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## Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville shale development, north-central Arkansas

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### Abstract

Exploration of unconventional natural gas reservoirs such as impermeable shale basins through the use of horizontal drilling and hydraulic fracturing has changed the energy landscape in the U.S.A. providing a vast new energy source. The accelerated production of natural gas has triggered a debate concerning the safety and possible environmental impacts of these operations. This study investigates one of the critical aspects of the environmental effects; the possible degradation of water quality in shallow aquifers overlying producing shale formations. The geochemistry of domestic groundwater wells was investigated in aquifers overlying the Fayetteville Shale in north-central Arkansas, where approximately 4,000 wells have been drilled since 2004 to extract unconventional natural gas. Monitoring was performed on 127 drinking water wells and the geochemistry of major ions, trace metals, CH<sub>4</sub> gas content and its C isotopes ( $\delta^{13}\text{C}_{\text{CH}_4}$ ), and select isotope tracers ( $\delta^{11}\text{B}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ ) compared to the composition of flowback-water samples directly from Fayetteville Shale gas wells. Dissolved CH<sub>4</sub> was detected in 63% of the drinking-water wells (32 of 51 samples), but only six wells exceeded concentrations of 0.5 mg CH<sub>4</sub>/L. The  $\delta^{13}\text{C}_{\text{CH}_4}$  of dissolved CH<sub>4</sub> ranged from -42.3‰ to -74.7‰, with the most negative values characteristic of a biogenic source also associated with the highest observed CH<sub>4</sub> concentrations, with a possible minor contribution of trace amounts of thermogenic CH<sub>4</sub>. The majority of these values are distinct from the reported thermogenic composition of the Fayetteville Shale gas ( $\delta^{13}\text{C}_{\text{CH}_4}$  = -35.4‰ to -41.9‰). Based on major element chemistry, four shallow groundwater types were identified: (1) low (<100 mg/L) total dissolved solids (TDS), (2) TDS > 100 mg/L and Ca-HCO<sub>3</sub> dominated, (3) TDS > 100 mg/L and Na-HCO<sub>3</sub> dominated, and (4) slightly saline groundwater with TDS > 100 mg/L and Cl > 20 mg/L with elevated Br/Cl ratios (>0.001). The Sr ( $^{87}\text{Sr}/^{86}\text{Sr}$  = 0.7097 to 0.7166), C ( $\delta^{13}\text{C}_{\text{DIC}}$  = -21.3 to -4.7‰), and B ( $\delta^{11}\text{B}$  = 3.9 to 32.9‰) isotopes clearly reflect water-rock interactions within the aquifer rocks, while the stable O and H isotopic composition mimics the local meteoric water composition. Overall, there was a geochemical gradient from low-mineralized recharge water to more evolved Ca-HCO<sub>3</sub>, and higher-mineralized Na-HCO<sub>3</sub> composition generated by a combination of carbonate dissolution, silicate weathering, and reverse base-exchange reactions. The chemical and isotopic compositions of the bulk shallow groundwater samples were distinct from the Na-Cl type Fayetteville flowback/produced waters (TDS ~10,000-20,000 mg/L). Yet, the high Br/Cl variations in a small subset of saline shallow groundwater suggest that they were derived from dilution of saline water similar to the brine in the Fayetteville Shale. Nonetheless, no spatial relationship was found between CH<sub>4</sub> and salinity occurrences in shallow drinking water wells with proximity to shale-gas drilling sites. The integration of multiple geochemical and isotopic proxies shows no direct evidence of

contamination in shallow drinking-water aquifers associated with natural gas extraction from the Fayetteville Shale.

## 1. Introduction

The combined technological development of horizontal drilling and hydraulic fracturing has enabled the extraction of hydrocarbons from unconventional sources, such as organic-rich shales, and is reshaping the energy landscape of the U.S.A. (Kargbo et al., 2010; Kerr, 2010). Unconventional natural gas currently supplies ~20% of US domestic gas production and is projected to provide ~50% by 2035 (USEIA, 2010). Therefore, ensuring that unconventional natural gas resource development results in the minimal possible negative environmental impacts is vital, not only for domestic production within the U.S.A., but also for establishing guidance for worldwide development of shale gas resources. Recent work in the Marcellus Shale basin demonstrated a relationship between CH<sub>4</sub> concentrations in shallow groundwater and proximity of drinking water wells to shale-gas drilling sites in northeastern Pennsylvania, suggesting contamination of shallow groundwater by stray gas (Osborn et al., 2011a). In addition, a previous study has shown evidence for natural pathways from deep formations to shallow aquifers in northeastern Pennsylvania that may allow leakage of gas or brine, and might pose a potential threat to groundwater in areas of shale gas extraction (Warner et al., 2012). While previous studies have focused on the Pennsylvania and New York portion of the northern Appalachian Basin, many other shale-gas basins currently are being developed that have not been examined for potential effects on water quality. One of the critical aspects of potential contamination of shallow aquifers in areas with shale-gas development is the hydraulic connectivity between shale and other deep formations and overlying shallow drinking water aquifers. Here the quality and geochemistry of shallow groundwater directly overlying the Fayetteville Shale (FS) in north-central Arkansas is investigated. The Fayetteville Shale is an unconventional natural gas reservoir with an estimated total production of 906 billion m<sup>3</sup> (USEIA, 2011). Since 2004, approximately 4,000 shale-gas wells have been drilled there, including both vertical wells and, more recently, horizontal wells.

