

Isotope Approach to Assess Hydrologic Connections During Marcellus Shale Drilling

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Abstract

Water and gas samples were collected from (1) nine shallow groundwater aquifers overlying Marcellus Shale in north-central West Virginia before active shale gas drilling, (2) wells producing gas from Upper Devonian sands and Middle Devonian Marcellus Shale in southwestern Pennsylvania, (3) coal-mine water discharges in southwestern Pennsylvania, and (4) streams in southwestern Pennsylvania and north-central West Virginia. Our preliminary results demonstrate that the oxygen and hydrogen isotope composition of water, carbon isotope composition of dissolved inorganic carbon, and carbon and hydrogen isotope compositions of methane in Upper Devonian sands and Marcellus Shale are very different compared with shallow groundwater aquifers, coal-mine waters, and stream waters of the region. Therefore, spatiotemporal stable isotope monitoring of the different sources of water before, during, and after hydraulic fracturing can be used to identify migrations of fluids and gas from deep formations that are coincident with shale gas drilling.

Introduction

Marcellus Shale of the Appalachian Basin is one of the largest unconventional gas resources in the United States. To achieve economic gas production from Marcellus Shale, a technique known as hydraulic fracturing, or “fracing,” is adopted. During hydraulic fracturing, a mixture of water, sand, and chemicals is injected thousands of feet underground under high pressure to open new and existing fractures in shale formations and release natural gas. Public concern with Marcellus Shale gas development is that the quality of underground sources of drinking water (USDW) and surface waters might be degraded. Several thousand feet of lower permeability rocks like shales and siltstone separate the Marcellus Shale from USDW’s. These rocks should prevent gas and saline brines from the Marcellus Shale and other deep formations from migrating upward and mixing with shallow fresh water aquifers. Debate is still on-going over the volume of water that the Marcellus Shale contains and its potential to impact

shallow drinking water aquifers if hydrologic connections are induced through hydraulic fracturing (Engelder 2012; Warner et al. 2012; Haluszczak et al. 2013). Higher dissolved methane concentrations were reported in areas close to active shale gas drilling areas in Susquehanna County, Pennsylvania (Osborn et al. 2011). A subsequent study found that high groundwater methane concentrations were correlated with land topography, showing near surface geologic features and downward gradients as means for migration (Molofsky et al. 2011). However, there is still public concern that hydraulic fracturing may allow dissolved methane (commonly referred to as stray gas) and brines to migrate into drinking water supplies. It is also important to note that structural geology in areas of Marcellus Shale gas drilling is highly complex; this section of the Appalachians comprises several basement structures, faults, and fractures. As a result, the background concentrations of dissolved methane and brine can also be naturally high due to migration of brine and gas along preexisting natural faults and fractures over geological time scales (i.e., millions of years). Therefore, there is a need to (1) better understand the spatial and temporal variations in the baseline geochemical and isotopic signatures of water and gas sources in the region, and (2) develop a suite of natural geochemical tracers that can identify the origin of brine and methane in USDW’s.

The stable isotope signatures of waters in the streams and shallow aquifers are likely to be different from deeper/older aquifers, coal-mine waters, and produced waters due to variations in their recharge sources, water-rock interactions and biogeochemical reactions.

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Recent studies have demonstrated the utility of geochemical proxies to trace sources of waters in shale gas drilling areas of Pennsylvania (e.g., Osborn et al. 2011; Rowan et al. 2011; Chapman et al. 2012; Warner et al. 2012). These authors have demonstrated the use of elemental ratios (e.g., Sr/Ca, Ba/Sr, Sr/Cl, Ba/Cl, Li/Cl), and isotopic ratios of $^{228}\text{Ra}/^{226}\text{Ra}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{18}\text{O}/^{16}\text{O}$, and D/H to distinguish different brine sources. The aim of this study is to further this approach by testing the potential of O and H isotopic composition of water, C isotopic composition of dissolved inorganic carbon, and C and H isotopic composition of dissolved methane to distinguish different water and gas sources in an area of accelerating shale gas development in north-central West Virginia and southwestern Pennsylvania.

Study Area and Methodology

The study area lies in the Monongahela River Basin of southwestern Pennsylvania and north-central West Virginia (Figure 1). This study area was chosen because the Marcellus Shale is the primary gas play in this region and drilling is expected to expand rapidly. Structural geology of the study area is complex due to three distinct orogenic events that occurred from the Middle Ordovician to Permian (Bruner and Smosna 2011). The Marcellus Shale also underwent significant structural deformation, particularly during the last orogeny. Complex structural systems exist in the study area, accompanied by numerous basement structures, faults and fractures. These structural features can create preferential flow pathways for dissolved methane and water to migrate from one formation to another. In order to accurately assess the role of hydraulic fracturing the Marcellus Shale in creating new and/or additional pathways between different formations, it is important to understand the natural geochemical variability of waters in shallow aquifers and streams before hydraulic fracturing occurs. For this study, water and dissolved gas samples were collected from shallow groundwater wells in north-central West Virginia, and streams and coal-mine discharges in southwestern Pennsylvania and northern West Virginia. For isotopic end-member characterization, water and natural gas samples were collected from gas wells drilled in the Upper Devonian sands and Marcellus Shale in nearby Greene County of southwestern Pennsylvania. However, it is important to note that isotope signatures can vary geographically, therefore, when investigating potential water contamination or stray gas issues, localized signatures should be determined in order to confirm changes in hydrologic connections.

