserved with ultra pure nitric acid to a 2% acidification to prevent precipitation of solids and microbial growth. Acidification was done by first recording the weight of a polyethylene bottle (without the cap) labeled with the appropriate sample name. The filtered sample was then added to the bottle and the weight of the liquid was recorded. Finally concentrated ultra pure nitric acid was added to the sample to a 2% acidification by weight.

Later on the samples were acidified to a 4% level by weight. Many of the samples had been stored in a refrigerator for over two years, therefore to ensure complete dissolution of precipitates additional concentrated nitric acid was added to the samples that had only been filtered and acidified and had not been diluted for ICP-AES analysis. The additional nitric acid was added by weighing the amount of solution left in the bottle and then calculating how much nitric acid was in the solution. This was done by multiplying the weight (g) of the solution by 0.02. To calculate how much ultra pure nitric acid should be added to the solution to acidify the sample to a 4% level, the following calculation was used:

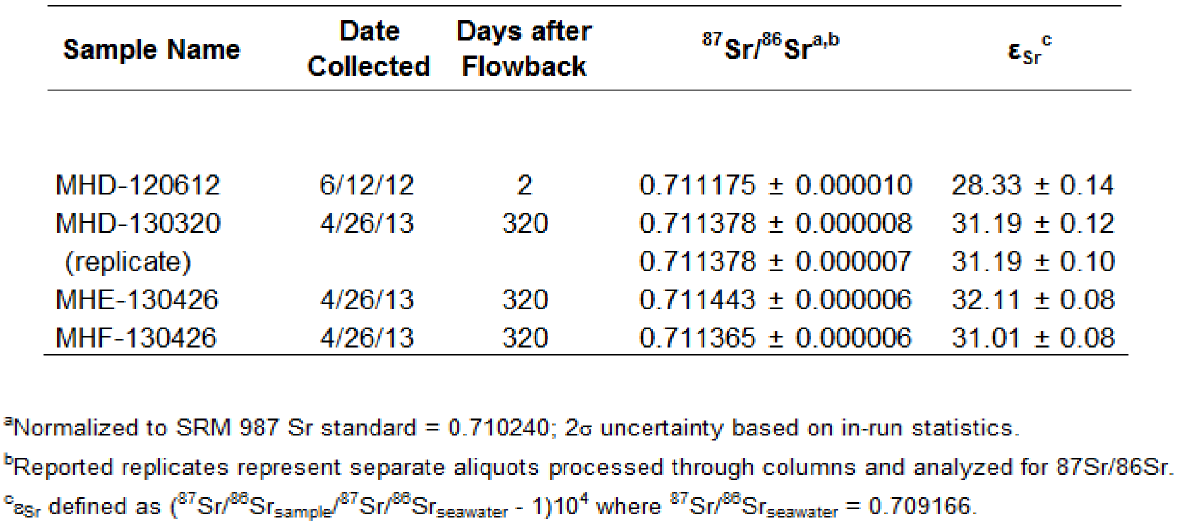
Amount of HNO3 to add = [(weight of solution (g)*0.04)-(weight of solution (g) *0.02)]/0.96

The calculated amount of ultra pure nitric acid was then added to the sample and the final weight and new acidification level was recorded.

APPENDIX B

B.1 SUPPLMENTARY DATA

Table B1. Marcellus horizontal well time series Sr isotope data. These represent additional analyses to the more complete data set reported by Capo et al. (2014).



Sample Name	Date Collected	Days after Flowback	^{87}Sr/^{86}Sr[a,b]	ε_{Sr}[c]
MHD-120612	6/12/12	2	0.711175 ± 0.000010	28.33 ± 0.14
MHD-130320	4/26/13	320	0.711378 ± 0.000008	31.19 ± 0.12
(replicate)			0.711378 ± 0.000007	31.19 ± 0.10
MHE-130426	4/26/13	320	0.711443 ± 0.000006	32.11 ± 0.08
MHF-130426	4/26/13	320	0.711365 ± 0.000006	31.01 ± 0.08

[a] Normalized to SRM 987 Sr standard = 0.710240; 2σ uncertainty based on in-run statistics.

[b] Reported replicates represent separate aliquots processed through columns and analyzed for 87Sr/86Sr.

[c] ε_{Sr} defined as ($^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater}$ - 1)10^4 where $^{87}Sr/^{86}Sr_{seawater}$ = 0.709166.

Table B2. Statistical analysis of change in Sr isotope composition (ε_{Sr}) after hydraulic fracturing.

	Pre-Hydraulic Fracture			**Post-Hydraulic Fracture**			**p-value: two-tailed distribution**
Well	Sample size	Mean ε_{Sr}	Variance	Sample size	Mean ε_{Sr}	Variance	
UD-2	3	152.63	1.505	17	152.09	0.702	0.545
UD-4	2	156.86	0.009	11	156.65	0.021	0.117
UD-5	6	165.65	0.375	15	166.12	0.759	0.180
UD-6	2	152.68	0.618	14	153.67	1.479	0.265
UD-7	2	156.17	0.144	12	156.53	0.044	0.410
MW-1	2	33.92	0.031	12	35.87	0.022	0.043

Table B3. Averaged elemental concentration data used to model produced water-ground water mixing (Fig. 10).

	Na	**Ca**	**Ba**	**Sr**	**Br**	**Cl**	**Total Ra activity**[a]
	- - - - - - - - - - - - - - - - - - - mg L^{-1} - - - - - - - - - - - - - - - - - - -						**pCi/L**
Marcellus Produced Water[b]	22,240	9,700	2,150	2,750	450	22,200	2,460
Upper Devonian Produced Water[c]	35,510	14,180	520	840	780	84,280	910
Ground Water[d]	9.27	30	0.13	0.32	0.04	6.25	0.42

[b] Radium activity values averaged from samples reported by Haluszczak et al. (2013), Rowan et al. (2011), and Dresel and Rose (2010) with total Ra from the latter estimated from ^{228}Ra values.

[b] Averaged from individual well samples reported by Hayes (2009), Chapman et al. (2012), Haluszczak et al. (2013), Warner et al. (2012) and Capo et al. (2014).

[c] Averaged from individual well samples reported by Osborn and McIntosh (2010) and Dresel and Rose (2010).

[d] Average of "Type A" groundwaters from Warner et al (2012).