In this study, water samples from 127 shallow domestic wells in the Hale, Bloyd and Atoka Formations in north-central Arkansas and six flowback/produced water samples from the underlying FS were analyzed in an attempt to identify possible groundwater contamination. Five of the produced water samples were collected within 21 days of fracturing (i.e., defined as flowback water) and a single sample was collected at about a year following hydraulic fracturing (i.e., defined as produced water). The concentrations of major anions (Cl, SO<sub>4</sub>, NO<sub>3</sub>, Br, and dissolved inorganic C [DIC]), cations (Na, Ca, Mg and Sr), trace elements (Li and B), and for a smaller subset of samples dissolved CH<sub>4</sub> and selected isotopic tracers (<sup>11</sup>B, <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>2</sup>H, <sup>18</sup>O, <sup>13</sup>C<sub>DIC</sub>, and <sup>13</sup>C<sub>CH4</sub>) were determined. Using multiple geochemical and isotopic tracers together with their geospatial distribution provides a multidimensional approach to examine potential groundwater contamination in areas of shale gas development. It is hypothesized that shallow groundwater could be contaminated by stray gas migration, possibly associated with poor well integrity, similar to earlier studies (Osborn et al., 2011a). Shallow drinking water could also be contaminated with deeper saline fluids at the same time as the stray gas migration associated with drilling. A third possibility would be natural migration and connectivity between the shallow drinking water aquifers and deeper, higher salinity formation waters through faults or other more permeable pathways (Warner et al., 2012). This study, in conjunction with a United States Geological Survey (USGS) report using the same major element data (Kresse et al., 2012), are to the authors' knowledge the first to report such a comprehensive geochemical evaluation of possible shallow groundwater contamination outside the Marcellus Shale basin (Osborn et al., 2011a; Warner et al., 2012).

## 2. Geologic Setting

The study area is located within the currently active development area for the FS in north-central Arkansas with the majority of samples collected in Van Buren County and the northern part of Faulkner County (Fig. 1). The area is characterized by a rugged and mountainous landscape to the north and rolling hills to the south, spanning the southern area of the Ozark Mountains, to the northern Arkansas River valley (Imes and Emmett, 1994). The bedrock in the study area comprises the Pennsylvanian-age Hale, Bloyd and Atoka Formations, which are composed of shale with interbedded minor occurrences of relatively permeable sandstone, limestone and coal (Cordova, 1963) (Fig. 2). The shale portion of the Atoka underlies the lowlands because of its lack of resistance to weathering (Cordova, 1963), and thin beds of coal are present throughout but limestone is only present in the north of the study area (Cordova, 1963). The Mississippian-age Fayetteville Shale is the target formation during drilling and lies approximately 500-2,100 m below the ground surface (mbgs), with the southern portion of the study area being the deepest. These formations are part of the Western Interior Confining System with groundwater flow restricted to the weathered and fractured upper 100 m of bedrock (Imes and Emmett, 1994). No one formation within this confining system, even where used for a drinking-water supply, forms a distinct aquifer regionally, and the regional designation as a confining unit indicates that on a regional scale these formations impede the vertical flow of water and confine the underlying aquifers. Domestic wells in the area typically provide limited groundwater yields (Imes and Emmett, 1994). The average reported drinking water well depth is 26 m and minimum and maximum of 7.8 m and 120 m, respectively. Wells drilled deeper than 100 m revealed a much more compacted and less permeable section of the formations (Imes and Emmett, 1994).

The underlying Fayetteville Shale production zone is ~ 17 to 180 m thick and occupies an area of approximately 6,500 km<sup>2</sup>; the area of groundwater samples for this study covered approximately 1/3 of the area of the production zone. The density of shale-gas drilling varied widely across the study area. For the set of drinking-water samples, the total number of unconventional shale-gas wells within 1 km (as measured from the well-head) of a given home ranged from zero to over 14 natural gas wells. This well density represents an area of moderate to intense unconventional shale-gas development similar to other areas of extensive shale gas developments, such as in NE Pennsylvania (Osborn et al., 2011a). Importantly, the Fayetteville Shale is the first oil and gas development in this study area. With no records that indicated the presence of historical conventional wells, which may provide possible conduits for vertical migration of stray gas and/or hydraulic fracturing fluids in other shale-gas plays. Saline water unsuitable for human consumption was identified between 150 to 600 mbgs but generally is at least 300 mbgs in the study area (Imes and Emmett, 1994).

The exposed and shallow subsurface geologic formations serving as local aquifers for Van Buren and Faulkner Counties are a series of dominantly sandstone and shale units of the Hale, Bloyd and Atoka Formations (Fig. 2). Subsurface geology, particularly with respect to lateral facies within the Fayetteville Shale, was poorly defined prior to development of gas, and most of the detailed stratigraphic and reservoir analysis were held as proprietary by the companies operating there.

The Fayetteville Shale is a black, fissile, concretionary shale, which contains pyrite and silica replacement fossils in some intervals. The Fayetteville Shale dips from north to south (Fig. 2). The highly organic-rich facies within the Fayetteville Shale is present in the middle and lower part of the formation. Vitrinite reflectance falls within 1.93 to 5.09 percent, which corresponds to the dry gas window (Imes and Emmett, 1994).