The 41 shallow groundwater wells (45 to 300 feet depth) sampled in this study represent nine geological formations (i.e., Conemaugh, Monongahela, Pottsville, Kanawha, Hampshire, New River, Chemung, Price, and Allegheny) that overlie the Marcellus Shale in north-central West Virginia (Figure 2). The nine formations range in age from Devonian to Permian and are composed primarily of sandstones, siltstones, shales, and limestones (Cardwell 1975; Mulder 2012). The samples

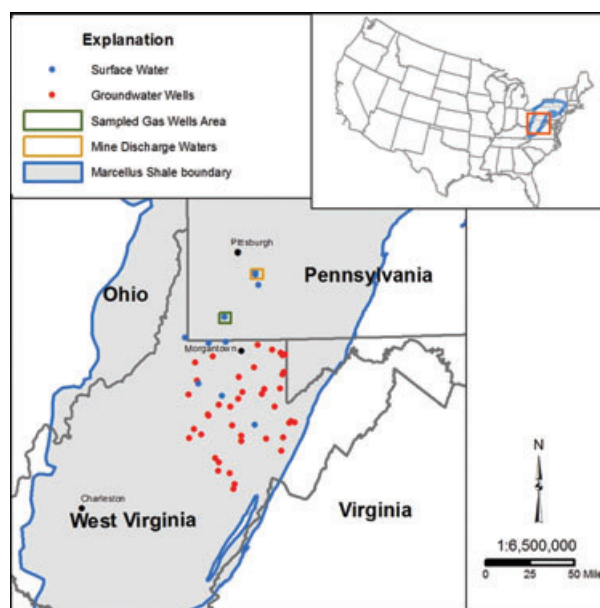


Figure 1. Map showing locations of the sampled groundwater wells, surface waters, and area of sampled coal-mine discharges and gas producing wells in Upper Devonian sands and Middle Devonian Marcellus Shale.

were collected during the summer of 2011 before any hydraulic fracturing activity occurred in this region (Mulder 2012). However, it is important to note that the long history of oil and gas drilling in this region can affect these baseline values. Water and gas samples were collected after two to three casing volumes of water were removed at rate less than 1 L/min through a Teflon hose line connected to the well plumbing. All samples were collected after field parameters (temperature, conductivity, pH, dissolved oxygen) were stabilized within $\pm 10\%$ of three consecutive readings. Samples were taken using existing well pumps at access points along the piping system, before treatment (if any). The coal-mine and stream waters were collected directly from the mine discharge portals and the flowing part of the stream, respectively. For end-member characterization, water and natural gas samples were collected from nine vertical gas wells drilled in Upper Devonian sands and Marcellus Shale approximately six years after hydraulic fracturing. In addition, two water and natural gas samples were also collected from two horizontal Marcellus Shale wells approximately 8 to 15 months after hydraulic fracturing. Since the water samples were collected from gas wells several months/years after hydraulic fracturing, it is presumed that the water coproduced with gas is representative of formation water. Also, it was not possible to obtain the produced water samples before gas-water separators at most of the sites. Hence, produced water samples were collected from a spigot on the bottom of the storage tanks at the well sites.

Water samples for $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were collected by filling an 8 mL glass threaded vial with no headspace, wrapped with parafilm, and refrigerated until analysis. For $\delta^{13}\text{C}_{\text{DIC}}$, the water was filtered through a

Age	Geological Unit			
Permian	Dunkard Group			
Pennsylvanian	Monongahela Group			
	Conemaugh Group			
	Allegheny Formation			
	Pottsville Group	Kanawha Fm.		
		New River Fm.		
Pocahontas Fm.				
Mississippian	Mauch Chunk Group			
	Greenbrier Group			
	Maccrady Formation			
	Price Formation			
Devonian	Hampshire Formation			
	Chemung Group			
	Brallier Formation			
	Harrell Shale			
	Mahantango Formation			
	Marcellus Formation			
	Onesou Thaw Stage	Tioga Bentonite		
		Onondaga Limestone	Huntersville Chert	Needmore Shale

Figure 2. Simplified stratigraphic column of the study area showing the nine sampled groundwater formations overlying the Marcellus Shale (modified after Cardwell 1975).

0.45- μm polyvinylidene difluoride filter with a 60 mL Luer-lock syringe and collected in a 10 mL Wheaton glass serum bottle. The water sample in the bottle was preserved by adding two to three drops of benzalkonium chloride to prevent biological activity. The bottle was then capped with Teflon septa and sealed with an aluminum cap. Water samples for dissolved methane were collected in a rinsed 5-gallon bucket using Teflon tubing connected to the groundwater sampler. The bucket was filled with sample water until the water level was above the height of the sample bottle, and the pre-rinsed methane sample bottle was fully submerged upright in the bucket with the sampling tube inserted. After approximately three sample bottle volumes were exchanged, the sample hose was quickly removed underwater and the sample bottle was capped underwater. Extra care was taken not to expose the sample to air; with no air bubbles present after being capped.

