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# The Geochemistry of Naturally Occurring Methane and Saline Groundwater in an Area of Unconventional Shale Gas Development

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## Abstract

Since naturally occurring methane and saline groundwater are nearly ubiquitous in many sedimentary basins, delineating the effects of anthropogenic contamination sources is a major challenge for evaluating the impact of unconventional shale gas development on water quality. This study investigates the geochemical variations of groundwater and surface water before, during, and after hydraulic fracturing and in relation to various geospatial parameters in an area of shale gas development in northwestern West Virginia, United States. To our knowledge, we are the first to report a broadly integrated study of various geochemical techniques designed to apportion natural and anthropogenic sources of natural gas and salt contaminants both before and after drilling. These measurements include inorganic geochemistry (major cations and anions), stable isotopes of select inorganic constituents including strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), boron ( $\delta^{11}\text{B}$ ), lithium ( $\delta^7\text{Li}$ ), and carbon ( $\delta^{13}\text{C}$ -DIC), select hydrocarbon molecular (methane, ethane, propane, butane, and pentane) and isotopic tracers ( $\delta^{13}\text{C}$ - $\text{CH}_4$ ,  $\delta^{13}\text{C}$ - $\text{C}_2\text{H}_6$ ), tritium ( $^3\text{H}$ ), and noble gas elemental and isotopic composition (He, Ne, Ar) in 112 drinking-water wells, with repeat testing in 33 of the wells (total samples=145). In a subset of wells (n=20), we investigated the variations in water quality before and after the installation of nearby (<1 km) shale-gas wells. Methane occurred above 1 ccSTP/L in 37% of the groundwater samples and in 79% of the samples with elevated salinity (chloride >50 mg/L). The integrated geochemical data indicate that the saline groundwater originated via naturally occurring processes, presumably from the migration of deeper methane-rich brines that have interacted extensively with coal lithologies. These observations were consistent with the lack of changes in water quality observed in drinking-water wells following the installation of nearby shale-gas wells. In contrast to groundwater samples that showed no evidence of anthropogenic contamination, the chemistry and isotope ratios of surface waters near known spills or leaks occurring at disposal sites (n=8) mimicked the composition of the Marcellus flowback fluids, and show direct evidence for impact on surface water by fluids accidentally released from nearby shale-gas well pads and oil and gas wastewater disposal sites. Overall this study presents a comprehensive geochemical framework that can be

46 used as a template for assessing the sources of elevated hydrocarbons and salts to water  
47 resources in areas potentially impacted by oil and gas development.

48  
49 **Keywords**

50 Water quality, hydraulic fracturing, methane, isotope tracers, shale gas, brines

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## 1. INTRODUCTION

55 Development of unconventional hydrocarbon resources from previously uneconomical  
56 black shales and tight sands through the advent of horizontal drilling and hydraulic fracturing  
57 technologies has revitalized the domestic energy industry in the U.S. and reduced dependency on  
58 coal combustion for electricity generation (USEIA, 2014). However, numerous environmental  
59 concerns, including the potential for compromised drinking-water quality, have tempered public  
60 opinions about the economic benefits of unconventional energy development in the U.S.  
61 (Jackson et al., 2014; Vengosh et al., 2014). For example, evidence for stray gas contamination  
62 in shallow drinking-water wells was reported in a subset of wells located less than 1 km from  
63 shale gas sites in Pennsylvania (PA) and Texas (TX) using both geospatial statistics and  
64 hydrocarbon and noble gas geochemistry (Darrah et al., 2014; Jackson et al., 2013; Heilweil et  
65 al., 2014; Osborn et al., 2011).

66 The debate around the potential for wide spread contamination from hydraulic fracturing  
67 stems from the lack of pre-drilling datasets that include a comprehensive suite of geochemical  
68 tracers. The nearly ubiquitous presence of naturally occurring inorganic and hydrocarbon  
69 contaminants in many areas of hydrocarbon extraction, and the potential for legacy  
70 contamination from conventional oil and gas development and other industries (e.g., coal) can  
71 also deteriorate water quality (Vengosh et al., 2014). Several studies have suggested that  
72 dissolved methane (CH<sub>4</sub>) and saline groundwater in shallow aquifers in the Appalachian Basin  
73 likely originated from natural processes (Baldassare et al., 2014; Darrah et al., 2015b; Molofsky  
74 et al., 2013; Schon, 2011; Siegel et al., 2015a; Siegel et al., 2015b; Warner et al., 2012).

75 The intense debate about these issues has been sustained for over five years, highlighting  
76 the need to better understand the critical factors that control the elevated levels of hydrocarbon  
77 gas and salts in groundwater systems globally. Indeed, answering these questions is a critical  
78 challenge in assessing the impacts of unconventional energy development and hydraulic  
79 fracturing on the quality of water resources. To address this debate, we must first develop a

80 robust understanding of the fundamental geochemical, hydrogeological, and environmental  
81 factors that control the composition and behavior of hydrological systems in a given area.

82 This presents a comprehensive suite of geochemical tracers that interrogates the  
83 fundamental geochemical interactions and crustal fluid flow processes that control groundwater  
84 geochemistry, using a case study in the North Appalachian Basin (NAB) of northwestern West  
85 Virginia. The Appalachian Basin is an archetypal energy basin with diverse tectonic and  
86 hydrological characteristics and energy development activities, and therefore constitutes an  
87 important area to study the potential impacts to water quality from shale gas development  
88 (Warner et al., 2012; Darrah et al., 2015b; Engle and Rowan, 2014; Ziemkiewicz and He, 2015).

89 While many studies have focused on Pennsylvania, less is known about the distribution  
90 of naturally occurring saline groundwater and methane in aquifers overlying the southwestern  
91 segments of the Marcellus Basin. Despite the long history of fossil fuel development, including  
92 both coal mining and conventional oil and gas drilling, there is limited historical geochemical  
93 information about these aquifers, particularly studies that integrate both aqueous concentrations  
94 and dissolved gas phase measurements. Two reports, one from the West Virginia groundwater  
95 atlas (Shultz, 1984) and another from eastern Kentucky coalfield, have identified saline  
96 groundwater in the region (Wunsch, 1992). The legacy of previous energy exploration and  
97 naturally occurring migration of saline water and natural gas to shallow aquifers are a set of  
98 additional factors that could complicate the delineation of potential contamination from recent  
99 shale gas development (Vengosh et al., 2014).

100 Previous applications of inorganic and isotopic tracers of dissolved salts and hydrocarbon  
101 and noble gas geochemical tracers have revealed the influence of the tectonic and  
102 hydrogeological setting on water quality and natural contamination in areas of oil and gas  
103 development both in the NAB and elsewhere (Darrah et al., 2015b; Engle and Rowan, 2014;  
104 Llewellyn, 2014, Lautz et al, 2014; Molofsky et al., 2013; Mortiz, 2015; Revesz et al., 2010;  
105 Schon, 2011; Sharma and Baggett, 2011; Siegel et al., 2015a; Siegel et al., 2015b; Warner et al.,  
106 2012, Warner et al., 2013b, Wunsch, 1992).

107 Here, we present a combination of integrated techniques applied to a longitudinal dataset  
108 as an improved framework to assess the geochemical processes that control groundwater  
109 geochemistry, as well as changes to surface water geochemistry during unconventional oil and  
110 gas operations. While we apply our framework to a specific area in this study, the ultimate aim

111 of this study is to contribute to the emerging body of knowledge about the risks to water  
112 resources from unconventional oil and gas development and to develop a standardized  
113 assessment tool for a more broad application to study the sources and migration of hydrocarbon-  
114 rich brines to water resources in the NAB and other hydrocarbon-rich basins.

115

116

## 2. BACKGROUND

### 2.1. Hydrological Background

118 The study area in northwestern West Virginia is part of the Appalachian Plateau  
119 Physiographic Province, where irregular, steeply sloping ridges, separated by narrow valleys and  
120 mountainous terrain characterize the topography. Bedrock in the region is dominated by cyclic  
121 sequences of sandstone, siltstone, shale, limestone and coal, which vary in thickness and lateral  
122 extent throughout the Appalachian Plateau (Wunsch, 1992). The aquifer rocks are composed of  
123 the Permian/Upper Pennsylvania Drunkard Group and the Upper Pennsylvanian Monongahela  
124 Group (Fig. 1 and 2). Locally, perched water tables are typical in some upland regions where  
125 intermittent shale layers act as local aquitards, which result in horizontal flow through cleated  
126 coal seam layers (Wunsch, 1992).

127 Where present, the unconsolidated alluvium provides the highest yields for domestic  
128 wells, while secondary fractures and bedding planes transmit water in the bedrock and the flow is  
129 highly variable (3.7 to 757 liters per minute) spatially because of vertical and lateral changes in  
130 fracture density, but with little variability across different geologic units. Shallow groundwater  
131 flow is dominated by shallow sets of vertical neotectonic fractures in the sandstone layers, with  
132 more intense fractures and thus higher hydraulic permeability in the valley bottoms (Wyrick and  
133 Borchers, 1981). Wells located in valley settings generally yield higher flow rates (~22.7L/min)  
134 than those in hillslopes and uplands (7.5 to 11.4 L/min). Lineaments, which experience the  
135 highest fractures and joint system intensity, are associated with the highest groundwater flow  
136 rates (Bain, 1972) and can be pathways for gas and brine migration.

137 In Tyler, Doddridge and Harrison counties groundwater is generally hard (hardness>120  
138 mg/L) with high manganese (Mn>50 ug/L) and iron (Fe>300 ug/L). However, similar to  
139 groundwater flow rates, hardness and metal levels are highly variable with some topographic  
140 controls. Groundwater wells located in valleys generally have higher alkalinity, pH, and total  
141 dissolved solids (TDS). Sodium (Na), pH, alkalinity, chloride (Cl) and total dissolved salt (TDS)

142 concentrations increase with well depth, while calcium and magnesium decrease. Generally,  
143 there is little difference in water quality and water type between different geologic units, with  
144 dominantly Ca-HCO<sub>3</sub> composition in most areas, followed by a Na-HCO<sub>3</sub> water type.

145 Based on the data from Shultz (1984), dissolved solutes in the shallow groundwater  
146 varied greatly from low salinity with Cl <10 mg/L to saline waters with Cl up to 2,200 mg/L. Na  
147 concentrations had positive correlations with increasing Cl concentrations ( $r^2 = 0.57$ ,  $p < 0.05$ ),  
148 with Na concentrations reported up to 970 mg/L. Groundwater with Cl > 250 mg/L has been  
149 observed in the area ranging from a few hundred to several thousand feet deep. Elevated Cl  
150 concentrations are found at shallower depths mainly in valley floors. Densely fractured zones  
151 provide nearly vertical highly permeable conduits for upward migration of deep-seated saline  
152 water. High Cl concentrations in groundwater have been also reported in areas of oil and gas  
153 development. Old deteriorating oil and gas wells can short-circuit the natural flowpaths and  
154 provide an area of localized contamination of groundwater (Shultz, 1984). Cl > 50 mg/L was  
155 reported in roughly 23% of wells surveyed (n=32 out of 139) conducted prior to shale gas  
156 development. A USGS survey of CH<sub>4</sub> in WV groundwater between 1997 and 2006 reported CH<sub>4</sub>  
157 contents up to 15 mg/L (21 ccSTP/L) (White and Mathes, 2006).

158

## 159 **2.2 Background of Study Design and Geochemical Techniques**

160 Previous studies in the NAB (northeastern PA) have demonstrated compelling evidence  
161 for naturally occurring gas and saline groundwater in regional aquifers. However, prior to the  
162 rapid rise of shale gas development and hydraulic fracturing, there was a lack of sufficient  
163 baseline water quality datasets in many of the areas of active unconventional energy  
164 development. Even when baseline water quality databases do exist, they typically consist of only  
165 major elements. For this reason, it can still be challenging to distinguish between naturally  
166 occurring salts and hydrocarbon gases in shallow groundwater and any possible anthropogenic  
167 contamination that could result from poor shale-gas well integrity (e.g., stray gas contamination)  
168 or accidental releases (e.g., surface spills of hydraulic fracturing fluids, produced water, or  
169 flowback fluids; Vengosh et al., 2014).

170 Several geochemical tools such as hydrocarbon isotopic and noble gas tracers have been  
171 previously developed to identify and distinguish water contamination from unconventional  
172 hydrocarbon production (Baldassare et al., 2014; Chapman et al., 2012; Darrah et al., 2014; Phan

173 et al., 2016; Sharma et al., 2014; Warner et al., 2014; Ziemkiewicz and He, 2015). In addition,  
174 Br/Cl ratios have been successfully employed to identify deep formation brines as the source of  
175 saline groundwater in the NAB, however they do not sufficiently distinguish naturally sourced  
176 brines from brines released from oil and gas activity (Warner et al., 2012; Ziemkiewicz and He,  
177 2015). Similarly, oxygen and hydrogen stable isotopes are typically enriched in brines (Sharma  
178 et al., 2014; Warner et al., 2014), however the relative proportion of a typical brine contribution  
179 to a blend that would generate saline groundwater is too small (i.e., <20% contribution) to  
180 observe significant changes in the stable isotope composition of salinized groundwater (Warner  
181 et al., 2014).

182 In contrast, the stable isotopes of strontium (Sr), boron (B) and lithium (Li) are more  
183 sensitive techniques to detect even small contributions of brines to a blend with fresh water  
184 (<1%) due to their distinct isotopic compositions in formation brines and the high concentrations  
185 of these elements in the brines (Warner et al., 2014). NAB oil and gas brines are typically  
186 enriched in radiogenic Sr, ( $^{87}\text{Sr}/^{86}\text{Sr}$  values ranging from 0.71000 to 0.72200), with Marcellus  
187 brines being less radiogenic (0.71000 to 0.71212) (Capo et al., 2014; Chapman et al., 2012;  
188 Warner et al., 2014) than Upper Devonian brines (0.71580 to 0.72200) (Chapman et al., 2012;  
189 Warner et al., 2014). Boron and Li isotope signatures in Marcellus hydraulic fracturing flowback  
190 fluids were distinct ( $\delta^{11}\text{B} = 25$  to  $31\text{‰}$  and  $\delta^7\text{Li} = 6$  to  $10\text{‰}$ ) from most surface waters ( $\delta^{11}\text{B} = 8$   
191 to  $20\text{‰}$  and  $\delta^7\text{Li} = 17$  to  $30\text{‰}$ ), and depleted compared to conventional NAB oil and gas brines  
192 ( $\delta^{11}\text{B} = 36$  to  $51\text{‰}$  and  $\delta^7\text{Li} = 10$  to  $23\text{‰}$ ; Phan et al., 2016; Warner et al., 2014). However, the  
193 application of these isotope systems for identifying groundwater contamination is limited  
194 without establishing a systematic dataset of the isotope signatures of pre-drill saline groundwater  
195 in the region.

196 The molecular and isotopic composition of natural gases can also help to distinguish  
197 between natural flow and anthropogenic hydrocarbon gas contamination. Natural gases are often  
198 classified as thermogenic, biogenic, or "mixed" sources, based on their molecular ratios (e.g.,  
199 wetness:  $\text{C}_2+/\text{C}_1$ ) along with carbon (C) and hydrogen (H) isotopic compositions (e.g., Bernard,  
200 1978; Clayton, 1991; Rice and Claypool, 1981; Schoell, 1980, 1983; Schoell, 1988).  
201 Thermogenic natural gases are typically more enriched in ethane ( $\text{C}_2\text{H}_6$ ) and heavier aliphatic  
202 hydrocarbons, and thermogenic  $\text{CH}_4$  is typically more enriched in  $^{13}\text{C}$  ( $\delta^{13}\text{C}-\text{CH}_4 > -55\text{‰}$ ) and  
203 hydrogen (e.g., Schoell, 1983). As thermal maturity increases, the  $\delta^{13}\text{C}$  of methane and ethane is

204 further increased. Conversely, biogenic gas is almost exclusively composed of CH<sub>4</sub> (C<sub>1</sub>/C<sub>2+</sub> ≥  
205 ~5,000), with a typically light δ<sup>13</sup>C-CH<sub>4</sub> between -55‰ and -75‰ (Schoell, 1983; Whiticar et  
206 al., 1985). However, methanogenesis, aerobic and anaerobic oxidation, sulfate reduction (thermal  
207 or bacterially driven), or post-genetic fractionation (e.g., fractionation during gas transport in the  
208 subsurface by diffusion) can alter the original composition of natural gases or lead to complex  
209 mixtures of natural gases from multiple sources.

210         Based on these considerations, the elemental and isotopic compositions of noble gases  
211 (e.g., helium (He), neon (Ne), argon (Ar)) have recently been utilized to provide additional  
212 constrains on the source of hydrocarbons gases in shallow aquifers (Darrah et al., 2014a; Darrah  
213 et al., 2015a; Darrah et al., 2015b; Jackson et al., 2013; Heilweil et al., 2015). The inert nature,  
214 low terrestrial abundance, and well-characterized isotopic composition of noble gases in the  
215 mantle, crust, hydrosphere, and atmosphere enhance their utility as geochemical tracers of crustal  
216 fluids such as groundwater (Ballentine et al., 2002). The noble gas composition of hydrocarbons  
217 and other geological fluids are derived from three primary sources: the mantle, atmosphere, and  
218 the crust (Ballentine et al., 2002). Previous work has demonstrated that the abundance of helium  
219 (i.e., <sup>4</sup>He) and air-saturated water major (e.g., N<sub>2</sub>) and noble gases (e.g., <sup>20</sup>Ne, <sup>36</sup>Ar) can be used  
220 to distinguish the presence of large volumes of gas-phase hydrocarbons and track the source and  
221 mechanism of fluid migration (Darrah et al., 2014; Darrah et al., 2015; Gilfillan et al., 2009;  
222 Heilweil et al., 2015).

223         Northwestern West Virginia is an area that has seen a rapid rise in unconventional oil and  
224 gas development, with over 3,000 unconventional gas wells drilled since 2008 (Fig. S1)  
225 (WVGES, 2012). With knowledge that shale gas development was imminent in the study area,  
226 we hypothesized that the collection and analyses of groundwater samples collected pre-, during-,  
227 and post-drilling would allow us to 1) evaluate temporal changes in groundwater geochemistry  
228 throughout the drilling processes; 2) determine the most sensitive geochemical parameters that  
229 can detect anthropogenic contamination relative to naturally occurring geochemical processes; 3)  
230 evaluate the source of the salinity and natural gas in shallow aquifers in this region; and 4)  
231 determine whether groundwater near shale gas development in this area is becoming  
232 contaminated by stray gas and other contaminants following shale gas development.

233         We conducted an extensive geochemical and isotopic analysis that included: (1) major  
234 and minor ions; (2) trace elements; (3) water isotopes (δ<sup>18</sup>O, δ<sup>2</sup>H); (4) isotopic ratios of dissolved



235 constituents ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{11}\text{B}$ ,  $\delta^7\text{Li}$ ,  $\delta^{13}\text{C-DIC}$ ); (5) molecular and isotopic composition of select  
236 dissolved gases ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{N}_2$ ,  $\delta^{13}\text{C-CH}_4$ ,  $\delta^{13}\text{C-C}_2\text{H}_6$ ); (6) tritium ( $^3\text{H}$ ); and (7) noble gas  
237 elemental and isotopic compositions ( $\text{He}$ ,  $\text{Ne}$ ,  $\text{Ar}$ ). To better address these questions, we  
238 integrate our geochemical data with time-series and geospatial analysis with respect to shale-gas  
239 wells and geological deformational features such as faulting, folding, and proximity to valley  
240 bottoms.

241 In parallel with the groundwater study, we also collected surface water samples near  
242 storage and disposal of oil and gas wastewater (OGW) areas in order to characterize the  
243 geochemical fingerprints of OGW in the research area. We used the geochemical composition of  
244 Marcellus flowback and produced waters (Warner et al., 2013a; Warner et al., 2014) as  
245 references to determine the source and magnitude of contamination of surface water from OGW.  
246 These geochemical fingerprints were also used as references to determine whether the saline and  
247  $\text{CH}_4$ -rich groundwater in northwestern West Virginia is derived from geogenic process or from  
248 direct contamination of leaking from nearby shale-gas wells.

249

250

### 3. MATERIALS AND METHODS

#### 251 3.1 Sample Survey

252 We examine the inorganic chemistry (anions, cations, trace metals), stable isotopes (O,  
253 H, B, Sr, Li), noble gas, tritium, and hydrocarbon (molecular ( $\text{C}_1$  to  $\text{C}_5$ ) and stable isotopic  $\delta^{13}\text{C-}$   
254  $\text{CH}_4$  and  $\delta^{13}\text{C-C}_2\text{H}_6$ ) compositions of 145 samples from 112 domestic groundwater wells in  
255 Doddridge, Harrison, Ritchie, Tyler and Wetzel counties in West Virginia, USA (Table 1). The  
256 typical depth of shallow drinking-water wells in our study was 35 to 90 m. A subset of wells  
257 ( $n=31$ ) was tested prior to shale gas drilling in Doddridge County starting in summer 2012 (open  
258 circle, triangle, and square according to water type defined below). Groundwater wells were  
259 selected based on their location in an area targeted for shale gas development and homeowner  
260 participation. An additional 79 wells were sampled in Doddridge ( $n=56$ ), Harrison ( $n=9$ ), Ritchie  
261 ( $n=5$ ), Tyler ( $n=6$ ) and Wetzel ( $n=3$ ) counties between 2012 and 2014, following installation of  
262 shale-gas wells and hydraulic fracturing in the area (crossed circle, inverted triangle, and  
263 diamond according to water type defined below). 55% of wells were located within 1 km of a  
264 shale-gas well. 20 wells were more than 1 km from a shale gas well when first sampled, but

265 retested at least once following installation of a shale gas well within 1 km during the study  
266 period. 8 wells that were less than 1 km of from a shale gas when initially sampled were retested  
267 during the study period.

268         Neither geological features, nor previous knowledge of water chemistry were considered  
269 during water well selection. Instead, we tried to randomly sample domestic water wells from  
270 across the study area to get a diverse suite of sample types. Four of the groundwater wells were  
271 located near OGW disposal or spill sites in the study area. Modern data was compared to  
272 groundwater data from 1982 reported by the West Virginia Department of Natural Resources  
273 (Shultz, 1984). We present data from this study with color-coded symbols, while historical data  
274 are identified by grey symbols. Pre- and post-drilling samples are indicated by symbol shape  
275 within the colors of the three water types identified in this study. An open circle denotes Type 1  
276 pre-drilling samples and post-drilling samples are denoted as a crossed-circle. Type 2 pre-drilling  
277 samples are denoted by a triangle and post-drilling samples are denoted as an inverted triangle.  
278 Type 3 pre-drilling samples are denoted by a square and a diamond denotes post-drilling  
279 samples.

280         Surface samples were collected from three spill sites, at the point nearest the origin (n=5)  
281 and in surface water downstream (n=8) and upstream (n=2) of the spill (Fig. 1; Table 3). We  
282 sampled streams near two deep well injection sites and one flowback spill that occurred on a well  
283 pad in Tyler County. The first injection well site in Lochgully, WV was sampled in October  
284 2013 and the second site in Ritchie County, WV was sampled in December 2013. The spill in  
285 Tyler County was identified on January 3, 2014 and the spill water was sampled directly on the  
286 same day and three days after the spill. Surface waters from Big Run Creek were collected  
287 upstream and at the point of entry for the spill water into the stream on January 6th and at points  
288 adjacent to the pad and downstream along Big Run Creek on February 23rd, 2014 along with  
289 water from Middle Island Creek, which is a drinking water source for the area.

290

### 291 **3.2. Field Methods**

292         Water samples from wells were collected prior to any treatment systems and were filtered  
293 and preserved in high density polyethylene (HDPE), air tight bottles following USGS protocols

294 (USGS, 2011). Samples were filtered through 0.45 micron filters for dissolved anions, cations  
295 and inorganic trace element isotopes (B, Sr, Li). Trace metal samples were preserved in 10%  
296 Optima nitric acid following filtering through a 0.45 micron filter. Samples bottles collected for  
297 stable isotopes of O, H and DIC were completely filled to minimized interaction with air or air  
298 bubbles and were kept sealed until analysis. Water chemistry samples were stored on ice or  
299 refrigerated until the time of their analysis.