The Hale Formation is made up of two members: the lower Cane Hill Member, which is typically composed of silty shale interbedded with siltstone and thin-bedded, fine-grained sandstone, and the

upper Prairie Grove Member composed of thin to massive limey sandstone. The Hale Formation thickness is up to 90 m (Imes and Emmett, 1994). The Cane Hill Member of the Hale Formation is exposed in the extreme northern part of Van Buren County (Fig. 2).

The Bloyd Formation in northwestern Arkansas is formally divided into five members, two of which are limestone members absent in the study area. The lower two thirds of the Bloyd Formation consists dominantly of very thin- to thinly-bedded sandstone with shale interbeds. The upper Bloyd is dominantly a shale with interbedded sandstone that is commonly calcareous; the sandstone units can reach a thickness of up to 24 m (Imes and Emmett, 1994). Total thickness for the Bloyd can exceed 120 m in the study area. Exposures of the Bloyd Formation are found in northern Van Buren County (Fig. 2).

The Atoka Formation in the study area consists of a sequence of thick shales that are interbedded with typically thin-bedded, very-fine grained sandstone. The Atoka Formation is unconformable with the underlying Bloyd Formation with a thickness of up to 7,500 m in the Ouachita Mountains (Imes and Emmett, 1994). The Atoka Formation is exposed throughout the southern portion of the study area (Fig. 2).

### 3. Materials and Methods

All shallow groundwater samples were collected from private drinking water wells by USGS personnel in July and November 2011. Methods for collection of field parameters (pH, temperature, and specific conductance) and water sampling followed standard USGS protocols (Wilde, 2006). These included sampling prior to any holding tanks or filtration, purging water wells until field parameters stabilized, followed by 0.45  $\mu\text{m}$  water filtering on site for water samples collected for trace and major ion analyses. Dissolved gas sample collection followed established protocols (Isotech Laboratories, Inc., 2012). Samples of FS water were collected from production wells (flowback or produced waters) by Arkansas Oil and Gas Commission personnel. Samples were labeled flowback waters if collected within 3 weeks of hydraulic fracturing (5 total samples) and produced water if collected more than 3 weeks after fracturing (1 sample;  $\sim 50$  weeks following fracturing). All water samples were preserved on ice and shipped to Duke University (Durham, North Carolina, USA), where they were refrigerated until analysis.

Samples for major cations, anions, trace metals, and selected isotopes (O, H, B, Sr and C-DIC) were analyzed at Duke University. Isotech Laboratories performed dissolved gas analysis for concentrations of  $\text{CH}_4$  and higher-chain hydrocarbons on 20 samples using chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry to measure  $\delta^{13}\text{C}_{\text{CH}_4}$ .

Dissolved  $\text{CH}_4$  concentrations and  $\delta^{13}\text{C}-\text{CH}_4$  were determined by cavity ring-down spectroscopy (CRDS) (Busch and Busch, 1997) on an additional 31 samples at the Duke Environmental stable Isotope Laboratory (DEVIL) using a Picarro G2112i. Dissolved  $\text{CH}_4$  concentrations were calculated using headspace equilibration, extraction and subsequent concentration calculation by a modification of the method of Kampbell and Vandegrift (1998). For each 1-L sample bottle, 100 mL of headspace was generated by displacing water with zero air ( $\text{CH}_4$ -free air) injected with gastight syringes equipped with luer-lock valves. Bottles were shaken at 300 rpm for 30 min to equilibrate headspace with dissolved  $\text{CH}_4$ . The equilibrated headspace was then extracted with gastight syringes while replacing the extracted volume of headspace with deionized water. The extracted headspace was then injected into Tedlar bags (Environmental Supply, Durham, NC) equipped with septum valves and introduced into the Picarro model G2112-i CRDS (Picarro, Inc., Santa Clara, CA). In some cases, dilution into a second Tedlar bag with  $\text{CH}_4$ -free air (zero-air) was required to keep the measured concentration in the optimal range for the instrument. Calculated detection limits of dissolved  $\text{CH}_4$  were 0.002 mg/L water. Reporting limits for reliable  $\delta^{13}\text{C}-\text{CH}_4$  were 0.1 mg/L, consistent with Isotech Laboratories (Illinois, USA) reporting values.



Concentrations and  $\delta^{13}\text{C}$  values were also corrected for instrument calibrations using known  $\text{CH}_4$  standards from Airgas (Durham, NC) and Isometric Instruments (Victoria, BC).

To confirm the accuracy of the CRDS results, a set of 49 field duplicate groundwater samples was collected and analyzed at Isotech using gas chromatography isotope ratio mass spectrometer (GC-IRMS). These groundwater samples were collected from North Carolina, New York, Pennsylvania and Arkansas in order to span a wider range of both concentrations ( $<0.002$  mg/L through values well above saturation  $\sim 100$  mg/L) and C isotope values ( $-30\text{‰}$  through  $-75\text{‰}$ ). The comparison of the field duplicates using these two independent methods showed good correlation for concentration ( $r^2=0.90$ ; Fig. 3a) and strong correlation for  $\delta^{13}\text{C}_{\text{CH}_4}$  ( $r^2=0.95$ ; Fig. 3b). Relative standard deviation of dissolved  $\text{CH}_4$  concentrations determined by CRDS on field duplicates was 9.8%. Reproducibility of  $\delta^{13}\text{C}$  measurements determined by CRDS for 8 field duplicate samples ranged from a minimum of 0.07‰ to a maximum of 1.0‰. Standard deviation of  $\delta^{13}\text{C}$  measurements ( $n=6$ ) on a laboratory check standard was 0.55‰ over the course of the project.