Produced gas samples were collected in 300 mL stainless steel high-pressure cylinders. The cylinders were attached directly to the $\frac{1}{4}$ " NPT sampling port of the wellhead prior to the gas undergoing any form of commercial processing. The cylinders were flushed through with gas from the wellhead for 5 min before the outer valve was shut and the cylinder was equilibrated at wellhead pressure. The cylinder valve closest to the wellhead was then shut and the gas was vented by opening the outer cylinder valve, closing this valve before complete positive pressure was lost. This purge

procedure was repeated five more times before both valves were closed sequentially from the outer valve to the valve closest to the sampling port. The gas cylinders were transported to the WVU Stable Isotope Laboratory and later shipped to Isotech Labs for natural gas characterization and isotope analysis.

The $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ in the water samples were measured with a continuous-flow gas-ratio mass spectrometer (Finnigan Delta Advantage) coupled with a Gasbench Device in the WVU Stable Isotope Laboratory. The reproducibility and accuracy were monitored by duplicate analyses of samples and internal lab standards and was better than 0.2‰ for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{13}\text{C}_{\text{DIC}}$, and 1‰ for $\delta^2\text{H}_{\text{H}_2\text{O}}$. All $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ values are reported in per mil (‰) relative to the international standards V-SMOW (Standard Mean Oceanic Water) and V-PDB (Pee Dee Belemnite), respectively. The $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ analysis of dissolved methane in water were performed on Delta S and Delta Plus XL dual-inlet IRMS at Isotech Labs, Champaign, Illinois, USA. An online gas chromatography—combustion—isotope ratio mass spectrometer (GC-C-IRMS) system was used for four samples having low dissolved methane concentrations. The isotopic composition of dissolved methane was analyzed through gas extraction from water by headspace equilibration. Duplicate samples consist of 10% of the total samples in smaller analysis sets and every 10th analysis is a duplicate sample within larger sets of analyses. The internal check standards for methane isotopes cover a wide range of natural gas samples contained in high volumes at Isotech Labs. Precision for methane isotopes at Isotech are $\delta^{13}\text{C}_{\text{CH}_4}$ -offline $\pm 0.1\%$, $\delta^{13}\text{C}_{\text{CH}_4}$ -online ± 0.4 , $\delta^2\text{H}_{\text{CH}_4}$ -offline $\pm 2\%$, and $\delta^2\text{H}_{\text{CH}_4}$ -online $\pm 5\%$.

Results

Oxygen, Hydrogen, and Carbon Isotopic Composition of Waters

The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ values of 64 water samples collected from shallow groundwater wells targeting nine geological formations, coal-mine water discharges and streams range from -7.2 to -10.6% , and -46.3 to -67.8% vs. V-SMOW, respectively. On the other hand, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ values of seven produced waters collected from wells producing from Marcellus Shale and Upper Devonian sands are more enriched in the heavy isotopes and range from -2.4 to -4.2% and -28.5 to -38.8% vs. V-SMOW, respectively (Figure 3; Table S1).

The $\delta^{13}\text{C}_{\text{DIC}}$ signatures of the 41 shallow groundwater samples collected from the nine geological formations show a wide range of isotopic values ranging from -1.1 to -23.5% vs. V-PDB. The $\delta^{13}\text{C}_{\text{DIC}}$ of six water samples collected from two coal-mine water discharges in different seasons range from -6.4 to -10.2% vs. V-PDB. The $\delta^{13}\text{C}_{\text{DIC}}$ values of 17 samples collected seasonally from streams throughout the sampling area range between -2 and -12.5% vs. V-PDB. Although there was isotopic variation among these water samples, more than 80% of

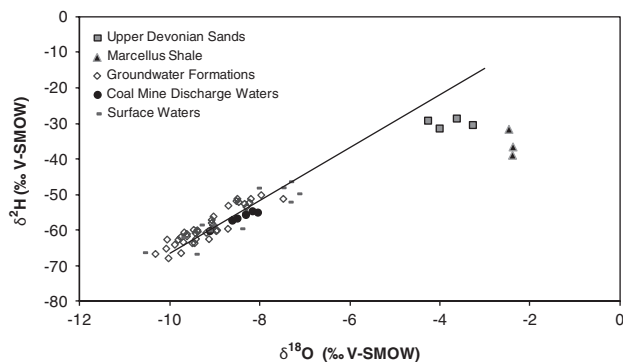


Figure 3. Plot of O and H isotopic composition of waters collected from all sites. Note all groundwater, surface water, and coal-mine discharge waters cluster along the Local Meteoric Water Line (LMWL) while the waters from Upper Devonian sands and Marcellus Shale have heavier O and H isotope signatures and they are much more enriched in oxygen compared to hydrogen.