300 Hydrocarbon gas samples for concentration and isotopic analyses were collected in the  
301 field using Isotube bottles obtained from Isotech Laboratories by procedures detailed by Isotech  
302 Laboratories (Isotech, 2011), stored on ice until delivery to Duke University, and analyzed for  
303 CH<sub>4</sub> (and where applicable C<sub>2</sub>H<sub>6</sub>) isotopic compositions of carbon. Dissolved gas samples for  
304 gas concentrations and noble gas measurements were collected in refrigeration-grade copper  
305 tubes that were flushed in-line with at least 50 volumes of sample water prior to sealing with  
306 stainless steel clamps according to standard methods reported previously (Darrah et al., 2013;  
307 Darrah et al., 2015;).

308

### 309 **3.3 Analytical Methods**

#### 310 **3.3.1 Water Chemistry**

311 Major anions (e.g., Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>) were measured by ion chromatography and major  
312 cations (e.g., Na, Ca, Mg) were measured by direct current plasma optical emission  
313 spectrometry. Trace elements (i.e., Li, B, V, Cr, Fe, Mn, As, Se, Sr, Ba) were analyzed by ICP-  
314 MS on a VG PlasmaQuad-3 calibrated to the NIST 1643e standard. The detection limit of the  
315 ICP-MS of each element was determined by dividing three times the standard deviation of  
316 repeated blank measurements by the slope of the external standard.

317

#### 318 **3.2.2. Isotope Chemistry**

319 <sup>11</sup>B/<sup>10</sup>B ratios were measured as BO<sub>2</sub><sup>-</sup> in negative mode and reported as δ<sup>11</sup>B normalized  
320 to NIST NBS SRM-951. Long-term measurements (n=60) of NBS SRM 951 standard yielded a  
321 precision of 0.6‰. Sr in the water samples was pre-concentrated by evaporation in a HEPA-  
322 filtered clean hood and re-digested in 3.5N HNO<sub>3</sub>. Sr was separated using Eichrom Sr-specific  
323 resin. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios were collected in positive mode on the TIMS and the standard NIST  
324 SRM 987 had an external reproducibility of 0.710265±0.000006. Li isotopes were measured by a

325 ThermoFisher Neptune MC-ICP-MS at BRGM (French Geological Survey) in France.  $^7\text{Li}/^6\text{Li}$   
326 ratios were normalized to the L-SVEC standard solution (NIST SRM 8545) and presented as  
327  $\delta^7\text{Li}$ . Long-term replicate measurements of NIST SRM 8545 standard yielded a precision of  
328 0.5% (Millot et al., 2004).

329 The stable isotopes of water (i.e.,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) were analyzed in the Duke Environmental  
330 Isotope Lab. These gases are chromatographically separated in the TCEA, and carried to a  
331 ThermoFinnigan Delta+XL ratio mass spectrometer via a Conflo III flow adapter. Raw delta  
332 values were normalized offline against known vs. measured isotope values for international  
333 reference waters VSMOW, VSLAP and IAEA-OH16. The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values are expressed in  
334 per mil versus VSMOW, with standard deviations of  $\pm 0.5\text{‰}$  and  $\pm 0.1$ , respectively.

335 Carbons isotopes in dissolved inorganic carbon ( $\delta^{13}\text{C-DIC}$ ) were measured at Duke  
336 University. Glass septum vials (Labco 11 mL Exetainers) were loaded into the thermostated  
337 sample tray of a ThermoFinnigan GasBench II and flushed for ~20 minutes each by autosampler  
338 with a two-way flushing needle and a carrier stream of UHP helium at ~30 mL/min. to remove  
339 air, and then were each injected with 100  $\mu\text{L}$  of liquid ortho-phosphoric acid. Sample waters  
340 were analyzed by ThermoFinnigan Delta+XL ratio mass spectrometer. Reference  $\text{CO}_2$  pulses are  
341 injected automatically before and after the six sample peaks. The calculated raw  $\delta^{13}\text{C}$  values of  
342 samples were then normalized offline against known vs. measured values for three carbonate  
343 standards that were analyzed during the run using the same acid reaction (NBS19, IAEA CO8,  
344 and Merck calcium carbonate). The first two are international reference materials and the third is  
345 an internal standard previously calibrated against the first two. The  $\delta^{13}\text{C}$  is expressed in per mil  
346 vs. VPDB, and the standard deviation is  $\pm 0.2\text{‰}$ .

347

### 348 **3.3.3. Dissolved Gas and Gas Isotope Geochemistry**

349 For samples where copper tube samples were not available, dissolved  $\text{CH}_4$  concentrations  
350 were calculated using headspace equilibration, extraction and subsequent concentration  
351 calculation by a modification of the Kampbell and Vandegrift (1998) method (Kampbell and  
352 Vandegrift, 1998) at Duke University. Calculated detection limits of dissolved  $\text{CH}_4$  were 0.002  
353 mg/L water. Procedures for stable isotope analyses of gas are summarized in Jackson et al.  
354 (2013). Reporting limits for reliable stable carbon isotopic compositions of methane ( $\delta^{13}\text{C-CH}_4$ )  
355 and ethane ( $\delta^{13}\text{C-C}_2\text{H}_6$ ) were consistent with Isotech Laboratories (Illinois, USA). Stable carbon

356 isotopes of methane and ethane were determined for all samples with CH<sub>4</sub> exceeding 0.1 cm<sup>3</sup>  
357 STP/L (n=97) and 0.001 cm<sup>3</sup> STP/L, respectively. The δ<sup>13</sup>C-CH<sub>4</sub> were determined by cavity ring-  
358 down spectroscopy (CRDS) (Busch and Busch, 1997) at the Duke Environmental Stable Isotope  
359 Laboratory (DEVIL) using a Picarro G2112i or newer generation G-2132i (NOTE: after May  
360 2014, the G221i was replaced with the newer generation G-2132i) or gas chromatographic  
361 separation using a Trace Ultra ThermoFinnigan followed by combustion and dual-inlet isotope  
362 ratio mass spectrometry using a Thermo Fisher Delta XL. For samples in which copper tubes  
363 were available, dissolved gas samples were measured by extracting the fluid from the copper  
364 tube on a vacuum line (Darrah et al., 2015). Copper tube samples were prepared for analysis by  
365 attaching the copper tube to an ultra-high vacuum steel line (total pressure= 1-3 x10<sup>-6</sup> torr),  
366 which is monitored continuously using a four digit (accurate to the nearest thousandths) 0-20 torr  
367 MKS capacitance monometer, using a 3/8" (0.953 cm) Swagelok ferruled connection. After the  
368 sample connection had sufficiently evacuated and pressure was verified, the fluid sample was  
369 inlet to the vacuum line by re-rounding the copper (Kang et al., 2016). After the fluid pressure  
370 had equilibrated, the sample was sonicated for ~30 minutes to ensure complete transfer of  
371 dissolved gases to the sample inlet line (Solomon et al., 1995).

372 From this gas volume, splits of samples were taken for the measurement of major gas  
373 components (e.g., N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub> to C<sub>5</sub>H<sub>12</sub>) using an SRS quadrupole mass spectrometer (MS)  
374 and an SRI gas chromatograph (GC) at Ohio State University with standard errors of <3%  
375 (Cuoco et al., 2013; Hunt et al., 2012; Kang et al., 2016). The average external precision was  
376 determined by measurement of a "known-unknown" standard, including an atmospheric air  
377 standard (Lake Erie, Ohio Air) and a series of synthetic natural gas standards obtained from  
378 Praxair. The results of the "known-unknown" average external precision analysis are as follows:  
379 CH<sub>4</sub> (1.27%), C<sub>2</sub>H<sub>6</sub> (1.68%), C<sub>3</sub>H<sub>8</sub> (1.34%), C<sub>4</sub>H<sub>10-n</sub> (2.08%), C<sub>4</sub>H<sub>10-i</sub> (2.11%), C<sub>5</sub>H<sub>12-n</sub>  
380 (2.78%), C<sub>5</sub>H<sub>12-i</sub> (2.81%), N<sub>2</sub> (1.25%), CO<sub>2</sub> (1.06%), H<sub>2</sub> (3.41%), O<sub>2</sub> (1.39%), and Ar (0.59%).  
381 CH<sub>4</sub> concentrations are reported as cc/L (the SI molar unit for gas abundance in water) at  
382 standard temperature and pressure (STP) where 1 mg/L of gas is equivalent to 1.4 cc STP/L.

383 An additional split of the gas was taken for the isotopic analysis of noble gases using a  
384 Thermo Fisher Helix SFT Noble Gas MS at Ohio State University following methods reported  
385 previously (Cuoco et al., 2013; Darrah and Poreda, 2012; Hunt et al., 2012). The average  
386 external precision based on "known-unknown" standards were all less than +/- 1.46% for noble

387 gas concentrations with values reported in parentheses ( $^4\text{He}$  (0.78%),  $^{22}\text{Ne}$  (1.46%), and  $^{40}\text{Ar}$   
388 (0.38%)). These values were determined by measuring referenced and cross-validated laboratory  
389 standards including an established atmospheric standard (Lake Erie Air) and a series of synthetic  
390 natural gas standards obtained from Praxair including known and validated concentrations of  $\text{C}_1$   
391 to  $\text{C}_5$  hydrocarbons,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ , and each of the noble gases. Noble gas isotopic  
392 standard errors were approximately  $\pm 0.0091$  times the ratio of air (or  $1.26 \times 10^{-8}$ ) for  $^3\text{He}/^4\text{He}$   
393 ratio,  $< \pm 0.402\%$  and  $< \pm 0.689\%$  for  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$ , respectively, less than  $\pm 0.643\%$   
394 and  $0.427\%$  for  $^{38}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$ , respectively (higher than typical because of  
395 interferences from  $\text{C}_3\text{H}_8$  on mass=36 and 38).

396 To evaluate the potential for *in-situ* radiogenic production and/or release of  $^4\text{He}$ , we  
397 analyzed the U and Th in various aquifer outcrop samples collected in Doddridge County, WV.  
398 Analyses were conducted by standard methods using inductively coupled plasma mass  
399 spectrometry (ICP-MS) (Cuoco et al., 2013). Additionally, tritium ( $^3\text{H}$ ) analyses were performed  
400 on 56 groundwater samples to evaluate the contributions from modern meteoric water. Tritium  
401 ( $^3\text{H}$ ) concentrations were measured by the in-growth of  $^3\text{He}$  using a ThermoFisher Helix SFT  
402 noble gas MS at The Ohio State University following methods reported previously (Darrah et al.,  
403 2015; Solomon et al., 1995; Solomon et al., 1992).

404

### 405 **3.4. Graphical and Statistical Treatment of Data**

406 All maps, cross-sections, and well coordinates are plotted using ArcMap GIS 10.2.2.  
407 Geological and oil and gas well data were available from the West Virginia Geological and  
408 Economic Survey (WVGES, 2012). All graphics are plotted using R v. 3.2.0. Statistical  
409 evaluations including mean, minimum, maximums, Spearman correlations, standard deviations,  
410 and analysis of variance (ANOVA) were performed using R v. 3.2.0. Correlation coefficient,  $r$   
411 reported in the text was calculated as Spearman's rank correlation coefficient,  $\rho$ .

412 We present data from this study with color-coded symbols, while data from previous  
413 studies are identified by orange hexagon. Within all figures, the abundance of methane is  
414 preserved using a color intensity scale, where low methane concentrations close to 0 ccSTP/L are  
415 blue and range up to red for methane concentrations  $> 40$  ccSTP/L. Samples for which methane  
416 samples were not analyzed are shown as a grey symbol.

417

## 4. RESULTS

418

### 4.1 Groundwater quality

419

420 The dissolved solutes in the shallow groundwater in the study area varied from low  
421 salinity (Cl <50 mg/L) to saline waters (Cl up to 2400 mg/L), mostly in the deeper wells (depths  
422 ~100 m). Cl concentrations >50 mg/L were detected in 19% of wells surveyed in our study  
423 (n=27/145). Saline waters were typically also elevated in other major constituents (Fig. 3). For  
424 example, Br and Na concentrations had strong positive correlations with Cl ( $r = 0.79$ ,  $p < 0.05$  and  
425  $r = 0.62$ ,  $p < 0.05$ , respectively; Fig. 4). Br concentrations ranged from below detection limits  
426 (<0.02 mg/L) to 15.2 mg/L, and Na concentrations ranged from below detection limits (<0.1  
427 mg/L) to 1,362 mg/L. DIC in groundwater was also positively correlated with Cl ( $r = 0.35$ ,  
428  $p < 0.05$ ) and concentrations ranged from 42 to 836 mg/L (Fig. 4). Ca, Mg and SO<sub>4</sub> in the  
429 groundwater, however, did not show any correlation with salinity (Fig. 4). SO<sub>4</sub> concentrations  
430 were relatively low in groundwater, ranging from below detection limits up to 50 mg/L, while Ca  
431 concentrations ranged from below detection limits up to 346 mg/L, and Mg concentrations  
432 ranged from below detection limits up to 233 mg/L.

433 Some trace elements were strongly associated with the salinity of the groundwater (Fig.  
434 S2). B and Li, specifically, had higher concentrations in the saline water. Li concentrations  
435 ranged from below detection limits (0.1 µg/L) to 72 µg/L, and were positively correlated to Cl ( $r$   
436  $= 0.54$ ,  $p < 0.05$ ), while B concentrations ranged from 6 to 232 µg/L and correlated to Cl ( $r = 0.60$ ,  
437  $p < 0.05$ ; Fig. S2). Arsenic (As) was weakly correlated with Cl ( $r = 0.18$ ,  $p < 0.05$ ), while other  
438 trace elements, such as Ba and Sr, were not significantly correlated with Cl (Fig. S2 and S3). Sr  
439 concentrations were relatively high in the study area and ranged from below detection limits  
440 (<0.1 µg/L) to 2,782 µg/L, while Ba concentrations ranged from below detection limits (<0.1  
441 µg/L) to 4.2 mg/L. Ba and Sr were both correlated with Ca ( $r = 0.53$ ,  $p < 0.05$  and  $r = 0.68$ ,  
442  $p < 0.05$ , respectively; Fig. S3). These high correlations with Ca suggest that Sr and Ba  
443 concentrations are more likely influenced by water-rock interactions in the shallow subsurface  
444 than from the migration of a brine.

445 The Br/Cl (molar) ratios in the saline water (Cl >50 mg/L) ranged from very low values  
446 around  $2 \times 10^{-4}$  to brine-type waters with Br/Cl  $> 1.5 \times 10^{-3}$  (up to  $7.8 \times 10^{-3}$ ). These ratios are  
447 similar to ranges found in saline groundwater that have been impacted by deep formation brines  
448 in other regions of the Appalachian Basin (Warner et al., 2012; Wunsch, 1992). Based on the Cl

449 concentrations and Br/Cl ratios (Warner et al., 2012), we divide the water samples into three  
450 major water types. The first type (Type 1) is characterized by  $\text{Cl} < 50 \text{ mg/L}$  and has Ca-Na- $\text{HCO}_3$   
451 composition (n=118 samples) (Fig. 3). Type 2 (n=17) has elevated salinity ( $\text{Cl} > 50 \text{ mg/L}$ ) and is a  
452 Ca-Na-Cl type, with Br/Cl molar ratio between  $1.0 \times 10^{-3}$  and  $2.5 \times 10^{-3}$  and high correlation  
453 between Br and Cl ( $r = 0.97$   $p < 0.05$ ). Type 3 (n=10) also has elevated salinity ( $\text{Cl} > 50 \text{ mg/L}$ ) and  
454 is a Ca-Na-Cl type, but has a Br/Cl molar ratio  $> 2.5 \times 10^{-3}$  and a lower correlation between Br and  
455 Cl ( $r = 0.56$ ;  $p < 0.05$ ; Fig. 4). In addition to the difference in Br/Cl, Type 3 had lower Na/Cl  
456 ( $0.99 \pm 0.28$ ) and B/Cl ( $0.97 \pm 5.4 \times 10^{-4}$ ) ratios relative to those in Type 2 ( $2.68 \pm 1.87$  and  
457  $4.4 \pm 3.5 \times 10^{-3}$ , respectively) (Fig. 4). All Type 3 groundwater samples occurred within 750 m of a  
458 valley bottom. The majority of these Type 3 water samples were located in valley bottom  
459 characterized by the hinge of the Burchfield syncline (Fig. 2) (Hennen, 1912; Ryder et al., 2012).

460 The stable isotopes ( $\delta^{18}\text{O} = -5.9$  to  $-9.2\text{‰}$ ;  $\delta^2\text{H} = -24.1$  to  $-55.0\text{‰}$ ) of the shallow  
461 groundwater in the study area primarily fall along the local meteoric water line (LMWL =  $6.6$   
462  $\delta^{18}\text{O} + 2.4$ ) (Kendall and Coplen, 2001), with low deuterium excess relative to the LMWL in the  
463 more saline samples (Fig. S4).  $\delta^7\text{Li}$  values in groundwater from the study area ranged from  
464  $10.9\text{‰}$  to  $21.3\text{‰}$ , which are higher than the  $\delta^7\text{Li}$  of Middle Devonian-age brines ( $6\text{--}10\text{‰}$ ; Phan  
465 et al., 2016; Warner et al., 2014). The  $\delta^{11}\text{B}$  values of the groundwater were between  $12.7\text{‰}$  and  
466  $25.2\text{‰}$ , which are lower relative to the  $\delta^{11}\text{B}$  of the Devonian-age brines ( $25\text{--}31\text{‰}$ ) (Warner et al.,  
467 2014).

468 The saline groundwater had higher  $\delta^{11}\text{B}$  values ( $19.9 \pm 5.9\text{‰}$ ) than that of the low-saline  
469 ground water of Type 1 ( $16.1 \pm 5.8\text{‰}$ ,  $p < 0.001$ ), and also had lower B/Cl ratios ( $p < 0.001$ ) (Fig.  
470 5). The  $\delta^{11}\text{B}$  was statistically indistinguishable between Types 1 and 2 ( $p = 0.75$ ). The Li/Cl ratios  
471 were similar to B/Cl ratios, with lower ratios in the saline water ( $p < 0.001$ ). However,  $\delta^7\text{Li}$  values  
472 were only significantly higher in Type 2 water (mean =  $19.7 \pm 1.4\text{‰}$ ,  $p < 0.05$ ) compared to both  
473 Type 1 ( $16.8 \pm 5.3\text{‰}$ ) and Type 3 ( $16.4 \pm 5.2\text{‰}$ ) water.  $\delta^7\text{Li}$  in groundwater of types 1 and 3 were  
474 statistically indistinguishable ( $p = 0.83$ ).

475 Sr/Ca molar ratios were lower than values typically reported in the Appalachian brines  
476 ( $0.002$  to  $0.17$ ) (Warner et al., 2012), with values in the saline water ranging from  $0.0004$  to  
477  $0.022$  (Fig. 5). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ranged from  $0.71210$  to  $0.71333$ , and mean ratios were  
478  $0.71287 \pm 0.0002$  for Type 1,  $0.71279 \pm 0.0001$  for Type 2 and  $0.71294 \pm 0.0002$  for Type 3 (Table  
479 1). These  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are more radiogenic than typical Marcellus age brines ( $0.71000$  to



480 0.71212), but still less radiogenic than the Upper Devonian conventional produced water  
481 (0.71580 to 0.72200). The Sr/Ca and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the three-groundwater types were  
482 statistically indistinguishable from each other (in spite of the differences in salinity and Sr  
483 concentrations).

484 High concentrations of Ba and other trace metals were also observed in the saline  
485 groundwater (Table 1). Type 3 groundwater had higher Ba ( $1.9\pm 1.3$  mg/L,  $p<0.05$ ) than either  
486 Type 1 or 2, with concentrations exceeding the U.S. EPA maximum contaminant level (MCL) of  
487 2 mg/L in 4 out of 10 Type 3 saline waters, and 1 out of 17 Type 2 waters. Likewise, the saline  
488 groundwater of Type 3 had distinctively higher As concentrations ( $14.3\pm 15.7$   $\mu\text{g/L}$ ) relative to  
489 either Type 1 ( $5.4\pm 6.7$   $\mu\text{g/L}$ ) or Type 2 ( $4.9\pm 3.7$   $\mu\text{g/L}$ ) samples, but it was not statistically  
490 significantly ( $p=0.16$ ), and the MCL of 10  $\mu\text{g/L}$  was exceeded in 5 of the 10 Type 3 waters and 2  
491 out of 17 Type 2 waters. The MCL was also exceeded in 18 of the 119 low-salinity Type 1  
492 groundwater. Overall, arsenic exceeded the MCL level of 10  $\mu\text{g/L}$  in 25 well samples (17%).

#### 493 **4.2 Dissolved Gas Geochemistry**

494  $\text{CH}_4$  concentrations in groundwater from the study area ranged from below detection  
495 limits ( $\sim 0.01$   $\text{cm}^3$  STP/L) to 36.9  $\text{cm}^3$  STP/L (Table 2). Similar to previous studies in the  
496 Appalachian Basin, the upper limit is near saturation conditions for  $\text{CH}_4$  in fresh water  
497 (saturation for  $\text{CH}_4$  is  $\sim 35\text{-}40$   $\text{cm}^3$  STP/L at  $p(\text{CH}_4)= 1$  atm at  $10^\circ\text{C}$ ) (Darrah et al., 2014; Darrah  
498 et al., 2015b). Samples from this study area had  $\text{C}_2\text{H}_6$  concentrations that ranged from below  
499 detection limits ( $\sim 0.0005$   $\text{cm}^3$  STP/L) to 0.037 ccSTP/L,  $\text{C}_3\text{H}_8$  concentrations that ranged from  
500 below detection limits ( $\sim 0.0005$  ccSTP/L) to  $6.65 \times 10^{-4}$  ccSTP/L,  $\text{C}_4\text{H}_{10\text{-i}}$  concentrations that  
501 ranged from below detection limits ( $\sim 0.0001$  ccSTP/L) to  $2.68 \times 10^{-6}$  ccSTP/L,  $\text{C}_4\text{H}_{10\text{-n}}$   
502 concentrations that ranged from below detection limits ( $\sim 0.0001$  ccSTP/L) to  $2.24 \times 10^{-6}$   
503 ccSTP/L,  $\text{C}_5\text{H}_{12\text{-i}}$  concentrations that ranged from below detection limits ( $\sim 0.0005$  ccSTP/L) to  
504  $4.65 \times 10^{-7}$  ccSTP/L, and  $\text{C}_5\text{H}_{12\text{-n}}$  concentrations that ranged from below detection limits ( $\sim 0.0005$   
505 ccSTP/L) to  $4.32 \times 10^{-7}$  ccSTP/L (Table 2).

506 A one-way analysis of variance of all data from each water type found that groundwater  
507 Types 2 and Type 3 (high salinity types) had significantly higher ( $p<0.05$ )  $\text{CH}_4$  concentrations  
508 ( $13.4\pm 15$  and  $14.3\pm 15$  ccSTP/L, respectively) relative to the low salinity Type 1 ( $1.7\pm 3.2$   
509 ccSTP/L), but were not significantly different from each other.  $\text{CH}_4$  and Cl contents were

510 positively correlated when including all samples ( $r^2 = 0.70$ ,  $p < 0.05$ ; Fig. 6). CH<sub>4</sub> was also  
511 correlated with Br ( $r^2 = 0.68$ ,  $p < 0.05$ ), B ( $r = 0.47$ ,  $p < 0.05$ ), and Li ( $r = 0.71$ ,  $p < 0.05$ ; Fig. S5)  
512 across the whole dataset. In the saline samples, CH<sub>4</sub> was correlated with Cl ( $r = 0.60$ ,  $p < 0.05$ ), Br  
513 ( $r = 0.59$ ,  $p < 0.05$ ), and Li ( $r = 0.67$ ,  $p < 0.05$ ).