Major anions were determined by ion chromatography, major cations by direct current plasma optical emission spectrometry (DCP-OES), and trace-metals by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometry (ICP-MS). Four replicate samples showed good reproducibility ( $<5\%$ ) for both major and trace element concentrations. Strontium and B isotopes were determined by thermal ionization mass spectrometry (TIMS) on a ThermoFisher Triton at the TIMS laboratory in Duke University. The average  $^{87}\text{Sr}/^{86}\text{Sr}$  of the SRM-987 standard measured during this study was  $0.710266 \pm 0.000005$  (SD). The average  $^{11}\text{B}/^{10}\text{B}$  of NIST SRM-951 during this study was  $4.0055 \pm 0.0015$ . The long-term standard deviation of  $^{11}\text{B}$  in the standard and seawater replicate measurements was 0.5‰. DIC concentrations were determined in duplicate by titration with HCl to pH 4.5. Values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of water were determined by thermochemical elemental analysis/continuous flow isotope ratio mass spectrometry (TCEA-CFIRMS), using a ThermoFinnigan TCEA and Delta+XL mass spectrometer at DEVIL.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values were normalized to V-SMOW and V-SLAP. The C isotope ratio of dissolved inorganic C determined after acid digestion, on a ThermoFinnigan (Bremen, Germany) GasBench II feeding a ThermoFinnigan Delta+XL Isotope Ratio Mass Spectrometer (IRMS) in the DEVIL lab. Several mL (volume depending on DIC concentration) of each sample were injected into 11-mL septum vials that had each been pre-dosed with 150  $\mu\text{L}$  phosphoric acid and pre-flushed for 10 min with He at 50 mL/min to remove air background. Raw  $^{13}\text{C}$  of resulting  $\text{CO}_2$  was normalized vs Vienna Pee Dee Belemnite (VPDB) using NBS19, IAEA CO-8 standards, and an internal  $\text{CaCO}_3$  standard.

Natural gas well locations (representing locations of the vertical portion of the well) were obtained from the Arkansas Oil and Gas Commission database (Arkansas Oil and Gas Commission, 2012). Arkansas Oil and Gas Commission also provided  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  values for five flowback and one produced water sample. Historical water data were gathered from the USGS National Water Information System (NWIS) data base for the six counties that comprise the bulk of permitted and active gas production wells: Cleburne, Conway, Faulkner, Independence, Van Buren and White Counties (Fig. 2). The data set includes 43 groundwater samples collected near the study area prior to shale-gas development during 1948 and 1983 (USGS, 2013).

## 4. Results and Discussion

### 4.1 Geochemical characterization of the shallow groundwater

The 127 shallow groundwater samples were divided into four major water categories (Fig. 1 and Supplementary data). The first category was low-TDS ( $<100$  mg/L) and generally low-pH ( $\text{pH}<6.6$ ;  $n=54$ ) water. The second was a  $\text{Ca-HCO}_3$  water ( $n=40$ ), with moderate TDS ( $100>\text{TDS}<200$  mg/L). The third was a  $\text{Na-HCO}_3$  water with a wider range of TDS ( $100>\text{TDS}<415$  mg/L;  $n=24$ ). The fourth group

was classified as Ca-Na-HCO<sub>3</sub> water type with the highest TDS (200>TDS<487 mg/L) and slightly elevated Cl (>20 mg/L) and Br/Cl molar ratios > 1x10<sup>-3</sup> (n=9). The fourth group was identified because the elevated Cl and Br/Cl could potentially indicate contamination from the underlying saline formation water (see description below).

The C isotope ratio of dissolved inorganic C ( $\delta^{13}\text{C}_{\text{DIC}}$ ; n= 81 samples) ranged from -22‰ to -10‰ (Supplementary data). The low-TDS and Ca-HCO<sub>3</sub> water types had lower DIC concentrations but all water types had similar  $\delta^{13}\text{C}_{\text{DIC}}$ , while most water samples fell within a narrower and lower range of -20‰ to -17‰. In the Na-HCO<sub>3</sub> groundwater a positive correlation was observed between DIC concentrations and  $\delta^{13}\text{C}_{\text{DIC}}$  values ( $r^2=0.49$ ,  $p<0.05$ ; Fig. 4). The Sr isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) varied from 0.7097 to 0.7166 (Fig. 5a). Most of the Ca-HCO<sub>3</sub> waters had slightly lower  $^{87}\text{Sr}/^{86}\text{Sr}$  (mean =0.71259; n=12) relative to the Na-HCO<sub>3</sub> waters (mean =0.71543; n=13). Boron isotope ratios ( $^{11}\text{B}$ ) showed a wide range from 4‰ to 33‰, with a general increase of  $^{11}\text{B}$  with B content (Fig. 5b) with no systematic distinction between the water types ( $p>0.05$ ). The stable isotope composition of all water types did not show any distinctions ( $p>0.05$ ) related to the water composition (Supplementary data) and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  variations are consistent with the Local Meteoric Water Line (LMWL) (Kendall and Coplen, 2001) of modern precipitation in the region. This similarity suggests a common meteoric origin, and also indicates that all of the geochemical modifications presented below were induced from water-rock interactions along groundwater flowpaths in the shallow aquifers.