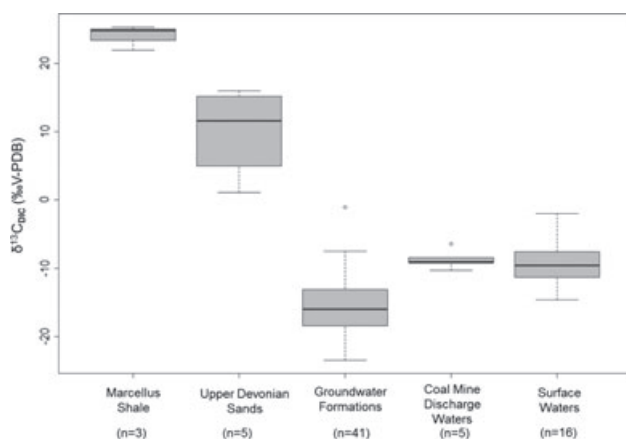


Figure 4. Box and whisker plot showing the variation in carbon isotope values of dissolved inorganic carbon in waters of different origin. Each box represents the inter-quartile range for each category, with the median value shown as the dark line. Each whisker represents values that are within 1.5 times the inter-quartile range. Outliers are shown as open circles.

the samples had $\delta^{13}\text{C}_{\text{DIC}}$ values lighter than -7‰ . In contrast, the $\delta^{13}\text{C}_{\text{DIC}}$ values of the seven produced waters were enriched in ^{13}C with their $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from $+1$ to $+25.3\text{‰}$ vs. V-PDB (Figure 4; Table S1).

Carbon and Hydrogen Isotopic Composition of Dissolved Methane and Produced Natural Gas

Dissolved methane concentrations and their corresponding carbon and hydrogen isotopic compositions were determined for the shallow groundwater samples collected in the study area. The dissolved methane concentrations in these shallow groundwaters range from 0 to 42 mg/L (Table S2). Of the 23 groundwater samples collected, 13 had dissolved methane concentrations high enough for isotopic analysis, that is, more than 0.1 mg/L. The $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ values range from -42 to -69‰ vs. V-PDB and -99 to -244‰ vs. V-SMOW, respectively.

For the majority of the dissolved gas samples, the higher hydrocarbon concentrations (i.e., C2, C3, C4) were below detection limits of the instrument (i.e., 0.3% for C₂ and 0.2% for C₃).

The range for $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ values of seven natural gas samples collected from gas wells producing from the Upper Devonian sands were -43.44 to -3.62‰ and -180.3 to -192.9‰ , respectively (Table S2). The natural gas from these wells had C2% in range of 3.8 to 5.5% and C3% of 0.1 to 1.3%. Natural gas samples collected from five gas wells drilled in the Marcellus Shale in Greene County, Pennsylvania had a $\delta^{13}\text{C}_{\text{CH}_4}$ range of -36.83 to -38.07‰ and a $\delta^2\text{H}_{\text{CH}_4}$ range of -164.4 to -166.8‰ . The C2% and C3% in the Marcellus gas samples ranged from 2.2 to 2.6% and 0.001 to 0.15%, respectively.

Discussion

O and H Isotope Composition of Waters

Oxygen and hydrogen form the water molecule itself, making these isotopic proxies good natural tracers for tracking the sources of water. On a global scale, meteoric waters show an excellent correlation between the O and H isotopic composition. This correlation is defined as the global meteoric water line (GMWL), defined by $\delta^2\text{H} = 8.13\delta^{18}\text{O} + 10.8\text{‰}$ (Rozanski et al. 1993). Deviations from the GMWL exist due to variations in the isotopic composition of source vapor mass, temperature, humidity, and evaporation which create Local Meteoric Water Lines (LMWL) of varying slopes and intercepts (Rozanski et al. 1993). The O and H isotopic compositions of waters in different groundwater aquifers will primarily be dependent on the time and season of recharge and water-rock interactions. The different water-rock interactions include exchanges with CO₂ and H₂S, hydration with silicates, evaporite dissolution, and high temperature exchange with rocks. These processes can impart unique O and H isotopic signatures and serve as natural tracers to distinguish waters from different formations and depths (e.g., Kharaka et al. 1973; Wittrup et al. 1987; Rostron and Holmden 2000).

The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ isotopic composition of all waters collected in this study were plotted in correlation to the predicted Local Meteoric Water Line (LMWL) constructed using the area's latitude, longitude, and altitude values (Bowen 2012). Groundwater samples from the nine geological formations, coal-mine discharges and streams plot close to the LMWL, indicating that meteoric recharge is the primary component of these waters (Figure 3). However, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ values of produced waters from the Upper Devonian sands and Marcellus Shale show much more enriched O and H isotope signatures with a shift toward the right of the meteoric water line. Evaporation of water in the storage tanks could result in a disproportionate loss of lighter isotopes of O and H in the remaining water pool, but this would result in the isotope values