514 Most of the Type 1 samples had CH<sub>4</sub> below 1.4 ccSTP/L, with a wide  $\delta^{13}\text{C-CH}_4$  range of  
515  $-96\text{‰}$  to  $-19\text{‰}$  and elevated C<sub>1</sub>/C<sub>2+</sub> ratios (mean =  $10,389 \pm 45$ ). A subset (30 out of 145) of  
516 low-salinity groundwater samples had CH<sub>4</sub> above 1.4 ccSTP/L, with most of these samples  
517 having  $\delta^{13}\text{C-CH}_4 = < -55\text{‰}$ . Types 2 and 3 groundwater with elevated salinity had much higher  
518 CH<sub>4</sub> contents on average, but had relatively low  $\delta^{13}\text{C-CH}_4$  (mean =  $-63.0 \pm 18.3\text{‰}$  in Type 2 and  
519 mean =  $-69.0 \pm 28.6\text{‰}$  in Type 3), an isotopic composition that is consistent with biogenic sources  
520 (Fig. 6) (Schoell, 1983; Whiticar and Faber, 1986). Types 1, 2 and 3 samples did display  
521 significantly heavier ethane isotope values, where sufficient ethane concentrations were available  
522 for isotopic analysis. The mean  $\delta^{13}\text{C-C}_2\text{H}_6$  were  $-35.87 \pm 1.80$ ,  $-38.25 \pm 0.87$ , and  $-37.60 \pm 0.54\text{‰}$   
523 for Types 1, 2, and 3, respectively. These values are consistent with the ranges observed for  
524 thermogenic gases derived from marine (e.g., shale) or terrestrial (e.g., coal) of organic matter.

525 Groundwater samples from the current study display N<sub>2</sub> ( $8.94 \text{ cm}^3 \text{ STP/L}$  to  $20.50 \text{ cm}^3$   
526  $\text{STP/L}$ ; average =  $12.71 \text{ cm}^3 \text{ STP/L}$ ) and Ar ( $0.21 \text{ cm}^3 \text{ STP/L}$  to  $0.41 \text{ cm}^3 \text{ STP/L}$ ; average =  $0.30$   
527  $\text{cm}^3 \text{ STP/L}$ ) concentrations that vary within 9% and 19% of air-saturated water (ASW) values  
528 ( $13.9$  and  $0.37 \text{ cm}^3 \text{ STP/L}$ , respectively) on average, assuming Henry's Law solubility  
529 equilibration conditions at atmospheric pressure (1 atm), 10°C, and ~600 meters of elevation  
530 (average elevation in the study area) (Table 2; Fig. 7). In fact, the majority of samples have N<sub>2</sub>  
531 and Ar that plot within 14% of the temperature-dependent ASW solubility line (Fig. 7).

532 In the current study, <sup>4</sup>He concentrations ranged from near ASW values ( $\sim 37.49 \times 10^{-6} \text{ cm}^3$   
533  $\text{STP/L}$ ) up to  $0.357 \text{ cm}^3 \text{ STP/L}$ , similar to the range observed in other parts of the Appalachian  
534 Basin (Darrah et al., 2015). All of the samples displayed <sup>3</sup>He/<sup>4</sup>He ratios that decreased from  
535  $1.021 R_A$  (ASW values plus small contributions from the in-growth of tritiogenic <sup>3</sup>He; Table 2)  
536 to a uniformly crustal isotopic composition of  $0.0166 R_A$  (where  $R_A = \text{the ratio of air} = 1.39 \times 10^{-6}$ )  
537 with increasing [<sup>4</sup>He] and <sup>4</sup>He/<sup>20</sup>Ne (Fig. 8). Note that this trend is largely consistent with other  
538 areas in the NAB, with the exception that the WV dataset do not show any evidence for a subset  
539 of samples with an anomalous mantle-derived composition as was seen in northeastern PA  
540 (Darrah et al., 2015b). The <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>21</sup>Ne/<sup>22</sup>Ne values ranged from 9.757 to 9.914 and

541 0.0276 to 0.0310, respectively. These values are within 1.4% and 7.3% of the anticipated air-  
542 saturated water values, respectively. The small increase in  $^{21}\text{Ne}/^{22}\text{Ne}$  reflects minor contributions  
543 of nucleogenic  $^{21}\text{Ne}^*$ , which is significantly higher in Type 2 and Type 3 waters as compared to  
544 Type 1. Similarly,  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$  values ranged from 294.50 to 308.77 and 0.1781 to  
545 0.1909, respectively. These values are within 4.5% and 1.3% of the anticipated air-saturated  
546 water values, respectively. The small increase in  $^{40}\text{Ar}/^{36}\text{Ar}$  reflects minor contributions of  
547 radiogenic  $^{40}\text{Ar}^*$ , which is significantly higher in Type 2 and Type 3 waters, as compared to  
548 Type 1.

549

### 550 **4.3 Spatial and statistical relationship between hydrogeological location and groundwater** 551 **geochemistry**

552 Previous studies have identified valley bottoms as an area with high occurrences of  
553 naturally saline, hydrocarbon-rich groundwater. Eight out of ten Type 3 drinking-water wells,  
554 were located less than 750m from the same valley bottom in the northwest corner of Doddridge  
555 County. The remaining Type 3 well (WV-503) was located in the valley bottom of an adjacent  
556 valley in west Tyler County. Both of these valleys intersect the Burchfield Syncline that runs  
557 through the study area. Seven of the Type 2 waters were also found within 750m of a valley  
558 bottom in northwest Doddridge County. The remaining Type 2 wells were located between 1,016  
559 and 8,241 m distance to a valley bottom.

560 The correlations of Cl ( $r=0.36$ ,  $p<0.05$ ) and Br/Cl ( $r=0.37$ ,  $p<0.05$ ) to valley bottoms  
561 were not high, but higher Cl concentrations and Br/Cl ratios were recorded in groundwater wells  
562 located closest to valley bottoms (Fig. S8).  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  concentrations were also weakly  
563 correlated with proximity to valley bottoms ( $r=0.15$ ,  $p<0.05$  and  $r=0.16$ ,  $p<0.05$  respectively).  
564 The  $\text{C}_1/\text{C}_2+$  ratio, on the other hand, was negatively correlated with distance to a valley bottoms  
565 (i.e. the ratio increased further away from the valley bottom) ( $r=0.4$ ,  $p<0.05$ ). The  $\text{N}_2$  and  $^{36}\text{Ar}$   
566 concentrations of groundwater from this study were also negatively correlated to valley bottoms  
567 ( $r= -0.13$ ,  $p<0.05$  and  $r= -0.24$ ,  $p<0.05$ ), with the lowest concentrations in groundwater wells  
568 closest to valley bottoms (Fig. S8). The carbon stable isotopes of methane showed no correlation  
569 with distance from valley bottoms ( $p=0.23$ ). Tritium showed no correlation with distance to a  
570 valley bottom.

571 The noble gases concentrations and gas ratios were also correlated with distance to valley  
572 bottoms (Fig. S8). For example, the  $^4\text{He}$  ( $r = 0.33$ ,  $p < 0.05$ ), the  $^4\text{He}/\text{CH}_4$  ( $r = 0.42$ ,  $p < 0.05$ ), and  
573 the  $^{20}\text{Ne}/^{36}\text{Ar}$  ( $r = 0.39$ ,  $p < 0.05$ ) were all weakly, but significantly correlated with proximity to  
574 valley bottoms so that higher values occurred in groundwater wells close to valley bottoms and  
575 are associated with more saline samples (Fig. S8). However, it is important to note that there is  
576 significant overlap between distances to the Burchfield Syncline and valley bottom in the current  
577 data set. Although the trends in  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $^{36}\text{Ar}$  could relate to gas-water interactions in the  
578 presence of a relatively low volume of free-gas phase hydrocarbons or the migration of an  
579 exogenous hydrocarbon-phase in the valley bottom, the lack of coherent fractionation between  
580  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $\text{N}_2/\text{Ar}$  suggests that phase-partitioning during fluid migration from depth to the  
581 shallow aquifer is more likely.

582

#### 583 **4.4 Spatial and statistical relationship between conventional and unconventional energy** 584 **development and water quality**

585 We did not observe any relationship between Cl and proximity of the drinking-water  
586 wells to the nearest shale gas drilling sites for any of the water types ( $r = 0.04$ ,  $p = 0.70$ ; Fig. 9). A  
587 Kruskal-Wallis test found that Cl concentrations in drinking-water wells  $< 1$  km from a shale gas  
588 well pad were statistically indistinguishable to values in drinking-water wells  $> 1$  km away from a  
589 well pad ( $p = 0.88$ ).  $\text{CH}_4$  concentrations did not increase with proximity to the nearest shale gas  
590 drilling sites ( $r = 0.10$ ,  $p = 0.89$ ; Fig. 9), and the  $\text{CH}_4$  concentrations in wells located  $< 1$  km from  
591 drilling were statistically indistinguishable from concentrations  $> 1$  km from drilling ( $p = 0.51$ ).  
592 However, the carbon isotopes of  $\text{CH}_4$  ( $\delta^{13}\text{C}-\text{CH}_4$ ) had a weak correlation with distance to a shale  
593 gas well ( $r = 0.28$ ,  $p < 0.05$ ), with significantly more negative values of  $\delta^{13}\text{C}-\text{CH}_4$  in drinking-water  
594 wells  $< 1$  km from a well pad (mean =  $-66.4\text{‰}$ ) than those located  $> 1$  km from a well pad (mean =  
595  $-59.8\text{‰}$ ,  $p < 0.05$ ). Conversely, there was no significant correlation between  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  and  
596 distance to a shale-gas well ( $r = 0.124$ ,  $p = 0.73$ ). The  $\text{C}_1/\text{C}_{2+}$  ratio had no relationship with  
597 proximity to a shale-gas well ( $p = 0.38$ ) (Fig. 9). However, the  $\text{C}_1/\text{C}_{2+}$  ratios were significantly  
598 higher than either the Marcellus or other productive natural gas horizons in the region or  
599 groundwater wells that experienced fugitive gas contamination in northeastern PA or elsewhere.  
600 Additionally, mean  $\text{C}_1/\text{C}_{2+}$  ratios in wells  $< 1$  km were not significantly different to the mean  
601 ratios in wells  $> 1$  km from a shale-gas well ( $p = 0.60$ ).

602 The only other parameter that showed a weak, but significant correlation to distance from  
603 oil and gas wells and valley bottoms was  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $r=0.32$ ,  $p<0.05$  and  $r=0.41$ ,  $p<0.05$ ). The  
604  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio increased in drinking-water wells with increasing distance from a shale-gas well  
605 and from valley bottoms (Fig. 9). Saline groundwater wells (both Type 2 and Type 3) within  
606 1km of a well pad had significantly lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than wells located  $>1\text{km}$  from a well  
607 pad ( $p<0.05$ , Kruskal-Wallis test). When considering all groundwater wells, there was no  
608 statistically significant difference in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in wells greater than or less than 1 km from a  
609 well pad ( $p=0.24$ , Kruskal-Wallis test). No significant ( $p= >0.10$ ) correlations were observed  
610 between distance from a shale-gas well and any other isotope or noble gas parameters (e.g.,  $\delta^{11}\text{B}$ ,  
611  $\delta^7\text{Li}$ ,  $^{13}\text{C-CH}_4$ ,  $^4\text{He/CH}_4$ ,  $^{36}\text{Ar}$ ,  $^{20}\text{Ne}/^{36}\text{Ar}$ , and  $^4\text{He}$ ). There was also no correlation observed for  
612 any parameters and number of shale-gas wells in a 1km radius.

613 It is also important to consider the legacy impact of other forms of conventional oil and  
614 gas development on water quality in the study area. Considering there are over 130,000 active,  
615 plugged, or abandoned conventional oil and gas wells in West Virginia, the extensive  
616 hydrocarbon production in West Virginia over the past 100 years could be a major influence on  
617 water chemistry and contamination, especially compared to the relatively short period ( $\sim 10$   
618 years) that hydraulic fracturing has been employed in the area. Only 7 of the 112-groundwater  
619 wells sampled in this study were located more than 1 km from a conventional (active or inactive)  
620 well. The  $^{36}\text{Ar}$  were weakly, positively correlated with distance to a conventional well ( $r=0.22$ ,  
621  $p<0.05$ ), but no other parameters showed any relationship with distance to the nearest  
622 conventional gas well. There were no significant correlations between the geochemical and gas  
623 parameters with the number of conventional wells within a 1km radius. The lack of correlations  
624 suggests that conventional oil and gas wells do not play a role in affecting the groundwater  
625 geochemistry in this study area in West Virginia, while a previous study in Colorado has  
626 suggested stray gas contamination associated with conventional oil and gas wells (Sherwood et  
627 al., 2016).

#### 628 629 **4.5 Pre- and post-drilling groundwater quality**

630 The data indicate that none of the 17 Type 1 wells that were retested after the installation  
631 of nearby shale gas wells showed any change in Cl as compared to the Cl measured in the initial  
632 Type 1 baseline testing (slope=0.9;  $r=0.79$ ;  $p<0.05$ ; Fig. 10), even in those located near shale gas

633 drilling sites. However, some groundwater wells with Type 2 and 3 water showed both  
634 significant increases and decreases in Cl after drilling, which are discussed further below. CH<sub>4</sub>  
635 contents of wells collected after installation of nearby shale gas wells did not change for the  
636 majority of the wells (for all 3 water types) relative to the baseline CH<sub>4</sub> data in wells collected  
637 prior to the shale gas drilling (slope=1.1; r=0.90; p<0.05; Fig. 10). Likewise, the δ<sup>13</sup>C-CH<sub>4</sub> of  
638 water collected after hydraulic fracturing was statistically indistinguishable to their respective  
639 values before drilling (slope=0.92, r=0.84; p<0.05; Fig. 10). δ<sup>13</sup>C-C<sub>2</sub>H<sub>6</sub> was only measured  
640 before and after in four samples but the isotope ratios all fall close to the 1:1 line between the pre  
641 and post-drilling samples.

642 These trends were also consistent for stable and noble gas isotopes (Fig. 10). Li and Sr  
643 isotopes ratios showed no changes in groundwater sampled post-drilling (slope=0.96, r=0.89;  
644 p<0.05 and slope=0.87, r=0.84; p<0.05, respectively). Neither the abundance of <sup>20</sup>Ne nor  
645 CH<sub>4</sub>/<sup>36</sup>Ar changed significantly over time either (slope =1.1, r=0.90, p<0.05 and slope =1.1,  
646 r=0.95, p<0.05, respectively), but other noble gas parameters did show some changes after  
647 drilling (Fig. 10). The <sup>4</sup>He/<sup>20</sup>Ne (slope = 0.97, r<sup>2</sup>=0.99, p<0.05), N<sub>2</sub> (slope =1.0, r<sup>2</sup>= 0.29,  
648 p<0.05), and <sup>36</sup>Ar (slope =1.0, r<sup>2</sup>=0.28, p<0.05) also do not show significant change with time,  
649 but the variability was much higher. The <sup>4</sup>He/<sup>20</sup>Ne in well WV-58, however, showed a dramatic  
650 increase from 179 to 503. The <sup>4</sup>He/CH<sub>4</sub> ratios showed little change in the saline samples  
651 (slope=0.93, r<sup>2</sup>=0.50, p<0.05), but either a large increase (up to 2x) or large decrease (up to 5x)  
652 in some of the freshwater samples (Fig. 10).

653 In two of the saline water samples (WV-36 and WV-38), we observed a >100% increase  
654 in Cl following shale gas drilling and hydraulic fracturing (Table 1), yet no changes were  
655 observed in the overall chemical composition for well WV-36 or in the B, Li, and Sr isotopes  
656 ratios of the saline groundwater collected after unconventional energy development.  
657 Groundwater in well WV-38 showed an increase in the Br/Cl ratio from Type 2 (Br/Cl=1.9x10<sup>-3</sup>)  
658 to Type 3 (2.9 x10<sup>-3</sup>). None of the diagnostic gas tracers (e.g., CH<sub>4</sub>, <sup>4</sup>He, <sup>4</sup>He/CH<sub>4</sub>, <sup>20</sup>Ne/<sup>36</sup>Ar,  
659 <sup>36</sup>Ar) showed any marked changes between sampling before and after installation of shale gas  
660 wells. One exception is a Type 1 well WV-3, which showed an increase in CH<sub>4</sub> from 2.8 to 21.0  
661 ccSTP/L after hydraulic fracturing, which is above the U.S. Dept. of Interior advisory limit, and  
662 yet did not correlate with an increase in Cl (Table 1) or other parameters. Despite the increase in

663 CH<sub>4</sub>, the  $\delta^{13}\text{C-CH}_4$  for this drinking-water well was very negative (-93‰) and, like other gas  
664 parameters (hydrocarbon composition, noble gases) did not change significantly through time.

#### 665 **4.6. Surface water contamination**

666 A spill on January 3<sup>rd</sup>, 2014 at a well pad in Tyler County was characterized by high  
667 salinity (Cl up to 18,000 mg/L), Br (278 mg/L), B (25.7 mg/L), Cr (679 $\mu\text{g/L}$ ), and Sr (76 mg/L)  
668 (Table 3). The variations of Br/Cl=( $6.8 \times 10^{-3}$ ),  $\delta^{11}\text{B}$  (27‰),  $\delta^7\text{Li}$  (11‰), and  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.70981)  
669 were consistent with the composition of Marcellus flowback waters (Chapman et al., 2012;  
670 Warner et al., 2014). We show that all of the downstream water collected at different dates had  
671 elevated Cl compared to the upstream values (2 mg/L), and high Br/Cl ratios similar to the spill  
672 waters (Fig. S9). Surface water directly adjacent to the spill site in Tyler County collected at two  
673 dates had up to twice the upstream Cl values (14 and 21 mg/L) and Br/Cl ratios that reflect  
674 mixing between the flowback and upstream surface water (Fig. S9). Run-off into Big Run Creek  
675 and the surface water at the run-off point sampled in February (more than a month after the spill)  
676 also had values that correspond to a mixing line between the flowback and upstream creek values  
677 (Fig. S9), indicating continued contamination of the stream from the spilled water. The  $\delta^{11}\text{B}$  and  
678  $\delta^7\text{Li}$  values in the run-off to Big Run creek were consistent with values in WV flowback (27 and  
679 14‰, respectively).

680 Surface water was also sampled near two disposal (i.e., injection) wells known to accept  
681 OGW; these surface waters also showed evidence of contamination. At both injection well sites,  
682 the oil and gas wastewater are stored in holding ponds prior to injection. Here, we sampled  
683 streams running adjacent to the injection pad and storage ponds, along with background surface  
684 water in the area. Two small streams directly downstream of the injection well in Lochgully and  
685 surface holding ponds had high Cl (mean = 470 mg/L), Sr (2 mg/L), Ba (2 mg/L), and Br/Cl ( $2.6$   
686  $\times 10^{-3}$ ), as well as  $\delta^{11}\text{B}$  (20‰) that are consistent with the Devonian-age brine (Warner et al.,  
687 2014). The injection well was permitted in 2002 and renewed for another five years in 2007. The  
688 surface storage ponds were closed in 2014, after we sampled in October 2013. Likewise, surface  
689 water next to the Hall injection well site in Ritchie Co. had elevated Cl (87 mg/L compared to an  
690 upstream of 16 mg/L) and Br/Cl ( $4.4 \times 10^{-3}$ ) and low Na/Cl (0.60) indicating possible  
691 contamination from the injection well site (Fig. S9). The Hall injection well is much recent and

692 was first permitted in 2013.

693

694

## 5. DISCUSSION

### 695 5.1 Tracing the source of the salinity and hydrocarbons in groundwater

696 The complex geology and tectonic history of the Northern Appalachian Basin (NAB) has  
697 led to diverse groundwater quality in the shallow aquifers. Saline groundwater in the NAB  
698 aquifers is relatively common and is frequently associated with the presence of hydrocarbon  
699 gases. However, findings of elevated salts and CH<sub>4</sub> in drinking-water wells near oil and gas  
700 development have prompted concerns about groundwater quality impacts from unconventional  
701 exploration of the Marcellus Shale. In some areas, stray gas from leaky, faulty, or damaged wells  
702 has been identified, but hydrocarbon-rich saline groundwater has typically only been associated  
703 with naturally occurring migration of deep formation brines (Darrah et al., 2014; Jackson et al.,  
704 2013b; Warner et al., 2012; Warner et al., 2013b). The timeline data in this study show that  
705 saline and hydrocarbon-rich groundwater was present in drinking-water wells prior to  
706 unconventional oil and gas development in the region, and the inorganic and gas geochemistry of  
707 both fresh and saline groundwater generally went unchanged in the first three years post-  
708 development in the suite of samples evaluated in this study. These observations suggest a natural  
709 source of hydrocarbon-rich brine mixing with shallow, young meteoric groundwater rather than  
710 contamination from nearby unconventional oil and gas development.

711 Salinity in the groundwater wells in the study area was lower (maximum Cl ~ 2,400  
712 mg/L) compared to groundwater sampled in northeastern Pennsylvania (Cl up to ~4,000 mg/L);  
713 however the range of Cl concentrations was very similar to the results of groundwater wells  
714 analyzed within the study area in a pre-existing 1982 study (Shultz, 1984). Additionally, the  
715 frequency of saline water wells was consistent with this historical data. Type 2 and Type 3 saline  
716 waters had Ca-Na-Cl composition with Br/Cl > 1.5 × 10<sup>-3</sup> that differ from the Type 1 fresh water  
717 with Ca-Na-HCO<sub>3</sub> composition, which is consistent with the brine compositions in Devonian-age  
718 produced waters in the NAB (Chapman et al., 2012; Dresel and Rose, 2010; Haluszczak et al.,  
719 2013; Warner et al., 2012). Ca-Na-Cl type water was also reported in the 1984 study, further  
720 supporting the presence of brine in groundwater prior to shale gas development in West Virginia  
721 (Shultz, 1984). The higher Br/Cl found in Type 3, but not in Type 2 water, with ratios up to



722  $\sim 4 \times 10^{-3}$  are similar to the ratios reported in Marcellus flowback water and accidental spills in  
723 northern West Virginia (Fig. 4; Ziemkiewicz and He, 2015; Harkness et al., 2015). Additionally,  
724 Type 3 waters were not present in groundwater sampled prior to shale gas development in the  
725 study area; however, it was detected in groundwater located more than 2 km from a shale-gas  
726 well.

727 Our data show that both Cl and Br/Cl ratios decrease with increasing elevation. Thus, the  
728 data show that saline waters with high Br/Cl ratios (mainly Type 3 waters) are more likely to  
729 occur in valley bottoms in this study area (Fig. S8). The relationships between salinity, brine  
730 contribution and location at the valleys have been observed in other parts of the NAB  
731 (Llewellyn, 2014; Warner et al., 2012). The increased fracturing in geologic formations below  
732 these features can induce higher hydraulic permeability and promote migration of deep fluids  
733 into the shallow aquifers, which supports natural migration of deep brines as the primary source  
734 of saline water. Additionally, several previous studies have suggested that increased levels of  
735 saline-rich and hydrocarbon-gas-rich fluids occur in valley bottoms assigned either based on  
736 topography or distances to nearest stream or river (Baldassare et al., 2013; Molofsky et al., 2013;  
737 Darrah et al., 2015; Siegel et al., 2015; Warner et al., 2012). By comparison, other studies have  
738 suggested the saline and hydrocarbon gas-rich fluids specifically occur within valley bottoms  
739 related to the eroded cores of highly fractured anticlinal structures (e.g., Darrah et al., 2015). The  
740 eroded cores of anticlines are not commonly observed in this region of WV because of the low  
741 amplitude nature of folding in this area.