Historical groundwater quality data from in or near the study area from the NWIS data base (Fig. 2) included 43 samples collected prior to shale-gas development between 1948 and 1983 (Table 1). Although collected from the same formations, the majority of historical samples were collected to the east, and only three sampling sites overlapped with the intensely sampled part of the study area (Fig. 2); therefore, a complete statistical comparison to historical data was not possible. However, the reported chemical composition of the water samples collected prior to shale gas development in the area was consistent with the Ca-HCO<sub>3</sub> and Na-HCO<sub>3</sub> water types, with a predominance of Na-HCO<sub>3</sub> water type in the Atoka Formation (Fig. 2) as reported in previous studies (Cordova, 1963). Likewise, the range of concentrations in this study fell within the minimum and maximum reported values in the NWIS (Table 1).

#### 4.2. Methane sources in shallow groundwater

Dissolved CH<sub>4</sub> concentrations were determined in 51 of the 127 water samples from wells collected for this study (Supplementary data). Methane was detected (>0.002 mg/L) in 63% of wells (32 of the 51), but only six wells had concentrations >0.5 mg CH<sub>4</sub>/L, with a single sample point (28.5 mg/L) above the potential recommended action level in the U.S.A. [10 mg/L] (Elt Schlager et al., 2001) (Fig. 6). Dissolved CH<sub>4</sub> concentrations were not higher closer to shale gas wells (Fig. 6 and Supplementary data), nor was any statistical difference (student t-test) apparent between concentrations in groundwater of 32 wells collected within 1 km of shale-gas production and 19 wells >1 km away from gas wells ( $p>0.1$ ; Supplementary data).

The C isotope ratios of CH<sub>4</sub> ( $^{13}\text{C}_{\text{CH}_4}$ ) was measurable in 14 of 51 samples (dissolved CH<sub>4</sub>>0.1 mg/L) and ranged from -42.3‰ to -74.7‰ (Fig 7), but the range in  $^{13}\text{C}_{\text{CH}_4}$  in the six samples with concentrations greater than 0.5 mg/L was systematically ( $p<0.01$ ) lower (-57.6‰ to -74.7‰). This result provides evidence for a predominantly biogenic origin of the dissolved gas (i.e., <-55‰) (Coleman et al., 1981; Whiticar et al., 1986; Grossman et al., 1989; Whiticar, 1999). Additionally,  $^{13}\text{C}_{\text{CH}_4}$  of 13 out of 14 samples with measurable  $^{13}\text{C}_{\text{CH}_4}$  did not overlap the reported values (Zumberge et al., 2012) for Fayetteville Shale production gas (Fig. 7). The only one sample with a  $^{13}\text{C}_{\text{CH}_4}$  value (-42.3‰) that approaches the values reported for shale gas had low CH<sub>4</sub> concentration (0.15 mg/L).

Samples with trace ( $<0.5$  mg/L)  $\text{CH}_4$  concentrations and  $^{13}\text{C}_{\text{CH}_4}$  values between  $-42$  and  $-60\text{‰}$  could reflect either flux of deep-source thermogenic gas (Schoell, 1980) or a mixture of biogenic and thermogenic gas. The sample with the highest  $^{13}\text{C}_{\text{CH}_4}$  value ( $-42.3\text{‰}$ ) also had a low  $\text{Cl}^-$  concentration ( $2$  mg/L). The combined low  $\text{Cl}^-$  and  $\text{CH}_4$  concentrations rule out likely contamination from underlying fluids (gas and water) (see discussion below). Further evidence for a biogenic origin of  $\text{CH}_4$  in the shallow groundwater was provided by the lack of detectable higher chain hydrocarbons ( $\text{C}_2 < 0.0005$  mol%) in the 20 samples analyzed at the commercial laboratory ( $\text{C}_2+$  was detected in only 1 of 20 samples analyzed). The single detection of a higher chain hydrocarbon ( $\text{C}_2 = 0.0277$  mol%) was in a sample with a relatively high  $\text{C}_1/\text{C}_2+$  ratio ( $\text{C}_1/\text{C}_2 = 730$ ), consistent with a biogenic source ( $\sim 1,000$ ) (Schoell, 1980; Coleman et al., 1981) (Supplementary data). The distribution of dissolved  $\text{CH}_4$  concentrations and  $^{13}\text{C}_{\text{CH}_4}$  values (Fig. 8a) suggest a local, shallow origin of dissolved  $\text{CH}_4$  unrelated to shale-gas extraction in the vast majority of samples.