plotting along a line with shallower slope with respect to LMWL. However, isotope values of produced waters from both formations do not plot along what would be expected as an evaporation slope; instead a horizontal shift to the right of the LMWL is observed (Figure 3). This right shift indicates large enrichments in ^{18}O relative to the meteoric waters. The values are similar to published values for the Appalachian brines (Siegel et al. 1990; Siegel et al. 2004; Warner et al. 2012). Similar isotopic enrichment in ^{18}O has been reported in brines from several sedimentary basins worldwide and is attributed to isotopic exchange reactions between waters and associated carbonate minerals (e.g., Clayton et al. 1966; Hitchon and Friedman 1969; Kharaka and Thordsen 1992). In this case, the exchange of deuterium is minimal, because the amount of water is large relative to hydrogen-bearing minerals in sedimentary rocks. Alternatively, it has been suggested that water-rock interactions involving gypsum dehydration could also result in enriched $\delta^{18}\text{O}$ values in the formation water (Holser 1979; Knauth and Beeunas 1986; Wilson and Long 1993). This is because gypsum precipitates from seawater under highly evaporative conditions (for the Marcellus Shale, this would have occurred during the Middle Devonian) incorporating more ^{18}O enriched evaporated water in its structure. Therefore, significant contribution from water released via gypsum dehydration would shift the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of the formation waters toward the right. The process of membrane filtration through shale formations has also been proposed to enrich the formation water in heavy isotopes (Graf et al. 1965). We hypothesize that any of these water-rock interactions could be responsible for the O and H isotopic signatures of produced waters from the Upper Devonian sands and Marcellus Shale. These unique O and H values could potentially serve as natural fingerprints to identify shallow groundwaters and surface waters that have received significant contribution from the produced waters.

Carbon Isotopic Composition of Dissolved Inorganic Carbon

The two primary sources of dissolved inorganic carbon (DIC) in natural waters are CO_2 derived from decaying organic matter and carbonate rock dissolution. The contribution of atmospheric CO_2 has been found to be negligible in most environments (Mook and Tan 1991; Clark and Fritz 1997). The average carbon isotope signature of these two contributing end members is very distinct. The average $\delta^{13}\text{C}$ of soil CO_2 in areas dominated by C3 vegetation (primarily all grass, trees and bushes in temperate regions), similar to the study area, is expected to be approximately -23‰ V-PDB (Aravena et al. 1992). On the other hand, the $\delta^{13}\text{C}$ of most carbonate rocks are around $0 \pm 2\text{‰}$. Most groundwaters receiving equal contributions from both these end members have $\delta^{13}\text{C}_{\text{DIC}}$ compositions ranging between -11 and -16‰ (Mook and Tan 1991). In our study, more than 77% of the 64 water samples collected from shallow aquifers, coal-mine discharges and streams had $\delta^{13}\text{C}_{\text{DIC}}$ signatures lighter than -9‰ (Figure 4; Table S1). Approximately 50% of

these have $\delta^{13}\text{C}_{\text{DIC}}$ values lighter than -13‰ , indicating greater contributions of carbon from isotopically lighter sources (i.e., carbon from soil organics and/or organic matter in the coals and shales with which they are interacting). The carbon isotope value of total organic carbon of the coal and shale solid samples collected from Pennsylvanian formations in the study area ranges from -21.6 to -25.4‰ vs. V-PDB (Sharma et al. 2013).

Water samples with enriched $\delta^{13}\text{C}_{\text{DIC}}$ signatures, that is, $\delta^{13}\text{C}_{\text{DIC}}$ values greater than -9‰ indicate larger contribution from dissolution of isotopically enriched carbonate rocks. Some of the more enriched $\delta^{13}\text{C}_{\text{DIC}}$ values in coal-mine discharge waters could also be attributed to degassing of isotopically light dissolved CO_2 species of total DIC due to high PCO_2 of these waters (Mook et al. 1974; Marlier and O'Leary 1984; Telmer and Veizer 1999; Doctor et al. 2008; Fonyuy and Atekwana 2008; Ali and Atekwana 2009; Atekwana and Fonyuy 2009; Sharma et al. 2013).

The $\delta^{13}\text{C}_{\text{DIC}}$ values of the produced water samples collected from wells drilled in Upper Devonian sands and Marcellus Shale have very high $\delta^{13}\text{C}_{\text{DIC}}$ signatures, with 85% of the total produced water samples having $\delta^{13}\text{C}_{\text{DIC}}$ signatures more than $+8.5\text{‰}$ (Figure 4; Table S1). Such heavy $\delta^{13}\text{C}_{\text{DIC}}$ signatures indicate occurrence of biogenic methanogenesis in highly reducing conditions due to preferential removal of ^{12}C by methanogens (e.g., Simpkins and Parkin 1993; Scott et al. 1994; Botz et al. 1996; Martini et al. 1998; Whiticar 1999; Hellings et al. 2000; Aravena et al. 2003; McIntosh et al. 2008; Sharma and Frost 2008; McLaughlin et al. 2011). Although the water samples collected from wells drilled in both Upper Devonian sands and Marcellus Shale have very high $\delta^{13}\text{C}_{\text{DIC}}$ signatures, it is important to note the $\delta^{13}\text{C}_{\text{DIC}}$ signatures of the three produced water samples from the Marcellus are more than $+21\text{‰}$ and more enriched in ^{13}C compared to Upper Devonian sands that have average $\delta^{13}\text{C}_{\text{DIC}}$ values of $+10.0\text{‰}$. The ^{13}C enriched signatures of DIC in these produced water samples indicates the possibility of biogenic methanogenesis in these formations. Quantitative PCR analysis of one of the produced water samples from the Marcellus Shale well shows the presence of *Methanosarcinales* sp., which includes methanol, methylamines, H_2 , and acetate utilizing methanogens (Sharma et al. 2011). These methanogens can use a wide variety of organic substrates to produce methane, demonstrating the potential of biogenic methanogenesis in these waters. It is also plausible that biogenic methanogenesis is occurring in the storage tanks from which waters are collected. However, one water sample collected directly from separator of Marcellus Well-3 also had an enriched $\delta^{13}\text{C}_{\text{DIC}}$ signature of $+21.4\text{‰}$ vs. V-PDB indicating these produced waters possibly have $\delta^{13}\text{C}_{\text{DIC}}$ signatures enriched in ^{13}C before they are discharged into the storage tank. The variation in ^{13}C enrichment between the waters produced from Marcellus Shale and Upper Devonian sands could possibly