742  $\text{CH}_4$  also had a significant relationship to valleys in the region (Fig. S6 and S7).  
743 Hydrocarbon gases may result from *in-situ* microbial or thermogenic production, and/or the  
744 migration of hydrocarbons from an exogenous biogenic or thermogenic source (e.g., Darrah et  
745 al., 2015). In general, results from this study are consistent with previously observed  
746 relationships between  $\text{CH}_4$  and elevated salinity. The strong correlation between Cl and  $\text{CH}_4$  in  
747 groundwater, particularly for Type 2 water ( $r = 0.76$ ,  $p < 0.05$ ), suggests that elevated  $\text{CH}_4$  is  
748 mainly arriving in the shallow groundwater along with a migrated brine (Fig. 4). Importantly, the  
749 high  $\text{CH}_4$  ( $> 1$  ccSTP/L) identified in groundwater wells is associated with elevated salinity, but  
750 not with distance to shale gas wells (Fig. 9), which appears to preclude an anthropogenic source  
751 for both hydrocarbon gases and salts. Historical data from WV also shows naturally high  $\text{CH}_4$   
752 (up to 21 ccSTP/L), and thus the values that were observed in this study do not appear atypical

753 for historical groundwater in the region (White and Mathes, 2006). Similar to what was shown  
754 by Darrah et al (2014; 2015b), we find that although CH<sub>4</sub> concentrations increase with Cl content  
755 until the point of methane saturation in groundwater. As CH<sub>4</sub> concentrations approach the  
756 saturation level (i.e., “bubble point” or CH<sub>4</sub> partial pressure of 1atm (p(CH<sub>4</sub>)=1atm) of methane  
757 (35-40 cm<sup>3</sup> STP/L) in groundwater at 1atm and 10°C for groundwater, there is a noticeable “roll  
758 over” in the plot of CH<sub>4</sub> versus Cl (Fig. 6). This roll over demonstrates how the conditions of gas  
759 saturation in water regulate the concentrations of CH<sub>4</sub> in groundwater.

760 By comparison to previous studies of the NAB, samples from this study area have lower  
761 C<sub>2</sub>H<sub>6</sub> concentrations (higher C<sub>1</sub>/C<sub>2+</sub>) on average and much more negative δ<sup>13</sup>C-CH<sub>4</sub> values.  
762 Although the Type 2 and Type 3 waters display heavier δ<sup>13</sup>C-CH<sub>4</sub> than Type 1 on average, the  
763 more negative δ<sup>13</sup>C-CH<sub>4</sub> signature in the saline groundwater of Type 2 and Type 3 indicates  
764 significant biogenic contributions of methane in all groundwater samples (Fig. 6), which is  
765 different from the more thermogenic-dominated (i.e., enriched in δ<sup>13</sup>C-CH<sub>4</sub>,) sources of  
766 hydrocarbon gases in groundwater from other regions of the Appalachian Basin (Baldassare et  
767 al., 2014; et al., 2014c; Jackson et al., 2013a; Molofsky et al., 2013; Osborn et al., 2011).  
768 Nonetheless, saline Type 3 groundwater samples showed positive linear correlations between  
769 CH<sub>4</sub> and δ<sup>13</sup>C-CH<sub>4</sub> (r=0.60, p<0.05) with Cl (r= 0.67, p<0.05; Fig. 6). Similar correlations were  
770 observed in earlier studies for the northeastern part of the Appalachian Basin, and are consistent  
771 with post-genetic fractionation during migration of CH<sub>4</sub>-rich brines to shallow aquifers (Darrah  
772 et al., 2015b; Darrah et al., 2014).

773 While δ<sup>13</sup>C-CH<sub>4</sub> <-55‰ and elevated C<sub>1</sub>/C<sub>2+</sub> can readily be interpreted as biogenic, as  
774 opposed to thermogenic in origin, the persistent presence of ethane (and in some cases propane),  
775 elevated helium, and the presence of methane with a more enriched δ<sup>13</sup>C-CH<sub>4</sub> have a less certain  
776 mode of formation (Fig. 6). The most confounding issue with the interpretation of a biogenic  
777 source of natural gases in this study area is the low, but persistent presence of higher aliphatic  
778 hydrocarbons such as ethane, propane, and in some samples trace amounts of butane and  
779 pentane. Further, the abundance of these higher order aliphatic hydrocarbons increases with  
780 increasing salinity and helium content, and is associated with a general increase in δ<sup>13</sup>C-CH<sub>4</sub>  
781 (discussed below) (Table 2; Fig. 6; 8). This trend is consistent with the presence of a mixture of  
782 thermogenic hydrocarbon gas in samples from this area (Darrah et al., 2014; 2015). Moreover,  
783 although there is a broad range of δ<sup>13</sup>C-C<sub>2</sub>H<sub>6</sub> (approximately -39 to -34 per mil) in groundwater

784 from Types 1, 2, and 3, ethane and isotopic values of  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  are consistent with the expected  
785 composition of thermogenic gases derived from either marine (e.g., shale) or terrestrial (e.g.,  
786 coal) organic matter (Faber and Stahl, 1984; Whiticar et al., 1994) throughout all sample types  
787 (Figure 6E).

788 In order to find a consistent explanation for all of the geochemical observations, we must  
789 first consider the series of geochemical processes that may change the molecular and isotopic  
790 composition of natural gas. Given the persistent presence of thermogenic natural gas, we start  
791 with the evolution of hydrocarbon stable isotopes during thermal maturation. During the  
792 generation of hydrocarbon gases by the thermocatalytic degradation of marine or terrestrial  
793 organic matter, there is an approximately linear, temperature-dependent relationship between the  
794  $\delta^{13}\text{C}$  values of methane, ethane, propane, and higher aliphatic hydrocarbons (Faber and Stahl,  
795 1984; Whiticar et al., 1985; Whiticar and Faber, 1986; Whiticar et al., 1994). Since only stable  
796 carbon isotopes of methane and ethane were available in the current study, we plot  $\delta^{13}\text{C}-\text{CH}_4$  vs.  
797  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  and the temperature-dependent relationship between these parameters, illustrated by  
798 the green line in Figure 6E. The classic interpretation of this plot is that samples that fall above  
799 the line represent mixing of various thermogenic components or methane oxidation, whereas  
800 samples that fall below the line indicate the addition of biogenic methane (Whiticar et al., 1994).  
801 Note that all of the samples fall below the line, indicating a significant mixture of biogenic  
802 methane with an apparently ubiquitous, and in this case, relatively low proportion of natural gas  
803 derived from a thermogenic source (Figure 6E).

804 Because  $\delta^{13}\text{C}-\text{CH}_4$  and  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  values are expected to increase with increasing thermal  
805 maturity (Faber and Stahl, 1984; Whiticar et al., 1985; Whiticar and Faber, 1986; Whiticar et al.,  
806 1994), decreasing  $\delta^{13}\text{C}-\text{CH}_4$  paired with the extent of increase in  $\text{C}_1/\text{C}_2+$  ratios may appear to be  
807 inconsistent with the anticipated trends for hydrocarbon maturation. However, we suggest that  
808 one potential parsimonious explanation may relate to a multiple stage process that progresses as  
809 follows: (1) initially a thermogenic natural gas migrates to shallow aquifers over geological time;  
810 (2) the range of  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  can be accounted for by *either* a) differences in the thermal maturity  
811 of natural gas that migrates to shallow aquifers over time (increasing the  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$  with a  
812 progressive increase in thermal maturity); b) the migration of multiple sources of thermogenic  
813 natural gas (e.g., shale gas plus thermogenic gas derived from coals); or c) aerobic oxidation of  
814 hydrocarbons after introduction to oxic/anoxic boundaries in shallow aquifers (Darrah et al.,

815 2015b); followed by (3) mixing with biogenic methane in the shallow subsurface following  
816 methanogenesis.

817 This processes would involve (1) the migration of a thermogenic natural gas with  
818 relatively enriched values of  $\delta^{13}\text{C-CH}_4$  and  $\delta^{13}\text{C-C}_2\text{H}_6$  and relatively low  $\text{C}_1/\text{C}_{2+}$  (as compared to  
819 groundwater geochemical composition observed in this study); (2) the  $\text{C}_1/\text{C}_{2+}$  composition of  
820 this natural gas would increase during fluid migration, potentially by a combination of solubility  
821 fractionation and aerobic oxidation during migration to the shallow aquifers (producing a range  
822 of progressively enriched  $\delta^{13}\text{C-CH}_4$  and  $\delta^{13}\text{C-C}_2\text{H}_6$  and elevated  $\text{C}_1/\text{C}_{2+}$ ); (3) mixing of  
823 thermogenic natural gases from either multiple sources *or* natural gas from varying thermal  
824 maturities, potentially followed by aerobic oxidation (both which would further increase the  
825 range of  $\delta^{13}\text{C-CH}_4$  and  $\delta^{13}\text{C-C}_2\text{H}_6$  and elevate  $\text{C}_1/\text{C}_{2+}$ ); followed by (4) the introduction of  
826 biogenic methane with depleted  $\delta^{13}\text{C-CH}_4$  ( $^{12}\text{C}$  enriched) and elevated  $\text{C}_1/\text{C}_{2+}$ , but without  
827 additional changes in  $\delta^{13}\text{C-C}_2\text{H}_6$ .

828 Based on the summation of data, we hypothesize that the persistent occurrence of ethane  
829 (and in some cases propane) and the ethane with this isotopic  $\delta^{13}\text{C-C}_2\text{H}_6$  values ranging from -39  
830 to -34 ‰ reflect an unambiguous presence of thermogenic natural gas that apparently migrated to  
831 the shallow aquifers, followed by the addition of biogenic methane. In combination, these  
832 coupled processes produce a distinguished geochemical composition of natural gas composed of  
833 a mixture of both post-genetically altered thermogenic natural gas and biogenic methane.

834 In support of this *ad hoc* hypothesis, is the presence of highly elevated [ $^4\text{He}$ ],  $^4\text{He}/\text{CH}_4$ ,  
835 and  $^{20}\text{Ne}/^{36}\text{Ar}$  (discussed further below) in the gas-rich end-member with relatively elevated  
836  $\delta^{13}\text{C-CH}_4$  and  $\delta^{13}\text{C-C}_2\text{H}_6$ . The majority of the data can be accounted for by simple two  
837 component mixing between a biogenic end-member and a thermogenic end-member that  
838 previously experienced post-genetic modification that increased the  $\text{C}_1/\text{C}_{2+}$  ratio without major  
839 changes in the  $\delta^{13}\text{C-CH}_4$  or  $\delta^{13}\text{C-C}_2\text{H}_6$ ; these conditions can be met by solubility partitioning  
840 during hydrocarbon gas migration (depicted by the dashed red line in Figure 6D).

841 In addition to the natural gas, this study investigates the origin of the saline groundwater.  
842 Boron and Li isotope variations in the saline groundwater reflect intensive water-rock  
843 interactions, which is consistent with this hypothesis. Thus, we hypothesize that the saline water  
844 originated from Upper Devonian brines with  $\delta^{11}\text{B} > 40\%$  and low B/Cl (Warner et al., 2014), but  
845 was modified through extensive water-rock interactions to form saline groundwater with lower

846  $\delta^{11}\text{B}$  of Type 2 and Type 3 water (Fig. 5). The high correlation of B/Cl with Na/Cl for Type 3  
847 water suggests that the B modification was induced by base-exchange reactions with the coal and  
848 shale rocks that also compose the aquifer, with typically lower  $\delta^{11}\text{B}$  (i.e.,  $\delta^{11}\text{B}\sim 15\%$  in  
849 desorbable B from marine clays; Spivack and Edmond, 1987). The  $\delta^7\text{Li}$  values in the  
850 groundwater wells mimic the composition of the Upper Devonian produced waters (Warner et  
851 al., 2014), which suggests lower contribution of Li from water-rock interaction. Nonetheless,  
852 these isotopic values were higher than the  $\delta^7\text{Li}$  fingerprints of the Marcellus flowback water  
853 ( $\delta^7\text{Li}<10$ ; Fig. 5), which is consistent with the lack of evidence for contamination from  
854 unconventional energy development (Phan et al., 2016; Warner et al., 2014).

855 The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in groundwater from the study area were less radiogenic than the  
856 typical high  $^{87}\text{Sr}/^{86}\text{Sr}$  measured in Upper Devonian brines ( $>0.716$ ) and slightly higher than the  
857  $^{87}\text{Sr}/^{86}\text{Sr}$  Marcellus flowback and produced waters ( $0.71121\pm 0.0006$ ) and spill water reported in  
858 this study ( $0.70981$ ; Table 3; Fig. 5; Chapman et al., 2012; Warner et al., 2012). The  
859 groundwater data are also different from the composition of Marcellus-like saline groundwater in  
860 northeastern PA reported by Warner et al. (2012).  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios reported for coals from the  
861 Pittsburgh, Allegheny and Kanawha formations in West Virginia (Vengosh et al., 2013) and  
862 Pennsylvania (Chapman et al., 2012), as well as leaching of U.S coals (Brubaker et al., 2013;  
863 Ruhl et al., 2014; Spivak-Birndorf et al., 2012), had a range of 0.70975 to 0.71910. Both  
864 leaching experiments of WV surface rocks and streams that discharged from valley fills in WV  
865 found that coal-bearing rocks have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  $\sim 0.7124$  (Vengosh et al., 2013), which is  
866 similar to the values measured in groundwater in this study. This similarity suggests that the  
867 deep-source of saline groundwater has interacted with the coal units imbedded in the deep or  
868 surface geology, causing the observed isotopic shift from the original isotope composition of the  
869 brine. Wunsch (1992) presented a hypothesis that groundwater in the lower NAB likely migrates  
870 along coal seams that have higher permeability than the interbedded shale layers found through  
871 shallow aquifers in the region. This preferential flowpath would induce intensive interaction with  
872 coal seams.

873 Overall, the integration of the isotope systematics of Sr, B, and Li in the investigated  
874 groundwater suggests that the saline groundwater originated from the Appalachian brines, but  
875 was modified by interactions with the local coal-bearing aquifer rocks. The difference in Br/Cl

876 ratios of Type 2 and 3 could be related to a different origin of the source brines. Produced waters  
877 from different geological formations in northern Appalachia have shown large variations in  
878 Br/Cl ratios, reflecting different degrees of evaporation and/or later modification by halite  
879 dissolution (Chapman et al., 2012; Dresel and Rose, 2010; Warner et al., 2012). The long-term  
880 migration of these presumably two different brine sources to the shallow aquifer in WV has  
881 involved interactions with the rock formations and modification of the original composition. In  
882 any case, the Li and Sr isotope compositions of the saline groundwater of Type 2 and 3 are  
883 different from those of the Marcellus brines and spill waters collected in this study, and clearly  
884 rule out the possibility of contamination from flowback or produced waters associated with  
885 unconventional energy development in the area. This interpretation is further strengthened by the  
886 fact that the chemistry of the saline groundwater prior to the shale gas drilling in the area was not  
887 modified throughout time following shale gas drilling and hydraulic fracturing.

## 888 **5.2 Determining transport mechanisms using noble gas geochemistry**

889 Geochemical studies in other regions of the NAB (northeast Pennsylvania, eastern  
890 Kentucky) identified mixing of shallow groundwater with possible deep brines with chemistry  
891 similar to that found in the Marcellus Shale (Warner et al., 2012). The flow paths that allow the  
892 migration from depth was attributed to a combination of deep high hydrodynamic pressure and  
893 enhanced natural flow paths (i.e. fracture zones) (Engelder et al., 2009). This model is  
894 particularly relevant in valleys due to increased regional discharge to lower hydrodynamic  
895 pressure in the valleys and greater fracturing and thus permeability of the subsurface in valleys.  
896 The presence of naturally occurring flow paths for fluid migration is important as it suggests  
897 there are connective pathways between shallow groundwater and oil and gas bearing formations  
898 that could allow for migration of hydraulic fracturing fluids. Noble gas studies in the  
899 Appalachian region support the model for long-range migration of hydrocarbon-rich brines over  
900 geological time from depth and mixing with shallow groundwater (Darrach et al., 2015; Darrach et  
901 al., 2014).

902 The abundance of dissolved atmospheric (ASW) gases (i.e.,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $\text{N}_2$ ) can also help  
903 to constrain the behavior of hydrocarbon gases (Aeschbach-Hertig et al., 2008; Gilfillan et al.,  
904 2009; Holocher et al., 2002; Holocher et al., 2003; Solomon et al., 1992). Previous research has  
905 shown that quantitative “stripping” of air-saturated water noble gases provide evidence for

906 fugitive gas contamination in some shallow drinking-water wells (Darrah et al., 2014). In  
907 contrast, *none* of the samples in this study, collected before or after shale gas drilling showed  
908 evidence for stripping or fugitive gas contamination (Fig. 7). The most obvious deviations from  
909 ASW composition in this study include concomitantly elevated levels of  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $\text{CH}_4$ , and  
910  $\text{C}_2\text{H}_6$ , which generally correspond to increasing salinity (Fig. 8 and S6) as was observed  
911 previously (Darrah et al., 2014; 2015).

912 The extent of "bubble enrichment" or "excess air" entrainment observed here is common  
913 in many aquifers (Aeschbach-Hertig et al., 2008; Heaton and Vogel, 1981) and reflects normal  
914 equilibration between the atmosphere and meteoric water during groundwater recharge. These  
915 findings were as expected for a typical shallow aquifer and consistent with an absence of obvious  
916 evidence for extensive gas-water interactions in this dataset (i.e., stripping related to fugitive gas  
917 contamination) (Weiss, 1971a, b). One noticeable difference from previous studies, is the lower  
918  $^{36}\text{Ar}$ , on average, for samples with the elevated  $\text{CH}_4$  concentrations in Types 2 and 3, which  
919 suggests the addition of  $\text{CH}_4$  may have induced minor two-phase effects (gas-liquid interactions)  
920 during transport in the aquifer (Fig. 7).

921 Noble gas isotopes and  $^3\text{H}$  data also provide additional insights for the origin of the  
922 different water types. Similar to other studies, all water types apparently reflect contributions  
923 from relatively young meteoric water as demonstrated by the presence of statistically  
924 indistinguishable ( $p < 0.05$ ) quantities of  $^3\text{H}$  (half-life  $\sim 12.4$  years) in all three subsets. In general,  
925 Type 1 water samples appear to reflect relatively young ( $^3\text{H}$ -active;  $< \sim 80$  years), low- $\text{CH}_4$ , and  
926 low salinity groundwater. By comparison, both Type 2 and 3 waters contain lower  $^3\text{H}$  levels  
927 (mean  $^3\text{H} = 4.5$  compared to 5.9 for the whole dataset), and thus indicate the likely migration of  
928 an old exogenous fluid into, and subsequent mixing with, fresh water in shallow aquifers on  
929 undetermined time scales. For these reasons, we conclude that the salinity and the majority of the  
930 dissolved  $\text{CH}_4$  reflect the migration of a deeper, exogenous source of  $\text{CH}_4$ -rich brines into the  
931 shallow aquifers over geological time coupled with the addition of methanogenic methane in  
932 the shallow subsurface. This argument conflicts with models of elevated  $\text{CH}_4$  controlled by  
933 hydrodynamic pressure (Molofsky et al., 2013; Siegel et al., 2015a) and instead suggests that  
934 valley bottoms with higher hydraulic permeability induced from higher fault and fracture  
935 intensity along deformational features, which may result in preferential pathways for the  
936 migration of deep fluids to shallow aquifers.

937            Important distinctions between Type 2 and 3 waters include the resolvable differences in  
938 the  $^4\text{He}/\text{CH}_4$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  ratios, which suggests a longer range of fluid transport for Type 3  
939 waters (Fig. 8). We interpret the noble gas differences as the result of the migration of a deeper  
940 source for Type 3 waters relative to Type 2 waters, potentially from an organic-rich shale-like  
941 source rock. This distinction is supported by the relatively higher Br/Cl of Type 3 groundwater,  
942 indicating a brine-rich source. This mechanism is consistent with the other geochemical and  
943 isotope differences observed between Type 2 and Type 3 waters. The B/Cl and Na/Cl ratios and  
944  $\delta^{11}\text{B}$  suggest that the Devonian brines that formed Type 3 waters had fewer interactions with the  
945 shallow aquifer host rocks relative to Type 2 waters.

946            Although we do observe a general trend of concomitantly increasing  $^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$   
947 and low  $^3\text{He}/^4\text{He}$  in samples that are rich in Cl and  $\text{CH}_4$ , we also found significant scatter in these  
948 relationships within the current dataset (Fig. 8 and S6). These data provide an important  
949 parameter by which to differentiate Types 2 and 3 from Type 1, but do not distinguish Types 2  
950 and 3 from each other. All Type 3 and the majority of Type 2 samples do display elevated  $^4\text{He}$ ,  
951  $^{20}\text{Ne}$ , and  $^4\text{He}/^{20}\text{Ne}$ , and low  $^3\text{He}/^4\text{He}$  in samples rich in Cl and  $\text{CH}_4$ , which is largely consistent  
952 with an exogenous crustal/radiogenic source of natural gas to the aquifer (i.e., a source of He  
953 external to the present aquifer lithologies) (Fig. 8 and S6).

954            By comparison to the He-rich samples, with a few exceptions, the majority of Type 1 and  
955 a subset of Type 2 samples have air saturated water-like  $^3\text{He}/^4\text{He}$  values that decrease with  
956 increasing  $^4\text{He}$  content, but does not decrease with increasing  $\text{CH}_4$  or Cl levels (Fig. 8). This  
957 trend appears to reflect a variable mixture between air-saturated water and crustal helium at  
958 moderate  $\text{CH}_4$  and Cl levels, which is consistent with a larger component of younger, biogenic  
959  $\text{CH}_4$ .

960            The  $^4\text{He}$  in groundwater, reflects a combination of: (1) atmospheric inputs; (2) *in-situ*  
961 production of  $^4\text{He}$  from  $\alpha$ -decay of U-Th in the aquifer rocks; (3) the release of  $^4\text{He}$  that  
962 previously accumulated in detrital grains; and (4) the flux from exogenous sources (Solomon et  
963 al., 1996; Zhou and Ballentine, 2006). The proportion of  $^4\text{He}$  from atmospheric inputs can be  
964 readily estimated from the abundance of other air-saturated water gases and the *in situ*  
965 production from  $\alpha$ -decay can be determined by measuring the U and Th of aquifer rocks (Table  
966 2). The steady-state production and accumulation for  $^4\text{He}$  in aquifer minerals (dominated by  
967 quartz and clay grains) was estimated as  $<2.94 \times 10^{-9} \text{ cm}^3 \text{ STP/L}$  of water/yr. Additionally, we



968 estimate that maximum release of radiogenic helium into aquifer waters that previously  
969 accumulated in crustal minerals over geologic time by conducting step-wise heating experiments  
970 on aquifers minerals to be on the order of  $\sim 0.71 \times 10^{-6} \text{ cm}^3 \text{ STP/L/yr}$ .

971 Based on these estimates, we find that the  $^4\text{He}$  that we observed (up to  $0.36 \text{ cm}^3 \text{ STP/L}$ )  
972 in the  $\text{CH}_4$ -rich and high salinity samples greatly exceeds the viable combined concentrations  
973 from  $^4\text{He}_{\text{ASW}}$ , the maximum  $^4\text{He}_{\text{in-situ}}$  production, and the expected release from  $^4\text{He}$  that  
974 previously accumulated in aquifers minerals, unless we assume a groundwater age of greater  
975 than 1.4 million years. Because of the consistent presence of  $^3\text{H}$  (with a half-life of 12.3 years)  
976 observed in groundwater from this study (2.48 to 8.48  $^3\text{H}$  units overall and 3.67 to 5.11 in Type 3  
977 waters), in combination with water isotopes that are consistent with the post-glacial (post-  
978 Pleistocene) local meteoric water line (Fig. S4), we suggest that these groundwater samples  
979 represent a mixture between young meteoric water and an exogenous source of hydrocarbon-rich  
980 diluted brines in the shallow subsurface. We conclude that Type 3 waters unambiguously require  
981 an exogenous source of  $^4\text{He}$  that mixes with relatively fresh meteoric water, while Type 2 waters  
982 likely reflect a mixture of both components. Clearly, on average the majority of Type 1 samples  
983 appear to reflect shallow, relatively young meteoric water with some exceptions that have higher  
984  $^4\text{He}$  and lower  $^3\text{He}/^4\text{He}$ .

985 In addition to  $^4\text{He}$ , other noble gas data are consistent with the hypothesized migration of  
986 an exogenous fluid. In others parts of the Appalachian Basin, we previously interpreted strong  
987 correlations between ratios of thermogenic to air-saturated water gases to each other and to  
988 increasing salt content as variable additions of a thermogenic hydrocarbon gas-rich brine  
989 (dominated by  $\text{CH}_4$  with minor  $\text{C}_2\text{H}_6$  and other crustal components such as  $^4\text{He}$ ) to  $^3\text{H}$ -active, and  
990 hence, relatively recent meteoric water (dominated by ASW components such as  $\text{N}_2$  and  $^{36}\text{Ar}$ ) in  
991 shallow groundwater conditions (Darrah et al., 2014; Darrah et al., 2015b). Although the  
992 collection of geochemical data likely indicates a different origin for these gases in this study area  
993 (i.e., coal beds or a lower thermal maturity shale gas), in combination, the data suggests the  
994 coherent migration of hydrocarbon gases, salts, and radiogenic helium from deeper exogenous  
995 sources.