If the  $\text{CH}_4$  was sourced from biogenic processes within the shallow aquifers, the ground water chemistry should provide further support for its biogenic origin (Aravena et al., 1995). Median dissolved  $\text{CH}_4$  concentrations were highest in the  $\text{Na-HCO}_3$  water type, with positive correlations to Na and DIC ( $r^2 = 0.46$  and  $0.79$ , respectively; Fig. 8b and c). In addition, the positive correlation between DIC concentrations and  $^{13}\text{C}_{\text{DIC}}$  values ( $r^2 = 0.49$ ,  $p < 0.05$ ; Fig. 8e) could suggest that methanogenesis is occurring within the formations, perhaps within the minor coal beds (Imes and Emmett, 1994) under reducing conditions. If the minor concentrations of observed  $\text{CH}_4$  were sourced from microbial  $\text{CO}_2$  reduction, generation would be expected of  $^{13}\text{C}_{\text{CH}_4}$  of  $-70\text{‰}$  to  $-80\text{‰}$  (Coleman et al., 1981) parallel to elevated residual  $^{13}\text{C}_{\text{DIC}}$  (e.g.,  $> +10\text{‰}$ ) during  $\text{CH}_4$  production (Aravena and Wassenaar, 1993). However, in the study the majority of the  $^{13}\text{C}_{\text{DIC}}$  values are significantly lower ( $-20\text{‰}$  to  $-17\text{‰}$ ), demonstrating that methanogens are not the main control of  $^{13}\text{C}_{\text{DIC}}$  in the aquifer. In the low TDS water only trace levels ( $\text{CH}_4 < 0.8$  mg/L) of dissolved  $\text{CH}_4$  were recorded ( $n=9$ ) and only two low-TDS samples had detectable higher  $^{13}\text{C}_{\text{CH}_4}$  ( $-42.3$  and  $-59.6\text{‰}$ ). These values could indicate either a minor presence of thermogenic gas in the shallow aquifers or bacterial oxidation (Coleman et al., 1981).

#### 4.3. Water-rock interactions and mixing with external fluids

The geochemical variation from low TDS,  $\text{Ca-HCO}_3$  and  $\text{Na-HCO}_3$  water types infer different modes of water-rock interaction. The low-TDS waters could reflect an early stage of groundwater recharge without much mineralization induced from water-rock interaction, while the  $\text{Ca-HCO}_3$  waters suggest dissolution of carbonate minerals in the aquifers. A  $\text{Na-HCO}_3$  water type typically (e.g., Cheung et al., 2010) indicates silicate weathering and ion exchange processes (e.g., reverse base-exchange reaction). In the majority of the shallow groundwater samples, regardless of the water type, DIC nearly balanced the sum of Na, Ca and Mg concentrations (in equivalent units; Fig. 9). DIC could be generated in the shallow aquifers by weathering of silicate minerals in the shale, dissolution of marine carbonate by  $\text{H}_2\text{CO}_3$  produced through oxidation of organic matter, or bacterial  $\text{SO}_4$  reduction. Silicate weathering would mobilize Na, Ca, Mg and Sr with a radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  signature and B with a wide  $\delta^{11}\text{B}$  range from  $0\text{‰}$ , which would characterize structural B in silicate minerals (Lemarchand and Gaillardet, 2006), to  $15\text{--}20\text{‰}$  in “desorbable” B on marine clay surfaces (Spivack and Edmond, 1987). The  $\delta^{13}\text{C}_{\text{DIC}}$  value would reflect the isotopic fractionation between DIC species and would be expected to be similar to the composition of the  $\text{H}_2\text{CO}_3$  that triggered the silicate weathering ( $\sim -22\text{‰}$ ). If, instead, dissolution of marine carbonate minerals was occurring, one would expect contributions of Ca, Mg and Sr with a low  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\sim 0.7082$ ) for the Pennsylvanian-age marine formation (Burke et al., 1982), and B with  $\delta^{11}\text{B}$  of a marine carbonate signature ( $\sim 20\text{‰}$ ) (Vengosh et al., 1991). Dissolution of marine carbonate would generate  $\text{HCO}_3^-$  with  $\delta^{13}\text{C}_{\text{DIC}} \sim 11\text{‰}$ , assuming a closed system with equal proportions of marine calcite



dissolution ( $\delta^{13}\text{C}_{\text{DIC}} \sim 0\text{‰}$ ) and  $\text{H}_2\text{CO}_3$  ( $\delta^{13}\text{C}_{\text{DIC}} \sim -22\text{‰}$ ), and that all DIC-bearing species would be in isotopic equilibrium (McCaffrey et al., 1987). Carbonate dissolution could contribute Ca that would be exchanged with Na from exchange sites on clay minerals, resulting in Na- $\text{HCO}_3$  water. In such a scenario, the Ca concentrations would be inversely correlated with Na.

Examining all of these geochemical and isotopic constraints, it is clearly shown that neither of these two mechanisms (i.e., silicate weathering versus marine carbonate dissolution combined with base-exchange reaction) were explicitly consistent with the geochemical variations measured in the shallow groundwater in this study. For example, in most of the groundwater samples, including those defined as the Na- $\text{HCO}_3$  type, Na was positively correlated with Ca, indicating contributions from both elements that would reflect silicate weathering. In contrast, the most DIC-rich (Fig. 10a) waters showed an inverse relationship between Na and Ca (Fig. 10b) that typically mimics reverse base-exchange reactions. Likewise, all of the water types showed a positive correlation ( $r^2=0.79$ ) between Na and B concentrations (Fig. 10c), a combination that could reflect mobilization from exchangeable sites on clay minerals. The most DIC-rich waters have a lower Ca/Na ratio and lower Na relative to B concentration (Fig. 10c), inferring a different source. The  $\delta^{11}\text{B}$  of the Na- $\text{HCO}_3$  waters (16.5‰ to 33‰; Fig. 5b) was also consistent with B sourced from exchangeable sites on marine clay minerals.