indicate different stages of biogenic methanogenesis and/or variation/mixing of water sources.

The $\delta^{13}\text{C}_{\text{DIC}}$ signatures enriched in ^{13}C in these produced waters can hence be used to track the produced waters in shallow groundwater aquifers and surface waters of the region. Similar isotope approaches have been found to be valuable in tracking sources and the fate of methanogenic waters in several studies (Atekwana and Krishnamurthy 2004; Sharma and Frost 2008; McLaughlin et al. 2011; Sharma and Baggett 2011).

C and H Isotope Compositions of Methane

Isotopic signatures of methane ($\delta^{13}\text{C}_{\text{CH}_4}$, $\delta\text{D}_{\text{CH}_4}$) can be used in conjunction with natural gas compositions to fingerprint methane originating via biogenic vs. thermogenic processes and its level of thermal maturity (e.g., Stahl 1973; Coleman et al. 1977; Bernard 1978; Schoell 1980, 1983; Faber and Stahl 1984; Chung et al. 1988; Clayton 1991; Hunt 1996; Whiticar 1994, 1996, 1999). Due to their ability to characterize natural gas, stable isotopes have been used for stray gas identification in the shale gas drilling areas of Appalachians (Laughrey and Baldassare 1998; Osborn et al. 2011). The $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ compositions of dissolved methane in shallow groundwaters plotted on the dual isotope plot show that the majority of the samples fall within the boundaries of thermogenic, CO_2 reduction and a mix between the two (Figure 5). None of the dissolved methane samples lie within the boundary of acetate fermentation which is the dominant pathway of microbial methane production in shallower freshwater aquifers. The natural gas samples collected from gas wells producing from the Upper Devonian sands and Marcellus Shale all fall well within the boundary of thermogenic gas; with the former having lighter $\delta^{13}\text{C}_{\text{CH}_4}$ signatures compared to the latter due to the greater thermal maturity (Figure 5).

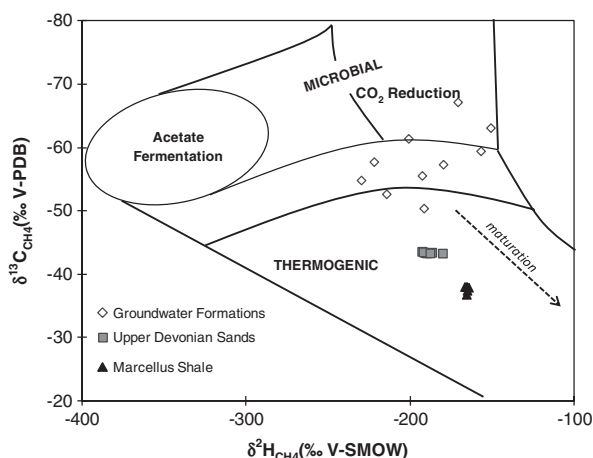


Figure 5. Plot showing C and H isotopic composition of dissolved methane in selected groundwater and natural gas samples collected from gas wells producing from Upper Devonian sands and Marcellus Shale collected in the study area (modified after Whiticar, [1999]).