996

#### 997 **5.4. Surface water impacts due to release of wastewater**

998 The clear evidence for surface water contamination at two injection well sites and from

999 the flowback spill in Tyler County, provide the basis for a geochemical “contaminated”  
1000 fingerprint that can be compared to the groundwater geochemistry in the study area. The  
1001 flowback spill water was associated with high salinity, high Br/Cl ratios and isotope ratios that  
1002 were similar to Marcellus flowback values reported in previous studies (Chapman et al., 2012;  
1003 Warner et al., 2014). The spill water was also characterized by relatively high  $\delta^{11}\text{B}$  (>27‰) and  
1004 low  $\delta^7\text{Li}$  (<15‰) values that are similar to the values found in Marcellus flowback and are  
1005 distinct from the Upper Devonian produced waters from conventional oil and gas wells. Water  
1006 samples collected 1.5 and 8 months after the spill show a continued release of flowback water to  
1007 the environment, with pools of water showing elevated salinity, Br/Cl ratios and Marcellus-like  
1008 isotope signatures. At 1.5 months after the spill, flowback-like water with elevated salinity, Li,  
1009 B, Ba, Sr, and other metals was found still running off into Big Run Creek and downstream of  
1010 the spill site in Big Run Creek. These samples had elevated concentrations of various inorganic  
1011 components compared to the upstream values, although the absolute concentrations levels were  
1012 below any ecological or drinking water standards.

1013         The  $\delta^{11}\text{B}$  values of the spill water from the Lochgully injection well sites were ~20‰,  
1014 which could reflect mixing of flowback water with surface water, or that the OGW released from  
1015 the storage ponds at the Lochgully site could be a mixture of both Upper Devonian produced  
1016 waters and Marcellus flowback. The streams running through the Lochgully site connect  
1017 downstream to Wolf Creek, which is a major drinking water source in the area. Other than  
1018 elevated Ba and Sr, no other trace elements contamination was found in the two small streams.  
1019 The surface water adjacent to the Hall injection well had elevated Cl, Br, Na, B, Sr and Ba  
1020 compared to the background surface water, which indicates possible contamination from the  
1021 OGW spills downstream from the injection well. These samples were collected during the winter  
1022 and there could be seasonal variations in the contribution of OGW to the environment.

1023         Overall, the surface water chemistry at these spill sites is consistent with the composition  
1024 of the Marcellus flowback, providing a strong evidence for contamination due to disposal and  
1025 storage of hydraulic fracturing fluids in West Virginia. The  $\delta^7\text{Li}$  values of the leaking flowback  
1026 fluid at the Tyler County site were lower compared to the regional saline groundwater in this  
1027 study, while the  $\delta^{11}\text{B}$  values were higher. This suggests that the B and Li isotope values in water  
1028 contaminated from unconventional activities should be distinct from naturally occurring brine

1029 salinization. These findings further support the conclusions from the time series data that the  
1030 saline groundwater found in the study site is not a result of releases of OGW from  
1031 unconventional oil and gas drilling activity in the area.

## 1032 **6. CONCLUSIONS**

1033 Similar to other areas in the Appalachian Basin, the occurrence of CH<sub>4</sub>-rich, saline  
1034 groundwater in shallow aquifers was found to be a widespread phenomenon and likely a result of  
1035 natural migration of deep brine- and natural gas-rich fluids combined with shallow water-rock  
1036 interactions. This three-year study has monitored the geochemical variations of drinking-water  
1037 wells before and after the installation of nearby shale gas wells, and provides a clear indication  
1038 for the lack of groundwater contamination and subsurface impact from shale-gas drilling and  
1039 hydraulic fracturing with the temporal resolution offered by the study. Saline groundwater was  
1040 ubiquitous throughout the study area before and after shale gas development, and the  
1041 groundwater geochemistry in this study was consistent with historical data reported in the  
1042 1980's. We observed significant relationships of Cl and Br/Cl ratios with tectonic and  
1043 topographic structures, but not with distance to shale gas wells. The variations of B, Li, and Sr  
1044 isotopes ratios in the groundwater samples were not consistent with the signature of hydraulic  
1045 fracturing fluids, but rather reflect upflow of Devonian-age brines that have migrated to the  
1046 shallow aquifers and were modified by water-rock interactions.

1047 Additional evidence comes from the relative distributions of hydrocarbon gases and air-  
1048 saturated water gases. Unlike previous studies that have identified fugitive gas contamination in  
1049 groundwater near shale gas wells in the northeastern part of the Appalachian Basin, we did not  
1050 observe significant deviations of CH<sub>4</sub>/<sup>36</sup>Ar (gas to water ratio) or <sup>4</sup>He/<sup>20</sup>Ne (thermogenic to air-  
1051 saturated water ratio) relative to Cl concentration (Fig. 10). While we did observe a subset of  
1052 samples with elevated CH<sub>4</sub> at low Cl concentrations, these samples all had very low δ<sup>13</sup>C-CH<sub>4</sub>,  
1053 which is consistent with microbial CH<sub>4</sub> and display near air-saturated water levels of <sup>4</sup>He (Darrah  
1054 et al., 2015). The occurrence of ethane and propane and the carbon isotope ratios of ethane  
1055 indicate that thermogenic gas contributes to the overall mixture of natural gas in the shallow  
1056 aquifers of WV. However, groundwater from this study area is dominated by biogenic CH<sub>4</sub>.  
1057 Importantly, it appears that both biogenic and migrated thermogenic gases in the shallow  
1058 groundwater are unrelated to shale gas development.

1059           The abundance of dissolved air-saturated water parameters and  $^4\text{He}$ , further support this  
1060 interpretation. With the exception of four samples that have significant excess air (denoted by  
1061 highly elevated  $^{36}\text{Ar}$ ), the only notable deviations from normal Henry's Law equilibrium values  
1062 are the significant excesses of  $^4\text{He}$  and  $^{20}\text{Ne}$  in  $\text{CH}_4$ - and the salt-rich groundwater samples noted  
1063 above. Both of these components are likely enriched in these aquifers by the migration of  
1064 exogenous  $\text{CH}_4$ - and salt-rich fluids, and potentially altered by minor gas-water interactions in  
1065 aquifer systems. Importantly, we did observe lower abundances of  $^{36}\text{Ar}$  and  $\text{N}_2$ , on average, in  
1066 samples with higher  $\text{CH}_4$  and Cl content, and thus we do not observe any evidence for  
1067 quantitative stripping of air-saturated water noble gases. Additionally, because the  $\text{N}_2/\text{Ar}$  does  
1068 not fractionation coherently with  $^{20}\text{Ne}/^{36}\text{Ar}$ , we conclude that the phase-partitioning that enriches  
1069  $^4\text{He}$  and  $^{20}\text{Ne}$  likely reflects migration of natural gas derived from an exogenous source. These  
1070 data also suggest that gas-water interactions occur at exceedingly lower volumes of gas with  
1071 respect to water, which further supports our observation for the lack of fugitive gas  
1072 contamination in the current study area.

1073           Trace metals, such as As, that are associated with potential health impacts also showed no  
1074 correlation with proximity to shale gas activities. Arsenic concentrations exceeding national  
1075 drinking water standards were detected also in wells tested before shale gas development. Wells  
1076 containing higher As concentrations were generally located in two regions of the study area, and  
1077 occurred in all 3 types of water, which points to natural (i.e., geogenic) sources of arsenic in the  
1078 aquifer. This observation is important for evaluating possible contamination processes because  
1079 some previous studies have associated elevated As with contamination from hydraulic fracturing  
1080 activities (Fontenot et al., 2013). Our data rules this out for this study area.

1081           It is clear from this and previous studies that risks to water resources from shale gas  
1082 development vary within and between basins. Stray gas contamination has been identified in  
1083 northeastern Pennsylvania and Texas (Darrah et al., 2014; Jackson et al., 2013), but not in  
1084 northeastern West Virginia (this study) or Arkansas (Warner et al., 2013b). However, surface  
1085 water impacts from spills and accidental release do seem to occur in all areas with hydraulic  
1086 fracturing such as Pennsylvania (Vengosh et al., 2014) and North Dakota (Lauer et al., 2016).  
1087 The integrated geochemical data presented herein rule out stray gas or brine contamination from  
1088 shale gas development in this study area. In contrast, we observed surface water contamination at

1089 three sites that originated directly from surface spills associated with unconventional oil and gas  
1090 activities. The chemistry of the spill water was identical to the composition of the Marcellus  
1091 flowback and/or produced waters. These results clearly demonstrate the advantage of integrated  
1092 geochemical tools for delineating the environmental effects of energy development, in addition  
1093 to geospatial analysis. The study also shows that surface processes like spills have immediate  
1094 effects, while groundwater quality is not impacted, even in a time scale of three years conducted  
1095 in this study. Future studies should adapt these and similar geochemical tools to evaluate the  
1096 long-term effects of intensive shale gas development in the NAB and other basins, and address  
1097 the potential for groundwater contamination over longer periods of time.

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1099

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1102

1103

### **CONFLICT OF INTEREST**

1104 The authors have no conflicts of interest to declare.

1105

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1116 **Figures Captions**

1117

1118 Fig. 1. Stratigraphic column of the carboniferous aquifers in the study area based on (Martin,  
1119 1998) showing interbedded layers of sandstone, limestone and coal.

1120

1121 Fig. 2. Location of private drinking-water wells and spill sites sampled in northwestern West  
1122 Virginia, superimposed on the local surface geology. Shale-gas wells and the direction and  
1123 length of lateral drills are also shown. The Arches Fork anticline (AFA) that divides Doddridge  
1124 County is show in green, while Burchfield Syncline to the north and Robbison Syncline to the  
1125 south of the AFA are shown in blue (Hennen, 1912; Ryder et al., 2012). No known faults are  
1126 described in the study area.

1127

1128 Fig. 3. Ternary diagrams that display the relative percent of (A) cations, and (B) anions in  
1129 groundwater samples in the study region. Type 1 groundwater (circles) is characterized as Ca-  
1130 Na-HCO<sub>3</sub> type water, while Type 2 (triangles) and 3 (squares) are Ca-Na-Cl type water.  
1131 Historical data from West Virginia collected in 1982 (orange hexagons) shows the presence of  
1132 both fresh and saline-type groundwater prior to shale-gas development in the region and could be  
1133 the result of natural mixing (Shultz, 1984). The abundance of methane is preserved by using a  
1134 blue-red color intensity scale, where methane concentrations of 0 ccSTP/L are blue and range up  
1135 to red for [CH<sub>4</sub>] >40 ccSTP/L. For samples from which methane was not analyzed, data is shown  
1136 with a grey symbol. The same color and label scheme is used for groundwater in all subsequent  
1137 figures.

1138

1139 Fig. 4. Bromide (A), Ca (B), Na (C), Mg (D), dissolved inorganic carbon (DIC) (E), and SO<sub>4</sub> (F)  
1140 versus chloride (Cl) concentrations in low-Cl Type 1 water and high-Cl Type 2 and Type 3  
1141 groundwater from the study area. Significant (p<0.05) positive linear correlations were found for  
1142 Br (r = 0.79), Na (r = 0.62), and DIC (r = 0.35) with Cl concentrations. Type 2 and Type 3  
1143 groundwater had lower Na/Cl ratios but no significant difference was found in the Na/Cl ratio  
1144 between Type 2 and Type 3 wells. Water types 2 and 3 had high Br/Cl (>0.0015) ratios with a  
1145 strong linear correlation between Br and Cl (r = 0.97 and r = 0.56), but with different Br/Cl  
1146 ratios, reflecting of mixing of freshwater with different brine-like sources.

1147

1148

1149 Fig. 5. Boron (A), lithium (B), and strontium (B) isotope and elemental variations in  
1150 groundwater from the study area.  $\delta^{11}\text{B}$  values in the saline water types were high compared to  
1151 the low-saline groundwater of Type 1 but lower than the composition of Upper Devonian brines,  
1152 and likely reflect contribution of deep-source brines modified by water-rock interactions with  
1153  $^{11}\text{B}$ -depleted rocks.  $\delta^7\text{Li}$  values, particularly in Type 2 and Type 1 waters, were mostly consistent  
1154 with values found in Upper Devonian brines, but not in the Marcellus Formation brines. The  
1155  $^{87}\text{Sr}/^{86}\text{Sr}$  rations in the groundwater samples were indistinguishable between the water types, and  
1156 were more consistent with values found in Appalachian coals (0.70975 to 0.71910) than the  
1157 Devonian age brines (Chapman et al., 2012; Vengosh et al., 2013).

1158

1159 Fig. 6. Variations of methane (CH<sub>4</sub>) (A) and ethane (C<sub>2</sub>H<sub>6</sub>) (B) concentrations,  $\delta^{13}\text{C}\text{-CH}_4$  values  
1160 (C) versus chloride concentrations; C<sub>1</sub>/C<sub>2+</sub> hydrocarbon ratios versus  $\delta^{13}\text{C}\text{-CH}_4$  (D);  $\delta^{13}\text{C}\text{-CH}_4$   
1161 versus  $\delta^{13}\text{C}\text{-C}_2\text{H}_6$  (E); and C<sub>1</sub>/C<sub>2+</sub> ratios versus  $\delta^{13}\text{C}\text{-C}_2\text{H}_6$  (F) in groundwater analyzed in this

1162 study. The majority of groundwater samples had  $\delta^{13}\text{C-CH}_4 < -55\text{‰}$  and elevated  $\text{C}_1/\text{C}_{2+}$  that can  
1163 be interpreted as biogenic. However, the positive correlations of  $\text{CH}_4$  and higher order  
1164 hydrocarbons ( $\text{C}_2\text{H}_6$ ) with Cl, the occurrence of higher order hydrocarbons, and the heavy  $\delta^{13}\text{C-}$   
1165  $\text{C}_2\text{H}_6$  all suggest the coherent migration of a gas-rich, saline fluid from deeper formations into  
1166 shallow aquifers, which is consequently diluted and presumably oxidized by meteoric water.  
1167 Maximum  $\text{CH}_4$  concentration is constrained by the upper level (saturation = 40 ccSTP/L at  $10^\circ\text{C}$   
1168 and 1 atm) for  $\text{CH}_4$ , resulting in an observed “roll over” as  $\text{CH}_4$  concentrations approach  
1169 saturation levels for shallow groundwater. No significant variations in the  $\delta^{13}\text{C-CH}_4$  values of the  
1170 groundwater were observed between different water types, with biogenic and thermogenic  
1171 signatures found in all three water types. The persistent presence of ethane and the values of  
1172  $\delta^{13}\text{C-C}_2\text{H}_6$  indicate a uniform background of thermogenic natural gas derived from Type II  
1173 (marine organic matter-shale) or Type III (terrestrial organic matter-coal) kerogen through the  
1174 study area. However, water samples with more enriched  $\delta^{13}\text{C-CH}_4 (> -55\text{‰})$  have a reduction in  
1175 the total amount of hydrocarbons and high  $\text{C}_1/\text{C}_{2+}$  in the residual hydrocarbon-phase, which  
1176 could reflect post-genetic modification of hydrocarbons by migration or oxidation.  
1177

1178 Fig. 7.  $^{20}\text{Ne}$  (A),  $\text{N}_2$  (B), and  $\text{CH}_4$  (C) versus  $^{36}\text{Ar}$  and  $\text{CH}_4$  versus  $^{20}\text{Ne}/^{36}\text{Ar}$  (D) in the shallow  
1179 groundwater wells in the study area. All Type 1 samples have  $^{36}\text{Ar}$  and  $\text{N}_2$  within 14% of the  
1180 temperature-dependent ASW solubility line, while the subset of methane-rich samples showed  
1181 noticeably elevated excess  $^{20}\text{Ne}$ . In contrast, none of the samples in this study, collected before  
1182 or after shale gas drilling showed clear evidence for stripping or fugitive gas contamination. One  
1183 noticeable difference from previous studies is the lower  $^{36}\text{Ar}$  on average for the samples with  
1184 elevated  $\text{CH}_4$  concentrations in Types 2 and 3, which suggests the addition of  $\text{CH}_4$  may have  
1185 induced minor two-phase effects (gas-liquid interactions) in the aquifer. Note also the elevated  
1186  $^{20}\text{Ne}/^{36}\text{Ar}$  in samples with high  $\text{CH}_4$ ; these values indicate significant two-phase migration during  
1187 transport to shallow aquifers.  
1188

1189 Fig. 8.  $^3\text{He}/^4\text{He}$  versus Cl (A),  $^4\text{He}/^{20}\text{Ne}$  (B),  $\text{CH}_4$  (C), and  $\delta^{13}\text{C-CH}_4$  (D);  $^4\text{He}/\text{CH}_4$  versus  
1190  $^{20}\text{Ne}/^{36}\text{Ar}$  (E); and  $^4\text{He}/^{20}\text{Ne}$  versus  $^4\text{He}/^{36}\text{Ar}$  (F) in shallow groundwater samples in the study  
1191 area. A general trend of concomitantly increasing  $^4\text{He}$  and low  $^3\text{He}/^4\text{He}$  in samples rich in Cl and  
1192  $\text{CH}_4$  suggest a source of  $^4\text{He}$  external to the aquifer formation, likely due to an exogenous  
1193 crustal/radiogenic source of natural gas to the aquifer. These data trends clearly distinguish  
1194 sample Types 2 and 3 from Type 1 ( $p < 0.01$ ), but not from each other, and are consistent with the  
1195 migration of a hypothesized exogenous, two-phase fluid, potentially of thermogenic origin, to  
1196 these aquifer systems.  
1197

1199 Fig. 9. Variations of Cl (A),  $\delta^{13}\text{C-CH}_4$  (B),  $\text{CH}_4$  (C),  $\text{C}_1/\text{C}_{2+}$  ratio (D),  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (E), and  
1200  $^4\text{He}/\text{CH}_4$  (F) across the study area in relation to distance to the nearest shale gas well (m). No  
1201 statistically significant relationships were observed between any of these geochemical tracers  
1202 and distance to the nearest gas well were observed. However, the carbon isotopes of  $\text{CH}_4$  ( $\delta^{13}\text{C-}$   
1203  $\text{CH}_4$ ) and  $\text{C}_1/\text{C}_{2+}$  ratios had weak correlations with distance to the nearest shale gas wells  
1204 gas well ( $r = 0.28$ ,  $p < 0.05$  and  $r = 0.27$ ,  $p < 0.05$ , respectively).  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were also  
1205 significantly correlated with distance to the nearest shale gas well ( $r = 0.40$ ,  $p < 0.04$ ).  
1206  
1207

1208 Fig. 10. Relationships between Cl (A), CH<sub>4</sub> (B), C<sub>2</sub>H<sub>6</sub> and heavier aliphatic hydrocarbons (C),  
1209 δ<sup>7</sup>Li (D), <sup>87</sup>Sr/<sup>86</sup>Sr (E), δ<sup>13</sup>C-CH<sub>4</sub> (F), <sup>4</sup>He/<sup>20</sup>Ne (G), CH<sub>4</sub>/<sup>36</sup>Ar (H), and <sup>4</sup>He/CH<sub>4</sub> (I) in shallow  
1210 groundwater wells before and after shale gas drilling and hydraulic fracturing in the study area.  
1211 Dash lines represent a 1:1 line, indication no change in time. All of these geochemical tracers  
1212 showed no changes in groundwater sampled post-shale gas development as compared to baseline  
1213 values, indicating no impact from shale gas development.  
1214



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## 1 Tables

2

3 Table 1. Major chemistry for groundwater samples. All ratios are in molar units. Blank entries  
4 indicate no analysis for that constituent.