In contrast, relatively low  $\delta^{13}\text{C}_{\text{DIC}}$  (-20‰ to -17‰) (Supplementary data) and radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7097 to 0.7166) (Fig. 5a) in the majority of the studied groundwater rule out the possibility that marine carbonate dissolution was the major process that controlled the generation of Ca- $\text{HCO}_3$  water. Nonetheless, given that the shale in the study area is carbonate-rich (Imes and Emmett, 1994), carbonate dissolution likely contributed Ca and  $\text{HCO}_3$ , with Ca exchanged with Na to generate Na- $\text{HCO}_3$  water. Reverse base-exchange reaction would remove Ca and Sr, and the uptake of Sr is not expected to modify its original isotopic ratio (i.e.,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the Pennsylvanian-age marine carbonate). One possible explanation for the high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is that the carbonate in the shale was diagenetically-modified from bacterial  $\text{SO}_4$  reduction with modified fluids containing radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  and depleted  $\delta^{13}\text{C}_{\text{DIC}}$  relative to the original composition of the marine carbonates. Given that the groundwater has a radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.7097 to 0.7166) that is similar to the composition of the local shale formations (Kresse and Hays, 2009), it was concluded that the water chemistry was controlled by *both* silicate mineral weathering and dissolution by diagenetically modified carbonate cement followed by ion-exchange reactions. Further study is needed to characterize the composition of the carbonate cement and delineate the specific mechanism that has caused evolution of the groundwater into a Na- $\text{HCO}_3$  composition.

The fourth shallow groundwater type, the higher- $\text{Cl}^-$  waters, shows a strong correlation between Cl and Br ( $r^2=0.89$ ; Fig. 11a) with a high Br/Cl ratio ( $>1 \times 10^{-3}$ ) that is similar to the elevated Br/Cl in the FS brine (see below). This geochemical composition could be interpreted as mixing of shallow groundwater with underlying formation water, similar to the salinization phenomena observed in NE Pennsylvania (Warner et al., 2012). However, the variations of other dissolved constituents such as B and Sr were not correlated with  $\text{Cl}^-$  (Fig. 11f-h), and their isotopic ratios, including  $^{87}\text{Sr}/^{86}\text{Sr}$  (Fig. 5a),  $\delta^{13}\text{C}_{\text{DIC}}$  (Fig. 4), and the majority of  $\delta^{11}\text{B}$  (Fig. 5b) were distinctly different from expected mixing relations with the FS brines (Supplementary data). This infers that the composition of the groundwater with ( $\text{Cl}^- > 20\text{mg/L}$ ) was modified by weathering and water-rock interaction. The ability to delineate the exact saline end-member that generated the saline groundwater is limited.

Finally, neither the Na- $\text{HCO}_3$  water type, nor the fourth water type with  $\text{Cl}^- > 20\text{ mg/L}$  were located closer to shale-gas wells (Supplementary data), which rules out the likelihood of salinization induced from shale gas exploitation and migration of fluids associated with natural gas wells. Instead, a geographical distribution of the water types was observed; the majority of Na- $\text{HCO}_3$  samples were

identified in the southern portion of the study area (Fig. 1) and at lower average elevations (Supplementary data), which could indicate increased Na and DIC in the southern portion of the study area, corresponding to a regional groundwater flow and increased water-rock interaction along regional flow paths (Imes and Emmett, 1994; Kresse et al., 2012) and/or greater predominance of shale lithology in the low lying regions (Cordova, 1963).

#### 4.4. The Fayetteville Shale flowback and produced waters

The FS flowback and produced water samples (Supplementary data) were saline (TDS ~ 20,000 mg/L), yet the present data show that the salinity is substantially lower than produced waters from other shale gas basins (e.g., Marcellus brine with TDS ~200,000 mg/L; Table 2). The FS saline water was composed of Na-Cl-HCO<sub>3</sub>, with a linear correlation ( $r^2=0.39$ ) between Cl<sup>-</sup> and Br<sup>-</sup> and a high Br/Cl ratio ( $\sim 4 \times 10^{-3}$  to  $7 \times 10^{-3}$ ; Fig. 11a). This composition infers modified evaporated seawater (seawater evaporation, salt precipitation, followed by dilution with meteoric water) with Na, Sr, Mg and Ca enrichments relative to the expected evaporated seawater curve (McCaffrey et al., 1987) (Fig. 11a-h). The  $\delta^{18}\text{O}$  (-2.1‰ to -0.5‰) and  $\delta^2\text{H}$  (-19.8‰ to -15.2‰) of the formation water samples plot to the right of the  $\delta^2\text{H}/\delta^{18}\text{O}$  LMWL (Kendall and Coplen, 2001) (Fig. 12). DIC content was elevated (800-1800 mg/L) compared to other produced waters in other shale basins in the U.S.A. (Table 2), and had a distinctive elevated  $\delta^{13}\text{C}_{\text{DIC}}$  (-12.7‰ to +3.7‰), which may reflect the composition of the injected hydraulic fracturing fluid or methanogenesis. Boron ( $\delta^{11}\text{B}=26\text{-}30\text{‰}$ ; Supplementary data and Fig. 5b) and Sr ( $^{87}\text{Sr}/^{86}\text{Sr}=0.7090\text{-}0.7111$ ; Supplementary data and Figure 5a) isotopic fingerprints were different than would be expected for unaltered Mississippian-age evaporated seawater, which would generate  $\delta^{11}\text{B}>39\text{‰}$  and a less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $\sim 0.7082$  (Burke et al., 1982). The  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activities were relatively low (14-260 pCi/L) (Supplementary data) compared to Appalachian brines (Rowan et al., 2011) with a  $^{228}\text{Ra}/^{226}\text{Ra}$  range of 0.1 to 0.5, which is similar to Appalachian brines. This relatively low Ra level could have important implications for management strategies and evaluation of possible environmental effects, following disposal of the flowback and produced waters.