Additional indicators, such as enriched $\delta^{13}\text{C}_{\text{DIC}}$ signatures more than $+10\text{‰}$, can also be used to identify microbial origins of methane (Simpkins and Parkin 1993; Scott et al. 1994; Botz et al. 1996; Martini et al. 1998; Whiticar 1999; Hellings et al. 2000; Aravena et al. 2003; Pitman et al. 2003; McIntosh et al. 2008; Sharma and Frost 2008; McLaughlin et al. 2011; Sharma and Baggett 2011). The $\delta^{13}\text{C}_{\text{DIC}}$ values of groundwaters from the nine shallow aquifers range from -23.4 to -1.1‰ (Table S1) and samples with heavier $\delta^{13}\text{C}_{\text{DIC}}$ signatures do not have higher methane concentrations, indicating that microbial methanogenesis is not dominant in these groundwaters. In addition, the hydrogen isotope composition of dissolved methane in these shallow groundwaters does not show any correlation with the hydrogen isotope composition of water in these aquifers (Figure 6), indicating that hydrogen in methane does not originate from formation water; a characteristic of microbial methanogenesis (Schoell 1980; Whiticar et al. 1986; Waldron et al. 1999). This further supports that dissolved methane in these groundwaters is of nonmicrobial origin and/or was formed in equilibrium with a different water source and has migrated into these shallow aquifers. The average $\delta^{13}\text{C}_{\text{DIC}}$ signatures of the produced water samples from Upper Devonian sands and Marcellus Shale are $+10$ and $+24\text{‰}$, respectively. These high $\delta^{13}\text{C}_{\text{DIC}}$ signatures are similar to produced waters from other shales and coalbeds where microbial methanogenesis is known to occur (e.g., Martini et al. 1998; McIntosh et al. 2008; Sharma and Frost 2008; McLaughlin et al. 2011; Sharma and Baggett 2011). On the other hand, the C isotopic compositions of produced methane gas samples collected from these wells are isotopically enriched with average $\delta^{13}\text{C}_{\text{CH}_4}$ isotope value of -37.6‰ vs. V-PDB and lie within the isotopic boundary of thermogenic gas. However, it is important to note that in deep subsurface formations biogenic methane as heavy as -40‰ can be produced by microbial reduction of a limited pool of isotopically heavy CO_2 (Claypool et al. 1985; Kotelnikova 2002). If the latter is the case, biogenic methane produced via CO_2 reduction might mimic $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of thermogenic methane. This suggests that either the contribution of microbial methane to the total gas produced by these reservoirs was not significant enough to shift the C and H isotopic signature of the produced gas OR the produced methane gas is a product of late stage CO_2 reduction in these reservoirs.

Another useful distinction between thermogenic and microbial/biogenic methane is the percentage of associated C_2+ hydrocarbons and the ratio of $\text{C}_1/\text{C}_2+\text{C}_3$. Thermogenic methane is formed by the slow breakdown of complex organic molecules into higher hydrocarbons, that is, pentane, butane, propane, ethane, and eventually the simplest C_1 hydrocarbon methane. Therefore, thermogenic methane is generally associated with higher % of C_2+ hydrocarbons. On the other hand, microbial methane is a by-product of the metabolic conversion of CO_2 and acetate by methanogens, which generally do not produce C_2+ hydrocarbons. Hence, less than 0.5%

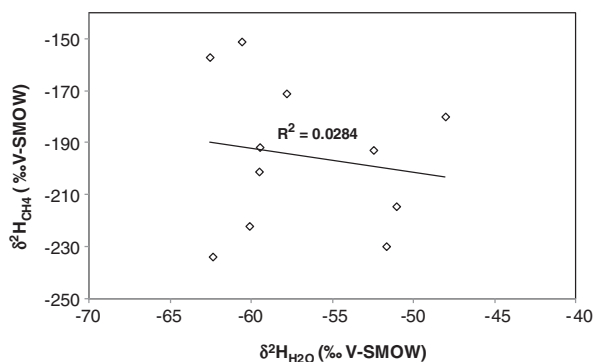


Figure 6. Graph depicting the relationship between the hydrogen isotope compositions of dissolved methane ($\delta^2\text{H}_{\text{CH}_4}$) and water ($\delta^2\text{H}_{\text{H}_2\text{O}}$) collected from the shallow groundwater wells targeting nine geological formations.

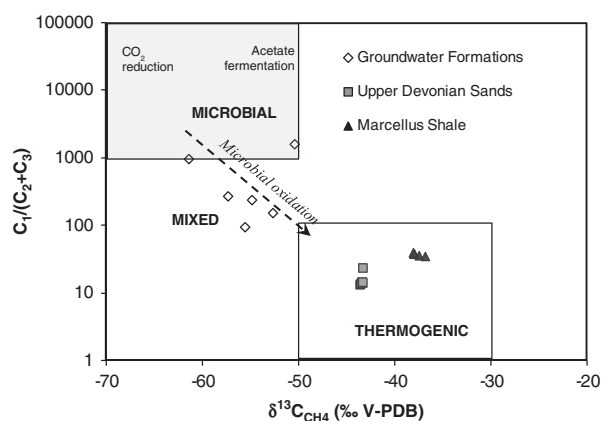


Figure 7. Distinguishing dissolved methane in groundwaters, produced gas from Upper Devonian sands and Marcellus Shale using molecular ratio $\text{C}_1/(\text{C}_2+\text{C}_3)$ with their $\delta^{13}\text{C}_{\text{CH}_4}$ (modified after Bernard [1978]).

of associated C_2+ hydrocarbons is a good indicator of microbial origins of methane (e.g., Stahl 1974; Whiticar et al. 1986; Whiticar 1994). Most of the groundwater samples collected in this study had C_2+ hydrocarbon % below the detection limit of the instrument (0.3% for C_2 and 0.2% for C_3), supporting microbial origin for dissolved methane. The six groundwater samples from the nine formations which had C_2+ hydrocarbons were also plotted on the Bernard diagram and they lie within the microbial and mixed boundaries of microbial and thermogenic (Figure 7).