Sample ID <sup>a</sup>	Type	Co. <sup>2</sup>	Distance to well (m)	Cl (mg/L)	Br/Cl (x10 <sup>-3</sup> )	Na/Cl (x10 <sup>-3</sup> )	DIC (mg/L)	<sup>13</sup> C-DIC (‰)	Ba (mg/L)	As (ppb)	Sr/Cl (x10 <sup>-3</sup> )	<sup>87</sup> Sr/ <sup>86</sup> Sr	B/Cl (x10 <sup>-3</sup> )	δ <sup>11</sup> B (‰)	Li/Cl (x10 <sup>-3</sup> )	δ <sup>7</sup> Li (‰)
WV-1a	1	DD	3104	3		49.0	289	-16.50	0.17	6.95	31.7		86.4		10.5	
WV-1b	1	DD	3104	3		48.5	278		0.31	6.27	48.5		76.1		11.3	
WV-2a	1	DD	1485	1		39.1	146		0.19	28.45	56.2		47.6		9.2	
WV-2b	1	DD	1485	2		26.3	143		0.19	26.76	36.3		27.6		5.4	16
WV-3a	1	DD	1951	2		41.4	253	-14.54	0.33	20.69	49.9		35.9		11.3	
WV-3b	1	DD	1951	3		44.5	250		0.37	24.86	54.6		24.3		9.3	
WV-4	1	DD	513	3		13.1	193	-15.74	0.69	5.67	61.3		22.6		8.2	
WV-5	1	DD	513	9		2.8	167	-14.92	0.74	9.59	21.8		5.2		1.9	
WV-6	1	DD	1937	1		25.8	195	-15.61	0.50	15.50	130.8		61.4		21.6	
WV-7	1	DD	1944	1		4.8	42	-15.90	0.05	0.07	46.0		164		1.8	
WV-8a	1	DD	599	3		27.3	229	-11.85	0.46	2.46	96.7		50.1		17.6	
WV-8b	1	DD	599	12		20.9	504	-15.21	0.05	11.59	1.3		48.9		3.2	
WV-8c	1	DD	599	3		31.1	227		0.44	1.85	73.3		36.6		12.6	
WV-10a	1	DD	939	21		6.6	172	-16.93	0.25	7.45	4.5		12.2		2.0	
WV-10b	1	DD	939	11		48	836	-15.90	0.06	6.59	4.2		51.5		6.3	
WV-10c	1	DD	939	20		10	292	-18.4	0.25	8.25	4.7	0.7130	12.6		2.1	18
WV-11	1	DD	488	5		13.0	174	-15.44	0.43	8.27	24.3		23.8		6.2	
WV-11b	1	DD	488	5		7.1	145		0.41	6.25	24.0		14.1		4.9	
WV-11c	1	DD	488	4		15.3	161		0.39	6.42	32.2		20.7		6.8	
WV-12	1	DD	491	5		13.9	174		0.42	7.82	26.0		26.7		6.8	
WV-21	1	DD	1032	23		6.5	298	-19.88	0.37	0.71	4.9		12.2		2.2	
WV-22	1	DD	69	8		11.5	228	-20.17	0.00	1.02	31.0		24.1		6.3	
WV-25	2	DD		51	1.8	4.2	344	-17.29	0.52	2.33	5.5	0.7126	7.2	20	1.1	18
WV-27a	1	DD	752	20		13.7	446	-14.27	0.09	0.54	1.9		16.3		1.9	
WV-27b	1	DD	752	25		11.8	471	-13.3	0.13	0.63	1.6	0.7130	12.4		1.4	19
WV-29a	2	DD	1420	53	1.6	0.3	374	-15.38	0.02	6.49	<0.1		7.3		0.1	
WV-29b	1	DD	1421	32		0.1	323.93		0.02	4.53	<0.1		8.6		<0.1	
WV-29c	1	DD	1420	45		6.9	396	-14.9	0.00	3.86	0.0		8.0		0.8	20
WV-31a	1	DD	893	5		19.9	219	-15.92	0.64	0.03	47.4		44.7		11	
WV-31b	1	DD	893	5		21.0	172		0.53	0.04	50.3		48.9		11.9	
WV-32a	1	DD	1576	1		6.6	65	-19.08	0.18	0.33	47.4		67.1		8.2	
WV-32b	1	DD	1576	1		6.2	62		0.14	0.25	39.1		30.6		6.1	
WV-33	1	DD	542	1		40.9	319	-17.73	0.66	7.31	206.6		116		26.1	
WV-36a	2	DD	757	159	1.7	6.6	619	-4.27	0.28	11.82	1.6	0.7128	3.9	26	0.9	20
WV-36b	3	DD	757	58	3.1	1.0	322	-8.5	0.55	13.26	3.0	0.7129	2.3		0.1	
WV-36c	2	DD	757	696	1.9	1.3	632		0.00	7.73	0.3	0.7128	0.8	25	0.2	20
WV-37a	2	DD	1126	793	1.7	0.1			0.53	0.00	0.3		0.3		0.1	
WV-37b	2	DD	1126	83	2.5	3.4	328	-17.8	0.00	0.35	0.4	0.7128	3.9		0.7	20
WV-38a	2	DD	1677	110	2.2	2.4	312	-14.94	0.50	3.62	1.3		3.5	23	1.0	
WV-38b	3	DD	1677	660	3.3	1.0	323	-14.7	0.33	3.33	0.2	0.7128	0.7		0.2	18
WV-39a	1	DD	1085	32		6.8	378.23	-18.39	0.14	10.55	2.8	0.7129	6.0	16	0.7	15
WV-39b	1	DD	1085	32		2.9	373.00	-14.2	0.57	10.80	11.7	0.7129	5.8	13	1.9	15
WV-39c	1	DD	1085	42		3.2	172.00		0.57	7.20	8.8		4.2		1.2	
WV-40a	1	DD	1351	29		5.7	338	-17.22	0.38	0.67	10.6	0.7129	9.6	17	1.7	17
WV-40b	1	DD	1351	19		<0.1	334		0.24	0.53	16.1		14.3		2.3	
WV-40c	1	DD	1351	20		7.5	340	-16.9	0.32	0.60	16.1	0.7129	14.0		2.4	18
WV-41a	1	DD	938	4		5.0	245	-18.62	0.68	1.05	72.7		16.7	18	3.8	
WV-41b	1	DD	938	5		6.5	235		0.82	1.26	75.7		21.9		4.2	
WV-51a	3	DD	212	347	7.6	0.4	203	-14.7	2.08	37.26	1.7	0.7128	0.5		0.2	13
WV-51b	3	DD	212	172	3.6	0.8	230	-18.0	0.91	41.79	2.0	0.7128	1.0		0.3	
WV-52a	3	DD	61	540	3.9	1.5	448	-16.8	4.22	1.04	0.2	0.7127	1.2	20	0.2	20
WV-52b	2	DD	61	337	2.4	1.6	387	-17.1	0.00	2.54	0.2	0.7127	1.9	21	0.2	20
WV-53	1	DD	861	41		1.3	149.00	-14.3	0.38	3.16	3.0	0.7133	2.4		0.6	14
WV-54	1	DD	903	31		5.9	314.84	-17.3	0.11	18.93	1.2	0.7130	12.1	16	1.0	20
WV-55b	1	DD	1677	3		26.6	214		0.42	0.38	62.8		81.7		8.6	
WV-55c	1	DD	1677	4		17.6	216		0.33	0.71	38.4		38.8		4.0	
WV-56	1	DD	2133	38		3.6	240.02	-17.9	0.40	1.65	3.6	0.7129	8.9	14	0.8	18
WV-57	1	DD	2133	6		14.8	210		0.35	2.04	20.2		39.7		3.9	
WV-58a	3	DD	2167	773	8.7	1.0	252	-5.3	2.74	0.62	1.4	0.7132	0.5	18	0.2	16
WV-58b	3	DD	2167	900	3.7	0.9	258	-8.7	3.39	2.30	1.2	0.7132	0.4	22	0.2	
WV-59	2	DD	2133	80	2.2	4.8	480	-12.7	0.08	3.71	0.3	0.7129	7.1	19	0.4	20
WV-60b	1	DD	2165	28		5.6	282	-19.7	0.05	4.90	0.4		13.0	17	0.7	21
WV-60c	1	DD	2165	29		7.4	298	-21.5	0.00	3.71	0.4		14.7		0.7	21
WV-61	1	DD	2222	30		2.4	193.84	-16.4	0.57	14.62	6.8	0.7121	6.6		1.0	18
WV-62b	1	DD	2107	17		4.2	191		0.58	6.82	9.8		10.0		1.4	
WV-62c	1	DD	2107	13		7.1	168		0.47	6.06	9.8		11.2		1.4	
WV-63	1	DD	2088	21		3.3	199		0.68	6.77	11.7		7.1		1.6	
WV-64a	3	DD	2258	383	4.2	1.2	251	-19.0	1.09	1.10	1.2	0.7130	1.4		0.2	18
WV-64b	3	DD	2258	509	3.4	1.2		-20.4	1.98	26.21	1.6	0.7130	0.9	18	0.2	18
WV-65	1	DD	1533	15		4.1	195		0.42	1.87	10.8		7.8		2.0	
WV-66b	1	DD	495	3		5.1	128		0.08	1.10	27.7		6.1		10.3	
WV-66c	1	DD	495	5		3.4	148		0.10	0.24	21.1		4.2		8.0	
WV-101b	2	DD	744	88	0.5	2.5	277		0.24	1.84	1.1	0.7129	2.8		0.4	21
WV-101c	2	DD	744	80	0.2	2.6	287	-18.8	0.18	2.19	1.2	0.7129	3.5		0.4	21
WV-102	1	DD	737	8		3.8	204		0.50	3.41	18.5		10.1		2.7	



WV-103	1	DD	737	11		10.8	191		0.02	6.57	<0.1		7.4		0.2	10.4
WV-104	1	DD	1514	2		36.5	221		0.66	1.99	58.6		84.2			
WV-105	1	DD	813	9		16.0	260		0.29	0.03	8.2		33.5		5.0	
WV-106	1	H	1011	2		39.6	313		0.42	1.66	178.4		47.9		16.2	
WV-107	1	DD	2107	3		4.9	181		0.64	0.44	209.0		52.0		11.6	
WV-108b	1	DD	755	4		14.8	221		0.17	1.22	73.0		35.9		9.8	
WV-108c	1	DD	723	3		24.8	246		0.21	1.11	83.9		36.8		10.7	
WV-109b	1	DD	929	4		14.6	232		0.78	0.00	71.0		33.4		10.5	
WV-109c	1	DD	929	3		30.0	238		0.77	0.00	96.7		46.8		13.9	
WV-110	1	T	526	2		3.9	74		0.10	1.05	28.3		36.6		0.7	
WV-111	1	T	503	3		24.5	199		0.11	7.92	26.6		50.9		3.9	
WV-112	1	DD	1223	2		20.4	201		0.52	4.82	120.7		28.0		15.8	
WV-113	1	DD	1265	8		0.9	118		0.21	0.26	5.6		2.4		7.5	
WV-116b	2	DD	5180	79	2.5	3.1	350		0.07	9.86	0.2		3.6		0.5	20
WV-116c	2	DD	5180	73	2.1	4.4	370	-18.5	0.04	12.10	0.2	0.7130	4.4	17	0.6	19
WV-117	1	DD	378	12		1.3	92		0.55	4.01	8.9		8.2		0.9	
WV-300	1	DD	1658	1		47.1	279		0.31	0.12	414.0		280		45.3	
WV-301b	1	DD	650	28		4.7	236	-13.1	0.57	9.48	8.8	0.7128	10.3		2.0	14
WV-301c	1	DD	650	48		3.2	249.00	-15.2	0.35	19.39	2.9	0.7128	6.7		0.9	17
WV-302b	1	DD	516	27		2.8	177	-18.1	0.59	19.18	7.2	0.7128	4.5		1.2	14
WV-302c	1	DD	516	2		28.0	169		0.47	22.83	61.1	0.7128	42.7		12.3	14
WV-303b	1	DD	552	14		3.9	154		0.45	12.96	14.3		10.1		2.8	
WV-303c	1	DD	552	18		3.0	160		0.46	9.84	10.5		5.0		2.0	
WV-304	1	DD	457	7		9.7	193		0.95	3.47	56.3		16.8		4.2	
WV-305	1	DD	542	<1		159.7	154		0.39	10.71	481.5		461		90.2	
WV-306	1	DD	542	<1		5.4	361		0.04	0.14	18.7		90.2	23	3.1	
WV-308	1	DD	1701	1		57.6	194		0.67	0.59	393.3		107		41.2	
WV-309	1	DD	1932	14		4.0	305		0.26	0.10	4.8		28.4		2.3	
WV-311	1	DD	1587	<1		169.8	161		0.75	1.39	1355		576		103.9	
WV-312	1	DD	1408	<1		47.1	186		0.33	0.04	586.0		223		56.5	
WV-313	2	DD	906	59	1.8	1.9	334		0.09	1.27	0.4	0.7127	12.6	16	0.8	20
WV-314b	2	H	389	2366	2.2	0.3	161	-14.4	0.77	4.39	0.5	0.7129	0.2	20	0.2	19
WV-314c	2	H	389	2232	1.8	0.9	492	-14.8	2.88	3.69	0.5	0.7129	0.2	17	0.2	19
WV-315	1	DD	2125	1		47.7	424		0.18	2.81	129.3		65.6		18.4	
WV-316	1	DD	2196	9		27.0	483		0.01	4.69	2.3		52.1		4.7	
WV-317	2	DD	2336	54	1.8	5.0	361	-14.8	0.02	4.92	1.2	0.7125	9.2	19	1.1	20
WV-318	1	DD	1114	1		8.0	56		0.04	0.00	30.5		40.4		3.3	
WV-319	1	DD	1117	<1		38.9	132		0.10	0.18	301.8		216		28.8	
WV-320	1	DD	912	2		73.1	246		0.00	16.83	<0.1		92.2		0.1	
WV-321	1	DD	830	5		3.7	261		0.39	0.44	85.6		17.3		20.8	
WV-322	1	DD	744	3		4.3	214		0.00	6.82	0.6		12.3		4.3	
WV-323	1	H	1025	47		2.3	252.00	-16.8	0.19	0.79	9.2	0.7133	2.7	13	1.1	16
WV-324b	1	H	964	24		2.3	188	-17.1	0.43	0.30	7.4	0.7131	3.8		1.4	15
WV-324c	1	H	964	37		0.8	182	-19.3	0.44	0.34	4.7		1.8		0.8	
WV-325	1	H	834	3		15.4	221		0.38	9.90	37.9		33.4		8.1	
WV-326	1	H	467	3		10.8			0.26	0.42	68.8		32.4		5.4	
WV-327	1	R	765	6		12.8	290		0.67	1.12	91.1		60.9		11.4	
WV-329	1	R	925	3		18.2	239		1.13	4.85	181.7		86.0		15.6	
WV-400	1	T	261	3		4.9	114		0.10	0.17	29.1		45.4		3.3	
WV-401	1	T	874	2		62.3	287	-18.4	0.12	0.17	84.5		134		14.3	
WV-412	1	DD	141	26		8.3	322	-16.2	0.00	0.28	<0.1		8.3		0.1	
WV-414	1	DD	912	6		22.6	246		0.21	0.43	20.9		35.0		5.3	
WV-417	1	DD	1177	21		12.3	400	-15.2	0.24	2.45	8.9	0.7127	20.1		2.5	
WV-427	1	R	615	5		22.9	337	-19.7	0.92	27.89	92.5		34.0		8.8	
WV-428	1	R	402	7		33.8	248	-18.9	0.22	15.58	10.7		64.9		5.4	
WV-429	1	DD	277	1		131.3	256	-20.6	0.10	3.50	25.1		273		25.1	
WV-435	1	H	184	3		<0.1	218		0.39	1.60	78.6		23.9		10.9	
WV-501	1	W	521	5		5.8	239		0.38	2.60	21.1		52.2		4.8	
WV-502	1	W	772	17		2.6	159		0.25	0.31	9.3		7.2		0.6	
WV-503	3	W	675	159	3.1	0.9	145	-19.6	1.41	15.70	1.8	0.7129	0.6		0.2	16
WV-504	1	T	478	5		5.3	193		0.24	2.58	34.7		23.8		4.5	
WV-505	1	DD	1806	5		38.0	328	-11.2	0.00	0.47	15.6		77.0		7.9	
WV-511	1	H	334	2		10.9	206		0.45	0.71	98.3		34.0		13.0	
WV-512	1	H	393	28		1.3	262	-19.5	0.80	3.01	11.3		2.3		0.8	
WV-514	1	H	840	6		1.9	340	-17.9	0.02	0.00	27.5		14.4		7.9	
WV-515	1	DD	1161	37		5.7	330.00	-21.2	0.52	1.37	7.4	0.7128	5.8		1.3	16
WV-516	1	DD	847	22		3.4	239	-21.4	0.79	8.13	14.1	0.7129	6.7		1.7	11
WV-517	1	DD	883	21		11.4	289	-18.0	0.09	0.00	1.9	0.7126	14.6	15	2.9	20
WV-519	1	DD	1397	20		1.9	224	-16.7	0.15	0.00	18.1		6.8		2.8	
WV-602	1	R		1		113.0	311		0.32	10.72	99.0		155		33.8	

<sup>a</sup>Timeline samples are labeled alphabetically (a = pre-drill, b or c are consecutive samples post-drill).

<sup>b</sup>County: DD=Doddridge, H=Harrison, R=Ritchie, T=Tylor, W=Wetzel

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14 Table 2. Dissolved hydrocarbon gas chemistry for groundwater samples. Blank entries indicate  
 15 no analysis for that constituent.

Sample ID*	[CH <sub>4</sub> ] (ccSTP/L)	[C <sub>2</sub> H <sub>6</sub> ] (ccSTP/L)	[C <sub>3</sub> H <sub>8</sub> ] (ccSTP/L)	[i-C <sub>4</sub> H <sub>10</sub> ] (ccSTP/L)	[n-C <sub>4</sub> H <sub>10</sub> ] (ccSTP/L)	[i-C <sub>5</sub> H <sub>12</sub> ] (ccSTP/L)	[n-C <sub>5</sub> H <sub>12</sub> ] (ccSTP/L)	C <sub>1</sub> /C <sub>2</sub> +	δ <sup>13</sup> C-CH <sub>4</sub> (‰)	δ <sup>13</sup> C-C <sub>2</sub> H <sub>6</sub> (‰)
WV-1a	0.34	2.81E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12048	-70.90	
WV-1b	0.09	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-2a	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-2b	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-3a	2.74	1.96E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	14025	-93.25	
WV-3b	15.33	1.22E-03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12578	-91.14	-34.2
WV-4	0.13	1.04E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12547	-70.03	
WV-5	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-6	0.59	3.70E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	16022	-87.56	
WV-7	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-52.86	
WV-8a	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-73.61	
WV-8b	0.15	1.71E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	8746	-59.55	
WV-8c	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-70.15	
WV-10a	0.39	3.95E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9767	-67.62	
WV-10b	0.07	6.24E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	11343	-64.19	
WV-10c	0.23	1.85E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12146	-69.84	
WV-11a	0.37	3.54E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	10550	-95.40	
WV-11b	0.41	3.10E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	13065	-95.95	
WV-11c	0.19	1.44E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	13145	-77.55	
WV-12	0.28	2.81E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9880	-95.40	
WV-21	2.48	2.24E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	11031	-50.59	
WV-22	0.97	1.69E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5750	-35.06	
WV-25	0.08	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-27a	8.81	1.54E-03	3.45E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5703	-62.85	-35.6
WV-27b	7.81	1.27E-03	3.44E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5985	-61.89	-36.2
WV-29a	2.39	6.01E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	3968	-69.41	
WV-29b	0.92	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-66.85	
WV-29c	2.36	4.75E-04	4.31E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4924	-59.36	
WV-31a	0.99	8.15E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12145	-57.74	
WV-31b	1.35	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-53.46	
WV-32a	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-32b	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-40.43	
WV-33	0.37	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-95.08	
WV-36a	27.99	1.42E-02	6.64E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1959	-64.35	-38.6
WV-36b	29.89	1.29E-02	6.65E-04	4.21E-07	3.85E-07	b.d.l.	b.d.l.	2201		-38.0
WV-36c	18.45	8.55E-03	1.65E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2154	-66.63	-38.6
WV-37a	4.44	9.82E-04	5.24E-07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4522	-67.36	
WV-37b	5.01	1.16E-03	5.98E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4114	-65.91	
WV-38a	13.41	5.27E-03	4.55E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2522	-65.07	-36.8
WV-38b	12.78	5.12E-03	9.56E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2453	-61.20	-38.2
WV-39a	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-31.91	
WV-39b	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-39c	d.n.r.	d.n.r.	d.n.r.	d.n.r.	d.n.r.	d.n.r.	d.n.r.			
WV-40a	0.58	6.58E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	8765	-63.73	
WV-40b	3.15	2.87E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	10988		
WV-40c	1.62	1.64E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9896		
WV-41a	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-41b	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-67.46	
WV-51a	1.84	2.78E-04	1.46E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	6580	-82.80	
WV-51b	1.37	1.84E-04	3.14E-07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	7423	-86.41	
WV-52a	9.26	1.81E-03	1.36E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5086	-79.65	-37.0
WV-52b	6.66	1.38E-03	6.21E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4617	-76.90	
WV-53	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-71.82	
WV-54	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-59.05	
WV-55b	2.05	1.43E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	14326	-58.48	
WV-55c	0.01	4.82E-07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12956		
WV-56	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-57	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-19.23	
WV-58a	25.52	8.50E-03	2.01E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2995	-50.69	-37.1
WV-58b	28.82	9.22E-03	4.25E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	3123	-47.89	-37.6
WV-59	8.45	1.41E-03	4.95E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5961	-67.77	
WV-60b	0.35	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-57.67	
WV-60c	4.16	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-60.28	
WV-61	2.28	3.48E-04	1.59E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	6518	-49.33	-38.8
WV-62b	1.19	9.01E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	13258	-46.26	
WV-62c	0.64	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-47.31	
WV-63	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-64a	2.05	4.43E-04	1.26E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4612	-78.70	
WV-64b	3.68	7.76E-04	7.35E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4326	-73.07	
WV-65	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-28.24	
WV-66b	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-65.11	
WV-66c	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-72.46	
WV-101b	0.27	5.06E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5365	-44.23	
WV-101c	0.24	3.68E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	6524	-47.59	
WV-102	0.16	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-77.31	
WV-103	0.14	1.10E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12625	-74.77	
WV-104	0.11	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-73.18	
WV-105	5.72	3.63E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	15749	-78.45	-35.0
WV-106	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-107	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-108b	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-50.26	
WV-108c	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-109b	0.07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-48.88	
WV-109c	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-110	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-57.05	

WV-111	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			-71.44
WV-112	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-113	0.06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-116b	0.96	3.20E-04	6.16E-06	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2932		-58.38
WV-116c	0.65	1.99E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	3257		-55.76
WV-117	0.07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			-91.36
WV-300	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-301b										
WV-301c	6.66	4.92E-04	7.47E-07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	13527		-69.11
WV-302b	2.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-302c	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-303b	1.05	1.17E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	8975		
WV-303c	0.24	2.52E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9357		
WV-304	2.65	2.80E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9457		
WV-305	4.37	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-306	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-308	2.24	2.33E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9645		
WV-309	2.14	2.17E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9845		
WV-311	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-312	0.22	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-313	7.41	5.99E-03	2.34E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1232		
WV-314b	36.87	3.70E-02	1.42E-04	2.68E-06	2.24E-06	4.65E-07	4.32E-07	992		-39.0
WV-314c	21.46	1.95E-02	9.55E-05	5.55E-07	6.21E-07	b.d.l.	b.d.l.	1097	-69.45	-38.3
WV-315	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-316	6.85	7.16E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9568		-35.1
WV-317	9.16	9.28E-03	7.95E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	979		
WV-318	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-319	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-320	2.14	2.20E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	9752		
WV-321	1.87	1.38E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	13615		
WV-322	0.09	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-323	5.20	2.05E-03	5.68E-07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2540		
WV-324b	1.65	1.90E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	8714		
WV-324c	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-40.38	
WV-325	0.57	4.91E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	11548		
WV-326	2.36	3.59E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	6579		
WV-327	3.14	2.77E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	11355		
WV-329	1.35	1.09E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12355		
WV-400	0.07	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-34.36	
WV-401	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-412	2.60	5.07E-04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5136	-60.93	
WV-414	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-48.40	
WV-417	0.29	3.26E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	8780	-65.30	
WV-427	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-70.68	
WV-428	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-51.72	
WV-429	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-54.78	
WV-435	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			
WV-501	0.74	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-63.74	
WV-502	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-54.28	
WV-503	0.70	5.95E-05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	11727	-60.40	
WV-504	0.08	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-52.95	
WV-505	1.12	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-58.55	
WV-511	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-58.67	
WV-512	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-68.27	
WV-514	0.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-61.49	
WV-515	0.89	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-59.03	
WV-516	1.99	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-74.17	
WV-517	1.77	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-60.94	
WV-519	0.19	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.		-66.24	
WV-602	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.			

16  
17  
18

<sup>a</sup>Timeline samples are labeled alphabetically (a = pre-drill, b or c are consecutive samples post-drill).

19 Table 3. Dissolved major and noble gas chemistry for groundwater samples. Blank entries  
 20 indicate no analysis for that constituent.

Sample ID <sup>a</sup>	[N <sub>2</sub> ] (ccSTP/L)	[ <sup>3</sup> He] (x10 <sup>6</sup> ccSTP/L)	[ <sup>36</sup> Ne] (x10 <sup>6</sup> ccSTP/L)	[ <sup>36</sup> Ar] (x10 <sup>6</sup> ccSTP/L)	<sup>3</sup> He/ <sup>4</sup> He (R/Ra)	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>38</sup> Ar/ <sup>36</sup> Ar	<sup>20</sup> Ne/ <sup>36</sup> Ar	<sup>3</sup> He/CH <sub>4</sub> (x10 <sup>3</sup> )	3H (T.U.)
WV-1a	13.00	46.5	169.8	1031.4	0.984	9.801	295.1	0.1896	0.165	137.3	
WV-1b	13.54	51.1	174.7	1098.1	0.961	9.811	295.7	0.1901	0.159	539.2	
WV-2a	10.99	43.0	125.5	895.4	0.914	9.803	295.3	0.1884	0.140	7002	
WV-2b	16.95	39.5	169.0	1234.5	1.021	9.781	295.4	0.1869	0.137	18453	
WV-3a	11.70	62.1	143.6	952.5	0.842	9.790	295.6	0.1886	0.151	22.6	
WV-3b	12.62	87.6	163.6	1069.1	0.851	9.772	295.4	0.1855	0.153	5.7	
WV-4	10.46	47.7	146.9	936.1	0.965	9.808	295.5	0.1881	0.157	366	
WV-5	13.78										
WV-6	11.95	45.2	136.0	946.3	1.014	9.815	295.8	0.1905	0.144	76.2	
WV-7	10.95	42.2	162.5	1004.4	1.006	9.785	296.4	0.1864	0.162	9894	
WV-8a	16.43	61.3	361.7	1346.6	0.871	9.782	295.3	0.1891	0.269	3648	5.4
WV-8b	15.48	67.1	342.1	1341.6	0.881	9.777	295.6	0.1897	0.255	450.0	6.3
WV-8c	15.99	57.5	358.0	1376.0	0.861	9.796	295.1	0.1894	0.260	3672	7.0
WV-10a	13.03	51.5	181.7	1044.5	0.912	9.791	295.3	0.1886	0.174	133.3	6.1
WV-10b	12.68	47.7	172.7	1032.0	0.905	9.804	295.7	0.1887	0.167	674.3	7.7
WV-10c	12.43	41.6	183.4	1023.4	0.921	9.776	295.2	0.1876	0.179	184.8	
WV-11a	14.35	81.1	183.5	1087.5	0.920	9.820	294.8	0.1857	0.169	217.3	
WV-11b	14.94	61.2	1100.5	180.4	0.881	9.802	295.7	0.1857	0.164	151.1	4.7
WV-11c	14.70	70.0	186.7	1036.4	0.875	9.824	295.7	0.1866	0.180	368.4	7.0
WV-12	14.65	72.2	192.1	1118.3	0.902	9.802	295.7	0.1874	0.172	259.6	
WV-21	11.56	63.4	141.2	962.8	0.946	9.791	295.7	0.1867	0.147	25.6	
WV-22	10.67	63.5	135.5	974.4	0.834	9.814	295.7	0.1866	0.139	65.5	
WV-25	12.64	6746.0	261.1	1020.3	0.045	9.863	295.4	0.1865	0.256	83284	
WV-27a	11.41	6315.0	402.4	897.9	0.021	9.817	299.0	0.1866	0.448	716.7	
WV-27b	9.84	5269.8	289.6	998.2	0.020	9.821	301.6	0.1896	0.290	675.1	4.7
WV-29a	10.26	8451.1	135.0	878.2	0.022	9.821	295.8	0.1904	0.154	3543	
WV-29b	10.97	7245.7	150.7	981.2	0.042	9.764	295.6	0.1897	0.154	7904	7.0
WV-29c	11.02	5146.7	158.4	944.3	0.036	9.771	295.6	0.1884	0.168	2181	
WV-31a	12.65	48.0	150.1	986.1	0.985	9.779	295.5	0.1879	0.152	48.5	
WV-31b	14.21	79.5	153.4	1148.5	0.940	9.802	296.2	0.1896	0.134	58.7	
WV-32a	13.97	82.1	147.0	1131.3	0.841	9.777	295.7	0.1877	0.130	5334	
WV-32b	14.68	71.2	143.1	1020.5	0.831	9.795	295.3	0.1871	0.140	22631	
WV-33	17.07	48.0	157.2	1257.2	1.006	9.792	295.4	0.1896	0.125	129.7	
WV-36a	10.09	91451.7	506.5	926.3	0.021	9.827	307.4	0.1890	0.547	3268	
WV-36b	10.41	101214.1	568.5	831.9	0.019	9.851	306.2	0.1866	0.683	3387	
WV-36c	10.78	96874.4	498.5	947.4	0.023	9.830	303.4	0.0186	0.526	5250	
WV-37a	11.32	3979.7	261.1	942.0	0.030	9.781	297.1	0.1874	0.277	895.6	
WV-37b	11.82	4026.7	234.7	963.7	0.036	9.789	296.1	0.1877	0.243	803.1	3.5
WV-38a	10.25	67154.7	438.5	868.3	0.019	9.831	299.1	0.1876	0.505	5008	3.0
WV-38b	12.45	54658.0	387.7	1074.6	0.025	9.762	298.0	0.1895	0.361	4276	2.5
WV-39a	14.16	868.0	219.4	1120.1	0.106	9.796	295.9	0.0187	0.196	242776	
WV-39b	13.59	961.4	206.8	1095.9	0.104	9.802	296.1	0.1904	0.189	47129	3.5
WV-39c											
WV-40a	12.05	128.1	169.2	1056.6	0.781	9.821	295.7	0.1904	0.160	222.3	
WV-40b	11.87	102.1	176.5	1033.9	0.792	9.802	295.1	0.1867	0.171	32.4	
WV-40c	12.02	119.7	163.6	1030.3	0.831		295.1	0.1874	0.159	73.7	5.1
WV-41a	11.99	61.2	146.1	946.8	0.871	9.777	295.7	0.1890	0.154	28588	
WV-41b	14.15	61.1	149.5	1148.6	0.970	9.761	296.4	0.1869	0.130	74099	4.1
WV-51a	13.87	4789.7	394.6	892.3	0.023	9.824	297.1	0.1874	0.442	2600	
WV-51b	14.24	6021.4	385.5	964.4	0.020	9.831	298.0	0.1841	0.400	4408	4.7
WV-52a	10.72	357154.6	601.1	769.3	0.019	9.851	298.5	0.1904	0.781	38558	5.1
WV-52b	9.98	298647.5	442.7	887.6	0.018	9.871	299.0	0.1877	0.499	44836	6.2
WV-53	12.14	436.4	172.7	1222.4	0.084		295.6	0.1901	0.141	16543	
WV-54	10.90	102.4	132.5	961.5	0.698		295.8	0.1899	0.138	11856	
WV-55b	12.15	41.7	132.4	927.1	0.874	9.781	295.7	0.1896	0.143	20.4	3.2
WV-55c	10.95	53.5	151.4	918.6	0.934	9.760	295.5	0.1897	0.165	8574	
WV-56	11.62	235.4	131.4	1031.8	0.180		296.0	0.1898	0.127	7954	
WV-57	20.50										
WV-58a	12.46	214324.1	1196.8	1070.7	0.018	9.914	308.8	0.1891	1.118	8398	3.7
WV-58b	13.21	193214.7	384.1	1116.2	0.023	9.897	306.5	0.1886	0.344	6705	3.0
WV-59	11.57	1326.4	235.5	1007.9	0.031	9.805	297.6	0.1900	0.234	157.0	
WV-60b	14.75	127.8	153.5	927.6	0.832	9.795	295.5	0.1878	0.165	368.3	
WV-60c	14.22	502.3	224.4	1156.5	0.190	9.824	296.5	0.1901	0.194	120.8	
WV-61	10.41	7698.5	173.0	983.1	0.020		295.6	0.1875	0.176	3376	
WV-62b	14.02	72.2	132.1	919.2	0.847	9.791	295.4	0.1866	0.144	60.4	
WV-62c	14.52	63.4	190.2	999.6	0.920	9.804	294.6	0.1901	0.190	99.3	2.0
WV-63	12.14	53.5	129.9	990.3	0.861	9.780	295.3	0.1866	0.131	1776	
WV-64a	14.16	7255.0	239.4	966.4	0.021	9.779	297.4	0.1876	0.248	3538	
WV-64b	13.88	8967.7	249.5	963.6	0.031	9.761	298.4	0.1879	0.259	2439	
WV-65	12.14	49.8	142.2	996.4	0.924	9.799	295.4	0.1894	0.143	4387	
WV-66b	12.18	68.5	160.1	970.9	0.871	9.778	296.1	0.1904	0.165	27665	
WV-66c	13.55	67.1	161.2	1099.1	0.931	9.791	295.4	0.1884	0.147	20884	
WV-101b	12.14	978.6	204.6	873.0	0.030	9.790	297.1	0.1864	0.234	3606	5.7
WV-101c	11.97	1021.4	215.7	917.2	0.021	9.804	297.0	0.1843	0.235	4251	8.3
WV-102											
WV-103	11.15	51.6	137.4	907.5	0.911	9.787	295.0	0.1893	0.151	371.7	
WV-104											
WV-105	11.55	59.9	124.4	905.2	0.868		295.7	0.1904	0.137	10.5	
WV-106	13.49	43.5	136.0	1020.5	0.972	9.801	295.7	0.1864	0.133	1058	
WV-107											
WV-108b	14.24	79.5	182.4	1006.1	0.801	9.824	295.7	0.1876	0.181	6011	
WV-108c											
WV-109b	12.84	43.1	179.7	937.0	0.957	9.806	295.6	0.1894	0.192	605	
WV-109c	12.68	46.2	176.5	968.8	0.986	9.791	295.3	0.1867	0.182	3729	
WV-110	19.15	72.4	143.0	1326.1	0.931	9.785	295.2	0.1861	0.108	1827	

WV-111	13.54	43.7	153.0	964.6	0.979	9.799	295.4	0.1876	0.159	1001	4.7
WV-112	12.20	80.1	136.4	1030.4	0.803	9.821	295.4	0.1881	0.132	14195	4.4
WV-113	11.90										
WV-116b	12.01	815.4	249.6	932.6	0.196	9.802	296.1	0.1886	0.268	852.5	7.1
WV-116c	11.84	906.2	241.7	1089.0	0.163	9.790	298.0	0.1904	0.222	1399	2.7
WV-117	13.45										
WV-300											
WV-301b											
WV-301c	14.01	75.1	168.7	969.5	0.751	9.810	295.1	0.1890	0.174	11.3	4.7
WV-302b	12.96	103.2	192.2	1097.6	0.852	9.779	296.0	0.1876	0.175	51.1	3.0
WV-302c	12.35	63.1	171.6	1037.6	0.951	9.780	295.3	0.1869	0.165	2951	
WV-303b	12.75	54.7	175.4	1053.0	0.965	9.795	295.7	0.1898	0.167	51.9	
WV-303c	13.06	61.1	183.5	1009.3	0.981	9.776	295.0	0.1890	0.182	259.4	5.6
WV-304	10.69	53.6	128.8	933.4	0.822	9.767	294.5	0.1866	0.138	20.2	
WV-305											
WV-306											
WV-308	11.72	53.2	147.5	1018.6	0.930	9.821	295.6	0.1843	0.145	23.7	
WV-309	12.66	68.4	138.0	962.1	0.831	9.804	295.6	0.1865	0.143	32.0	
WV-311	17.24	50.0	132.5	1232.4	0.981		295.7	0.1880	0.108	1259	
WV-312	13.95	60.8	146.0	988.0	0.975	9.811	295.6	0.1878	0.148	281.7	7.2
WV-313	9.97	72156.4	269.5	900.4	0.017	9.851	301.3	0.1880	0.299	9735	3.5
WV-314b	12.61	154214.6	452.4	931.4	0.019	9.821	300.1	0.1890	0.486	4183	3.1
WV-314c	12.03	243142.4	406.8	923.2	0.019	9.842	299.4	0.1892	0.441	11328	4.7
WV-315	11.66	46.2	143.4	982.0	0.924	9.797	295.4	0.1883	0.146	1711	5.2
WV-316	10.99	56.6	141.2	962.9	0.931		295.4	0.1899	0.147	8.3	8.1
WV-317	8.94	96548.4	204.7	702.3	0.023	9.794	299.6	0.1877	0.291	10536	2.7
WV-318	12.99	39.0	137.6	861.5	0.826	9.757	295.3	0.1875	0.160	1258	6.5
WV-319	11.49	60.0	137.9	930.8	0.964	9.764	295.4	0.1899	0.148	1764	5.0
WV-320	10.45	70.0	136.0	1036.6	0.921	9.800	295.6	0.1874	0.131	32.7	
WV-321	10.59	42.5	138.0	1114.5	0.981	9.791	296.5	0.1886	0.124	22.7	7.5
WV-322	11.59	49.4	153.9	995.6	0.952	9.787	295.7	0.1877	0.155	568.3	3.5
WV-323	9.69	2154.4	163.4	825.9	0.037	9.842	295.4	0.1851	0.198	414.5	
WV-324b	12.87	90.2	157.2	963.8	0.687	9.786	295.3	0.1888	0.163	54.6	
WV-324c	13.24	206.2	214.5	1335.3	0.398	9.789	295.4	0.1899	0.161	7800	
WV-325	11.50	55.0	136.0	976.1	0.942	9.792	294.8	0.1886	0.139	97.0	
WV-326	11.50	53.5	161.6	946.8	0.942	9.821	295.7	0.1909	0.171	22.7	
WV-327	16.69	72.7	127.0	1233.6	0.694	9.831	295.6	0.1879	0.103	23.1	
WV-329	12.97	42.7	126.0	919.8	0.980	9.802	295.3	0.1881	0.137	31.6	8.4
WV-400	11.95	51.6	143.5	979.2	0.941	9.798	296.1	0.1882	0.147	767.8	6.0
WV-401	11.95	65.1	130.0	946.8	0.880	9.802	295.7	0.1879	0.137	30429	6.6
WV-412	13.84	8270.0	324.8	940.1	0.036	9.762	299.4	0.1874	0.345	3179	2.5
WV-414	11.98										
WV-417	11.64	61.4	147.0	907.1	0.765	9.801	294.8	0.1894	0.162	215.0	7.4
WV-427	12.50	47.0	132.0	941.8	0.964	9.805	295.9	0.1899	0.140	1922	
WV-428	10.15										
WV-429	12.14	51.2	124.5	972.4	0.894	9.795	295.6	0.1879	0.128	5697	
WV-435	11.29	49.0	163.4	919.8	0.962	9.797	295.7	0.1881	0.178	8999	7.5
WV-501	14.66	59.5	168.4	1221.2	0.981	9.795	295.1	0.1895	0.138	80.2	2.1
WV-502	19.65	37.5	358.0	1320.6	0.979	9.820	294.9	0.1905	0.271	6608	
WV-503	13.70	635.8	241.2	1153.3	0.045	9.795	296.5	0.1899	0.209	911.5	
WV-504	12.64	52.2	156.5	1010.6	0.964	9.790	295.4	0.1905	0.155	692.0	3.5
WV-505	13.75	76.4	146.5	1188.1	0.950	9.760	294.7	0.1897	0.123	68.2	
WV-511	11.82	80.0	146.2	1216.5	0.940	9.781	296.0	0.1891			
WV-512	13.25	145.4	189.5	1157.1	0.846	9.801	295.5	0.1895	0.164	29786	4.1
WV-514	14.15	51.1	176.4	1192.6	0.960	9.764	295.0	0.1865	0.148	99770	2.4
WV-515	12.96	301.5	223.2	1279.5	0.405	9.804	296.5	0.1904	0.174	339.2	
WV-516	13.06	197.9	189.6	1040.6	0.345	9.805	294.6	0.1879	0.182	99.5	2.7
WV-517	14.05	59.5	179.5	1033.4	1.002	9.782	295.1	0.1876	0.174	33.7	2.5
WV-519	13.21	67.4	154.6	1082.6	0.964	9.790	296.0	0.1880	0.143	346.0	1.9
WV-602											

21 <sup>a</sup>Timeline samples are labeled alphabetically (a = pre-drill, b or c are consecutive samples post-drill).

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24 Table 4. Water chemistry for surface water associated with the flowback spill in Tyler County  
 25 and leaks from the two injection well sites. All ratios are in molar units. Blank entries indicate no  
 26 analysis for that constituent

Sample ID	Sample Descriptions	Date Sampled	Cl (mg/L)	Br/Cl (x10 <sup>-3</sup> )	Li (ppb)	B (ppb)	V (ppb)	Cr (ppb)	As (ppb)	Se (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	δ <sup>11</sup> B (‰)	δ <sup>7</sup> Li (‰)	<sup>87</sup> Sr/ <sup>86</sup> Sr
WV Flowback n = 13	From Ziemkiewicz and He (2015)		42683	4.8				ND	0.08	ND	1365		515			
Tyler - 1	Spill water in Field	1/3/14	18087	6.8	14151	25737	221	679	50.0	282	769376	289	53119	27	11	0.7098
Tyler - 2	Spill water in Field	1/6/14	2133	4.0	841	1600	16.5	51.8	3.4	20.9	55009	25.1	1837	28	14	0.7096
Tyler - 3	Pool by well pad	1/6/14	1031	5.6	413	790	8.1	26.0	2.2	12.8	27067	29.9	975	27	14	0.7096
Tyler - 4	Creek at runoff point	1/6/14	14	3.9	2.65	14.9	0.3	0.7	0.1	0.7	210	3.4	35.3			0.7111
Tyler - 5	Creek upstream	1/6/14	2	ND	0.3	8.6	0.2	0.3	0.1	0.4	67.2	1.7	27.5			
Tyler - 6	Run-off into Creek	2/23/14	669	3.9	197	340	5.3	69.1	5.2	89.0	8269	ND	601.0			0.7098
Tyler - 7	Big Run Creek by pad	2/23/14	21	3.7	3.0	19.6	0.2	0.7	0.2	0.7	267	0.1	44.7			
Tyler - 8	Big Run Creek	2/23/14	6	2.7	0.5	10.0	0.2	0.3	0.2	0.5	74.3	ND	27.8			
Tyler - 9	Middle Island Creek	2/23/14	9	2.5	0.6	9.0	0.2	0.4	0.2	0.6	61.0	ND	27.7			
Tyler - 10	Effluent from well pad	8/29/14	918	4.5	2.2	233	4.9	14.4	3.7	7.0	12519	3.8	1102			0.7095
Lochgully -1	Downstream Creek 1	9/14/13	575	2.1	11.6	0.4	2.5	<DL	<DL	<DL	2068	<DL		20		
Lochgully -2	Downstream Creek 2	9/14/13	367	3.0	33.9	24.1	1.4	<DL	<DL	<DL	1296	<DL				
Hall - 1	Upstream	12/18/13	16	2.7	0.7	20.4	0.4	0.9	0.1	ND	302	ND	74.0			
Hall - 2	Downstream 1	12/18/13	95	4.4	1.0	48.8	1.0	2.7	0.2	0.6	617	ND	127			0.7113
Hall - 3	Downstream 2	12/17/13	80	3.2	0.7	38.7	0.9	2.3	0.2	ND	526	ND	106			0.7113
WV-327	Groundwater well	12/17/13	6	1.8	12.4	105	0.4	0.1	1.1	ND	1247	1.2	765			
WV-329	Groundwater well	12/17/13	3	2.7	10.1	89.0	ND	0.1	4.9	ND	1487	0.7	1450			

27 ND = value below detection

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Figure 1


Age	Group	Unit	Generalized Geologic Section
Permian	Dunkard	Waynesburg / Dunkard Interbedded sandstone and limestone	
		Mather Sandstone	
		Waynesburg Coal	
		Monongahela Group	
Pennsylvanian	Monongahela	Conemaugh Group	
		Allegheny Group	
		Pottsville Group	