However, it is also important to note that processes such as microbial oxidation, migration and mixing could not only affect the isotopic signatures of methane but also the percentage of C_2+ hydrocarbons (Whiticar et al. 1986; Faber et al. 1992; Prinzhofer and Huc 1995). During the process of microbial oxidation, the ^{12}C and C_1 hydrocarbons are preferentially removed, shifting the isotope and hydrocarbon composition of remaining methane toward thermogenic end members (Bernard 1978; Coleman et al. 1981; Faber and Stahl 1984; Whiticar et al. 1986). As seen in Figure 7, five

of the shallow groundwater samples lie along the trend of microbial oxidation indicated by samples falling along the slopes ranging from 8 to 14 between the thermogenic and microbial end members (Coleman et al. 1981). If microbial oxidation is occurring, the CO_2 generated by oxidation of methane should result in high dissolved CO_2 concentrations in these waters. However, the dissolved CO_2 concentrations in four of five of these groundwater samples were below 2 mole% supporting microbial oxidation is not a dominant process (Table S2) and these samples most likely denote mixing and/or migration.

The process of migration discriminates against ^{13}C and higher C_2+ hydrocarbons as a result of the easier diffusion of lighter isotopes and molecules (i.e., ^{12}C and methane) compared to heavier ^{13}C and higher chain hydrocarbons. Therefore, the diffused/migrated gas would tend to have more ^{12}C , and therefore a more depleted $\delta^{13}\text{C}_{\text{CH}_4}$ signature (Coleman et al. 1977; Schoell 1983; Prinzhofer and Huc 1995; Prinzhofer and Pernaut 1997; Zhang and Kroos 2001; Schloemer and Kroos 2004). Hence, the deeper thermogenic or late stage CO_2 reduction gases migrating from the deeper oil and gas formations into shallow groundwater formations could attain the isotopic and molecular composition of recently produced microbial gas further complicating the determination of gas origin. Plots of C_1/C_2 vs $\delta^{13}\text{C}_{\text{CH}_4}$ composition of higher hydrocarbons can be used to distinguish migration vs. mixing (Chung et al. 1988; James 1990; Prinzhofer and Pernaut 1997; Prinzhofer et al. 2000). However, the concentration of higher hydrocarbon in these groundwater samples was not high enough for these analyses.

Several lines of evidence, that is, $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^2\text{H}_{\text{CH}_4}$, poor correlation between $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$, low $\delta^{13}\text{C}_{\text{DIC}}$, low dissolved $\text{CO}_2\%$ and expected discrimination against ^{13}C and higher C_2+ hydrocarbons during gas migration suggest that methane in the shallow groundwater samples is not of recent microbial origin. We propose that methane has migrated into these aquifers from deeper formations over millions of years, that is, geological time scales, through natural structural pathways and/or through abandoned oil and gas wells in the area, as there was no active shale gas drilling in this region at time of sample collection. The critical observation is that isotopic and hydrocarbon compositions of methane in shallow groundwater aquifers, Upper Devonian sands and the Marcellus Shale are all isotopically and compositionally distinct from one another and hence can be used to identify sources of dissolved methane. It is important to note that this study presents data from a specific section of the Marcellus Shale, but general trends found in the data can be applied to other areas of the Marcellus Shale gas play. To make accurate interpretations during site-specific investigations, well-defined geologic conditions should be determined for a confined geographic area.

Conclusions

The preliminary data collected from this rapidly expanding shale gas drilling region indicates that $\delta^2\text{H}_{\text{H}_2\text{O}}$,

$\delta^{18}\text{O}_{\text{H}_2\text{O}}$, and $\delta^{13}\text{C}_{\text{DIC}}$ of produced waters associated with shale gas drilling are different from overlying shallow groundwater aquifers, coal-mine discharges, and streams of the region and hence can be used to discern significant contributions from production waters. The $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta\text{D}_{\text{CH}_4}$ signatures of methane in shallow groundwaters, Upper Devonian sands and Marcellus Shale are also different and hence can be used to identify methane leaks associated with gas drilling and production. However, it is important to note that isotope signatures can vary spatially and temporally, therefore, when investigating potential water contamination or stray gas issues, localized signatures should be determined in order to confirm changes in hydrologic connections. Robust spatiotemporal isotope monitoring of waters and dissolved gases in aquifers prior to shale gas drilling can help better constrain variability and enable the use of stable isotope mixing models to understand the contribution from different end members. Incorporation of hydrological and geochemical data in isotope mixing models could further help in strengthening this approach.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. The carbon, oxygen, and hydrogen isotopic composition of waters collected from different water sources in the region

Table S2. The carbon and hydrogen isotopic composition of dissolved methane along with C1, C2, and C3%, methane and CO_2 concentrations in groundwater samples and produced gas from shallow Devonian Sands and Marcellus Shale First three letters of groundwater "site names" refers to the country of sampling. The dashes

denote that methane concentrations were below the detection limits of the GC and mass spectrometer

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