Figure 1

Figure 2

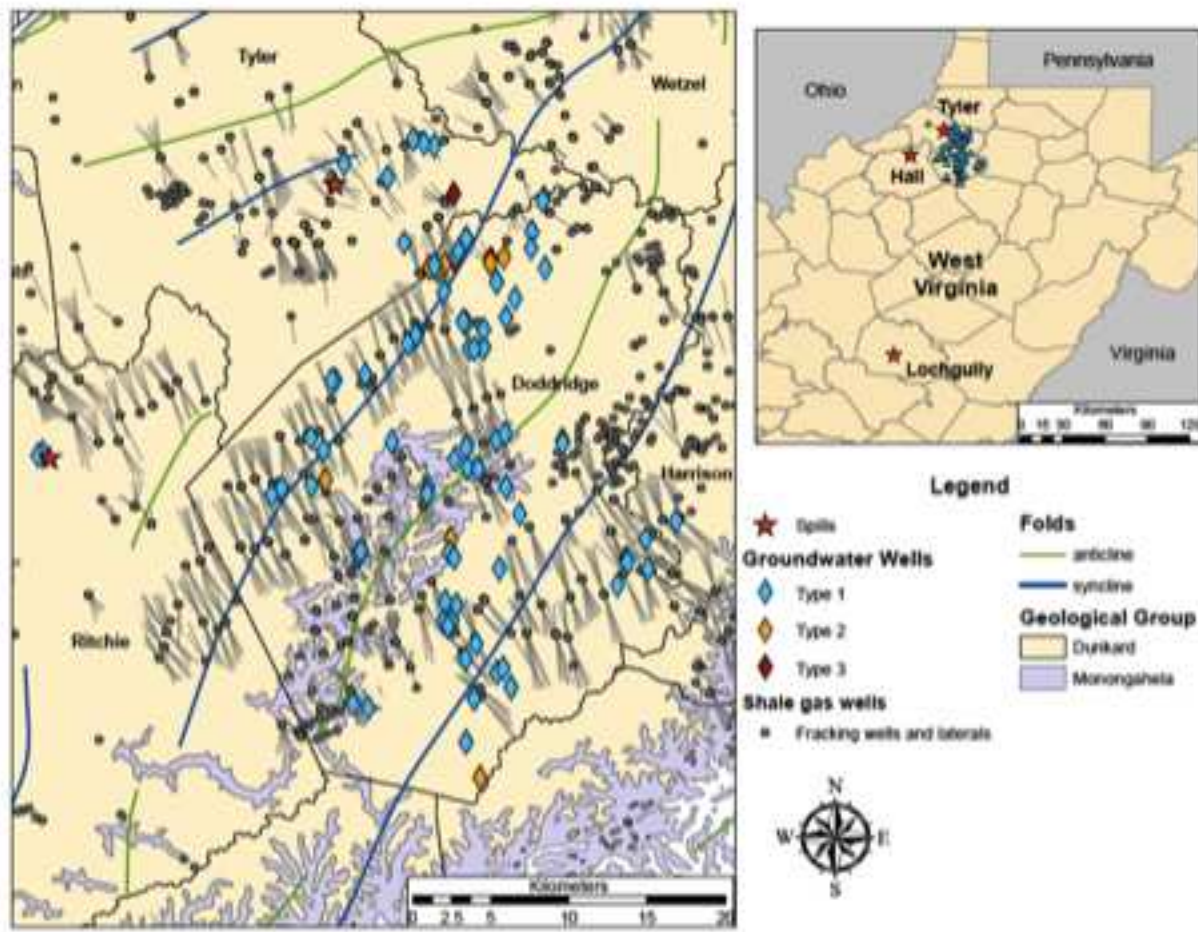


Figure 2



Figure 3

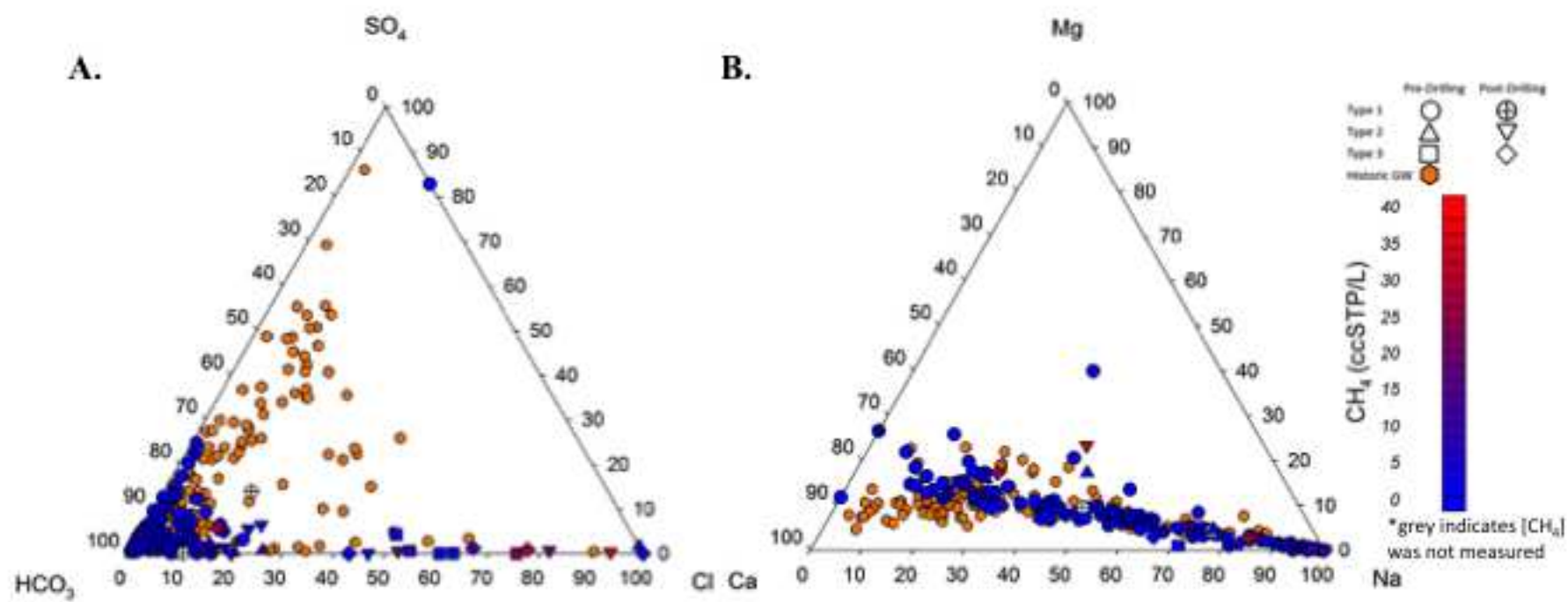


Figure 3

Figure 4

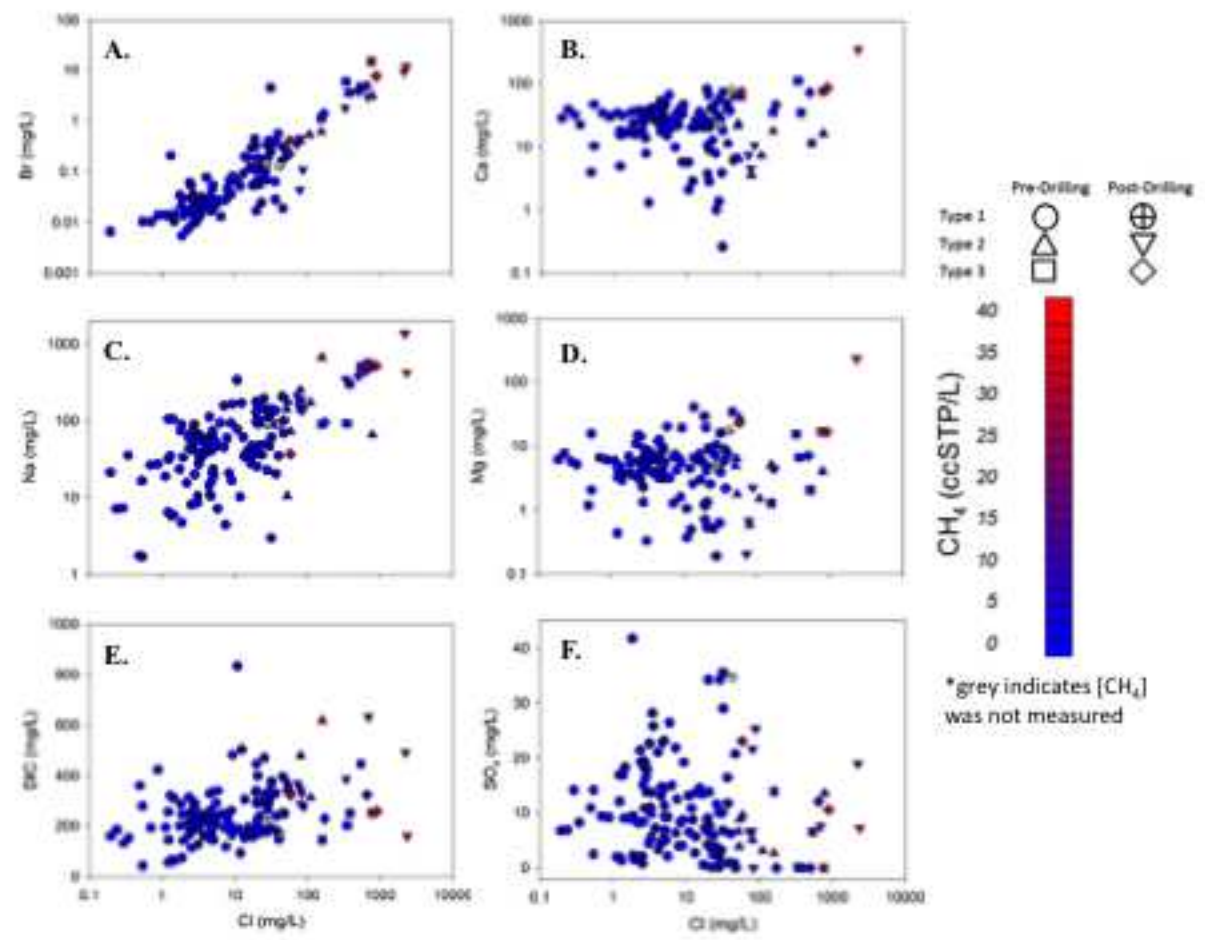


Figure 4

Figure 5

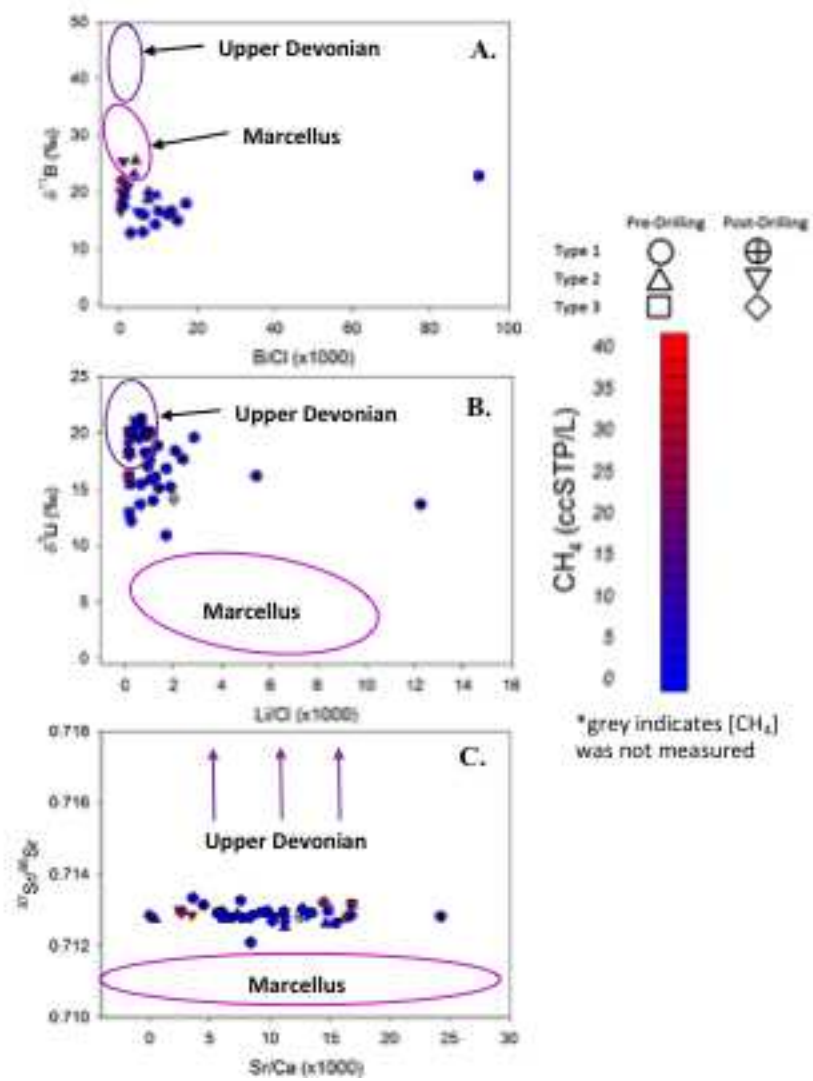


Figure 5

Figure 6

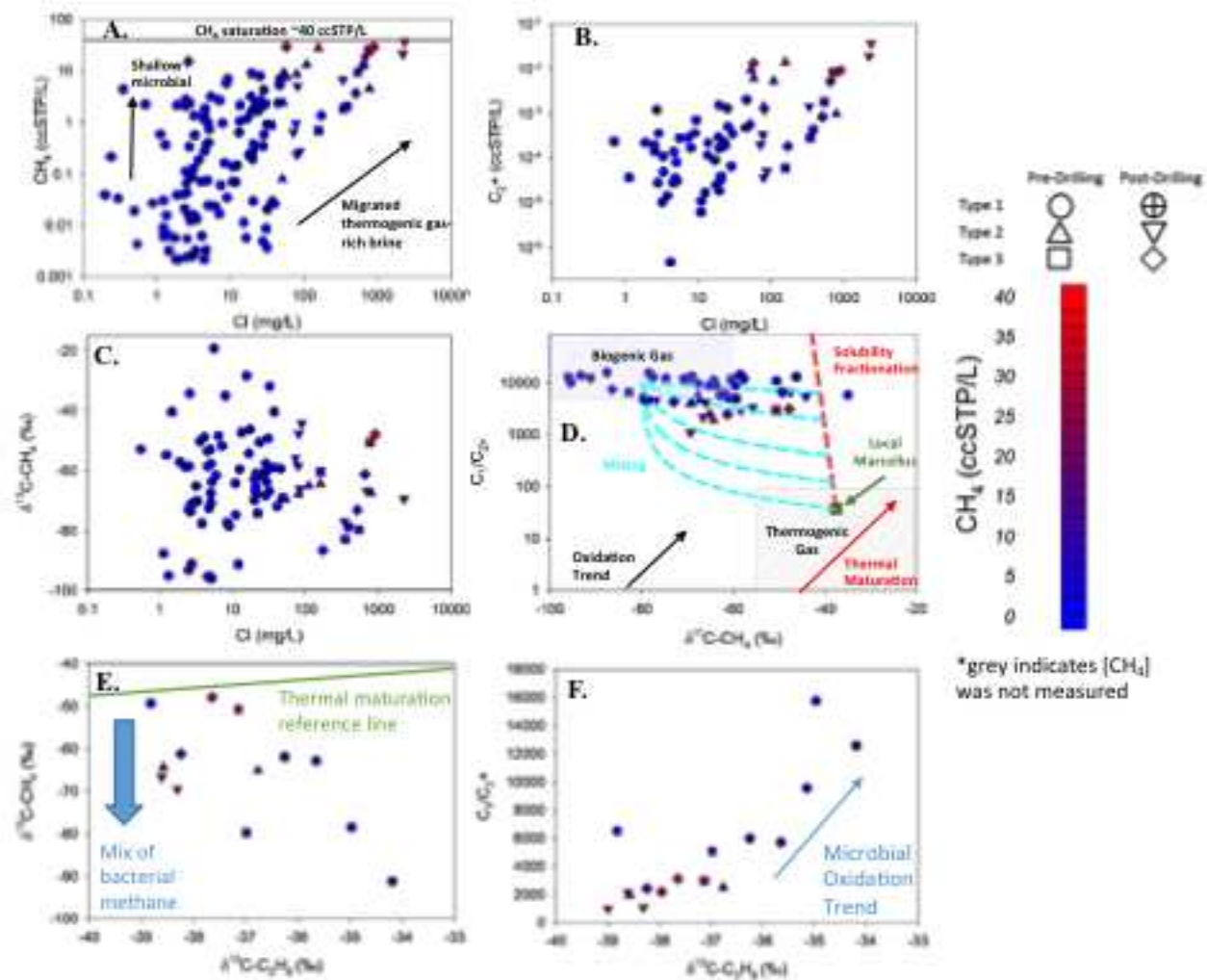


Figure 6

Figure 7

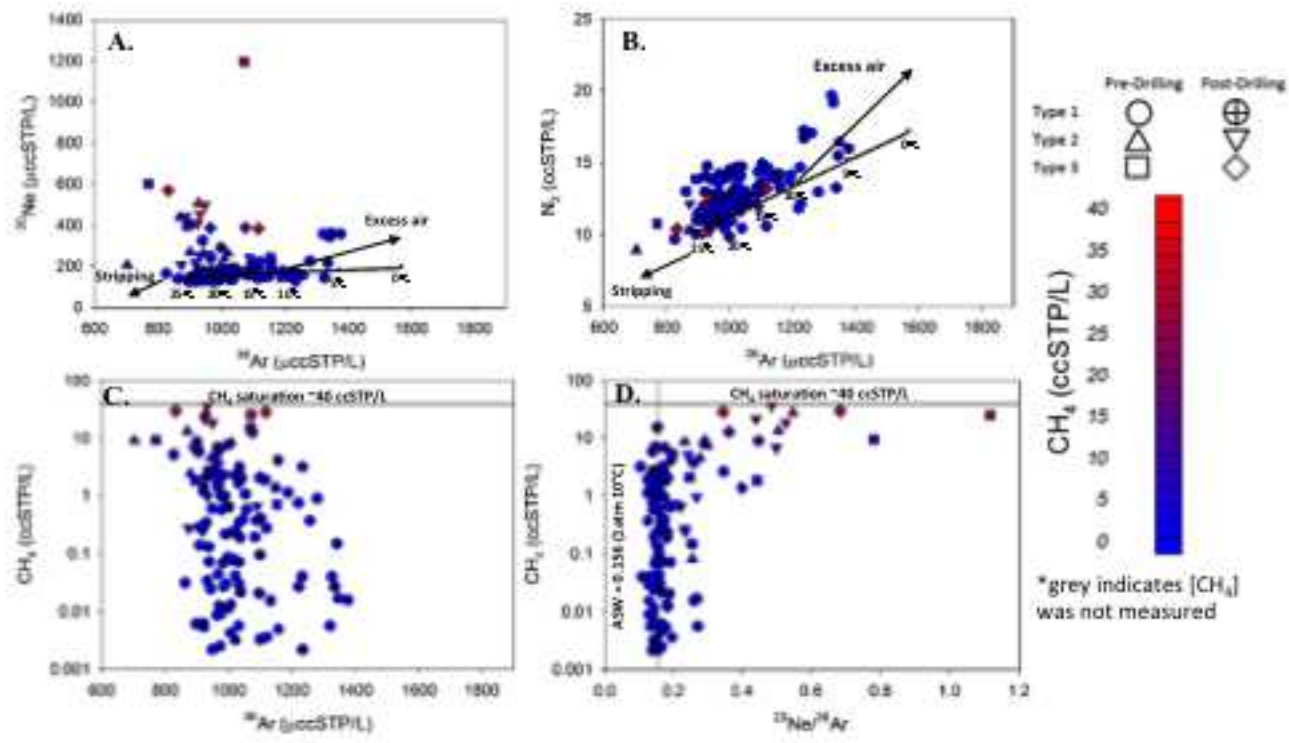


Figure 7

Figure 8

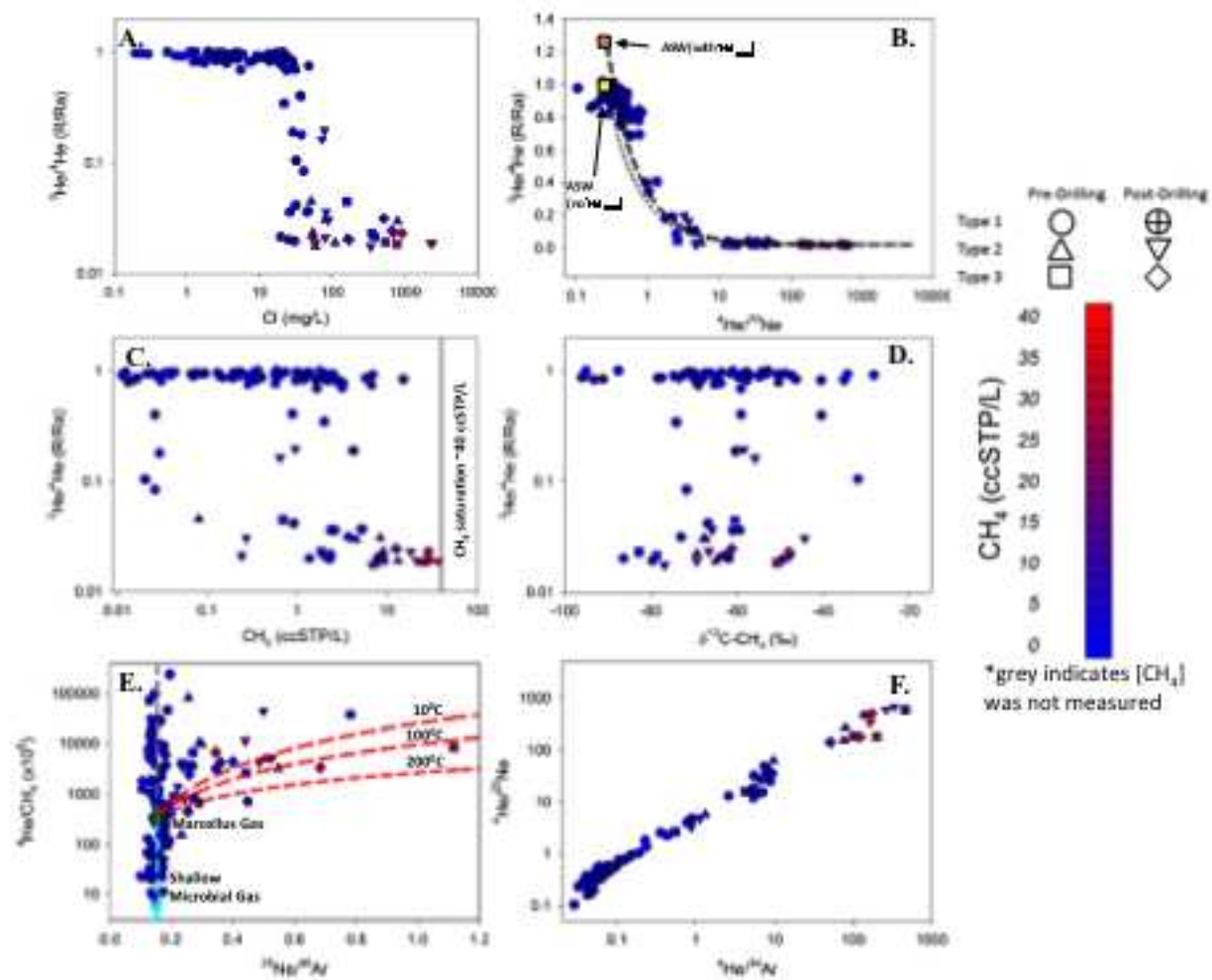


Figure 8

Figure 9

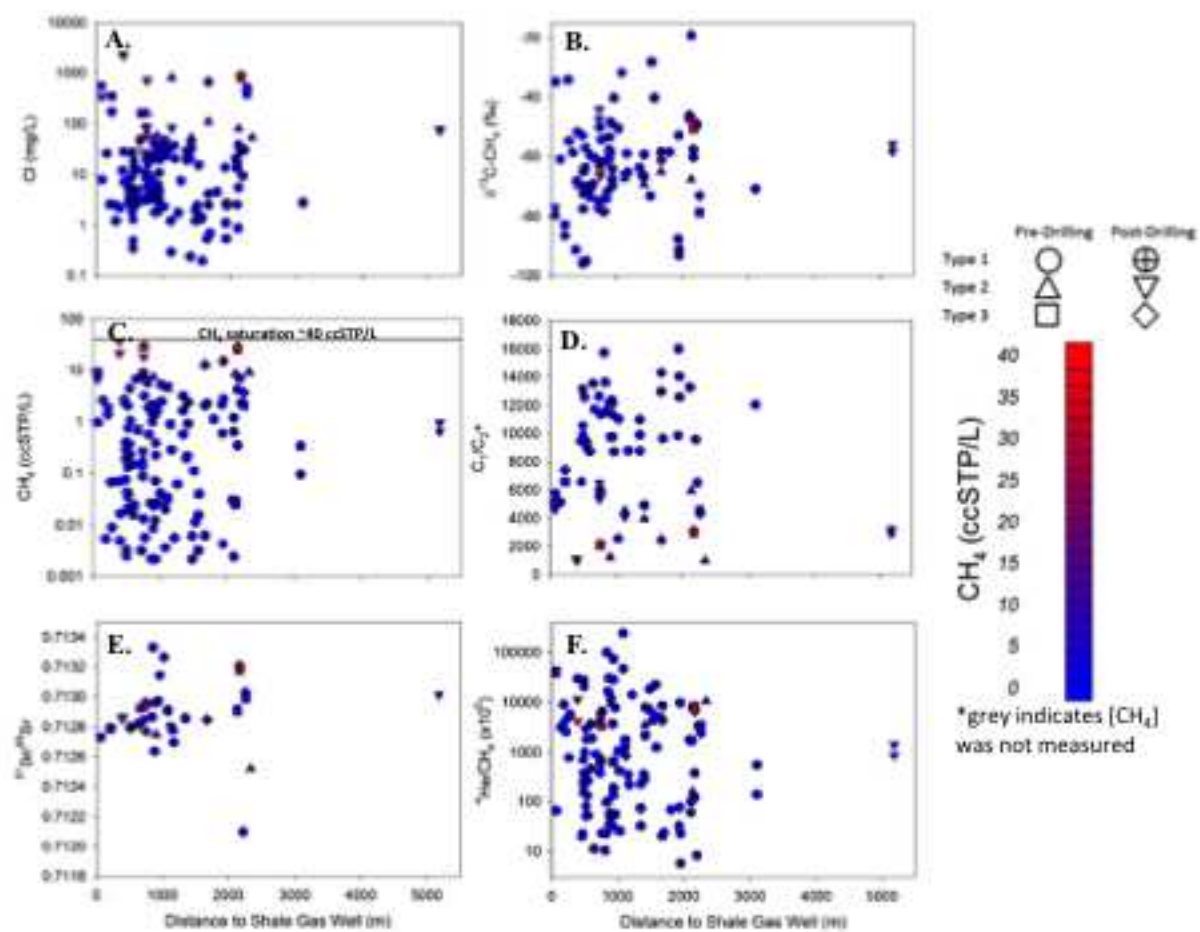


Figure 9

Figure 10

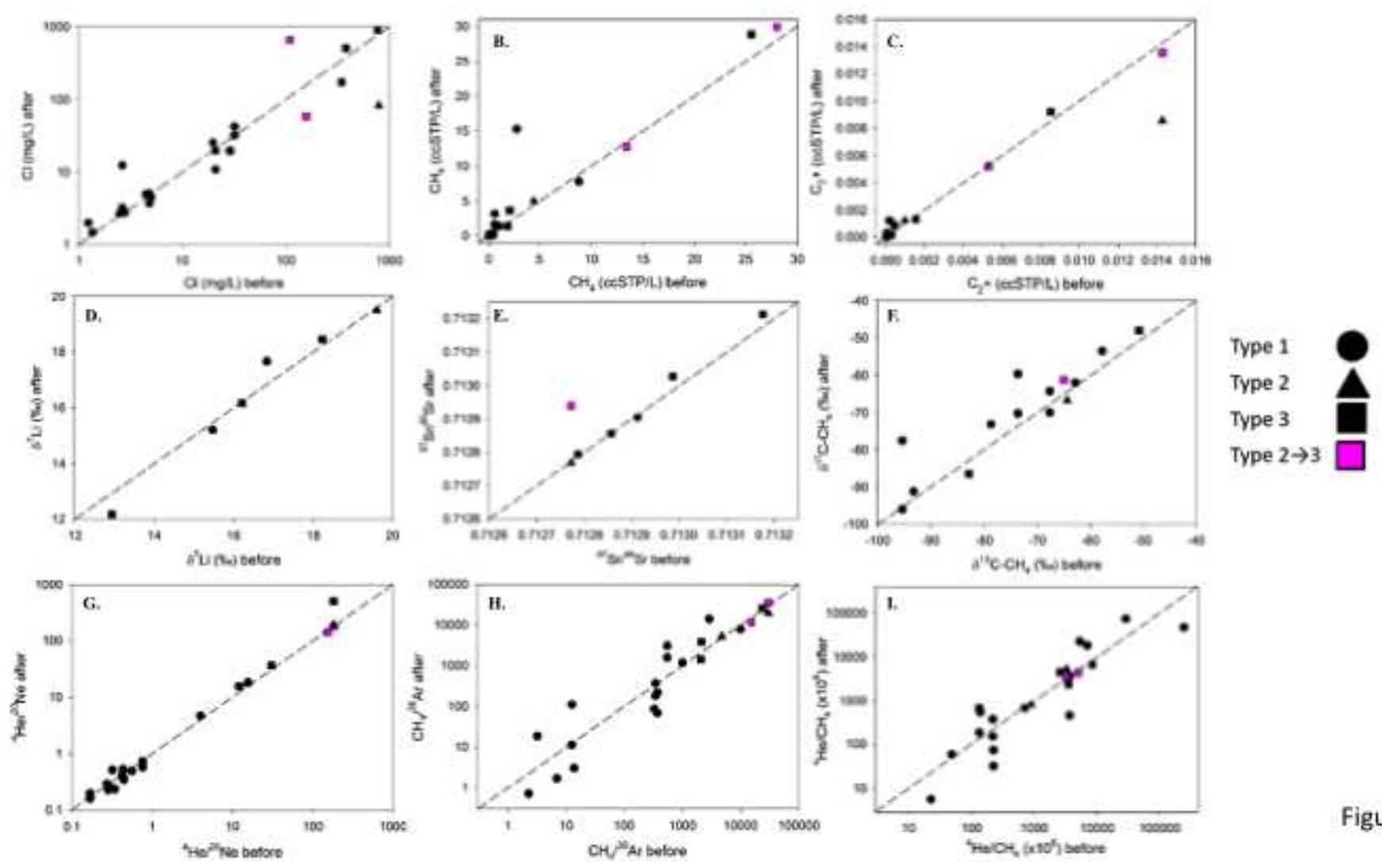


Figure 10