The chemical composition of the five flowback samples reflects mixing between the original formation water (represented by the produced water) and lower-saline water that was injected as fracturing fluids. Given the higher salinity of the formation water (relative to the injected water) its chemistry overwhelmingly controlled the composition of the flowback waters. Similar results were observed in the composition of flowback water from the Marcellus Formation (Haluszczak et al., 2013). Overall, the combined geochemical data from five flowback and one produced water samples indicate that the FS water is likely the remnant of seawater that evaporated beyond the halite saturation stage (McCaffrey et al., 1987). Similar to the Appalachian brines (Dresel and Rose, 2010; Warner et al., 2012) the evaporated seawater was modified by water-rock interaction that resulted in Na, Sr, Mg and Ca enrichments and alterations of the original marine  $^{11}\text{B}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic fingerprints. The brine was subsequently diluted by meteoric water with lower  $^{18}\text{O}$  and  $^2\text{H}$  values that reduced the original salinity to levels lower than seawater (TDS<32,000 mg/L).

Another unique characteristic of the FS is the substantial DIC enrichment that is inversely correlated ( $r^2=0.55$ ) with Cl<sup>-</sup> content (Fig. 11c) with high  $\delta^{13}\text{C}_{\text{DIC}}$  values (-12.7‰ to 3.7‰) relative to shallow groundwater (Supplementary data). This suggests that the FS water is diluted with DIC-rich water. The elevated positive  $\delta^{13}\text{C}_{\text{DIC}}$  could infer methanogenesis in the low-saline water that diluted the original FS brine. Alternatively, dissolution of the limestone matrix with a  $\delta^{13}\text{C}$  of  $\sim 1.0\text{‰}$  (Handford, 1986) coupled with reverse base-exchange reaction within the FS would generate Ca, Na (from base-exchange) and DIC with a positive  $\delta^{13}\text{C}_{\text{DIC}}$  signature. This is confirmed by the correlation of Na/Cl and Ca/Cl ratios and

inverse correlation of Cl with DIC (Fig. 11g, d and c). Combined, the chemistry and isotopic results indicate a major modification and dilution of the original FS brine composition.

## 5. Conclusions and Implications

This study examined water quality and hydrogeochemistry in groundwater from shallow aquifers in an attempt to delineate possible groundwater contamination. Three types of potential contamination were considered (1) stray gas contamination; (2) migration of saline fluids from depth that were directly associated with drilling and exploration of the underlying Fayetteville Shale; and (3) natural migration of saline fluids from depth through permeable geological formations. The results of this study clearly show lack of saline fluid contamination (scenario #2) in drinking water wells located near shale gas sites, which is consistent with previous studies in shallow groundwater in the Marcellus in northeastern Pennsylvania (Osborn et al., 2011a; Warner et al., 2012). However, the lack of apparent CH<sub>4</sub> contamination with thermogenic C isotope composition in shallow groundwater near shale gas sites in the Fayetteville Shale differs from results reported for shallow groundwater aquifers overlying the Marcellus Formation (Osborn et al., 2011a). It has been proposed that the stray gas contamination likely resulted from poor well integrity that allowed leakage and migration of CH<sub>4</sub> to the shallow aquifers (Jackson et al., 2011; Osborn et al., 2011a, b). In this study no direct evidence was found for stray gas contamination in groundwater wells located near shale gas sites and most of the CH<sub>4</sub> identified (mostly low concentrations) had a  $\delta^{13}\text{C}_{\text{CH}_4}$  composition that is different from the fingerprint of the Fayetteville Shale gas.

Likewise, this study did not find geochemical evidence for natural hydraulic connectivity between deeper formations and shallow aquifers (Warner et al., 2012) that might provide conduits for flow of saline fluids from depth to the shallow groundwater. The spatial distribution of the slightly saline groundwater (Cl>20 mg/L) that could be derived from dilution of the FS brine or another saline source was not associated with the location of the shale gas wells. Shallow groundwater samples for this study were collected from formations that are part of the Western Interior Confining System (Imes and Emmett, 1994). A previous investigation has shown that these formations impede the vertical flow of groundwater and restrict groundwater movement for domestic supply wells to only local near-surface flow systems (Imes and Emmett, 1994). The natural impermeability and apparent lack of deformation of these formations seems to prevent hydraulic connectivity that might allow the flow of saline fluids between deep saline formations and shallow drinking water aquifers in north-central Arkansas.

The lack of fracture systems that would enable hydraulic connectivity is very different from the geological formations overlying the Marcellus Shale in the Appalachian basin (Warner et al., 2012 and references therein). These differences could be explained by two structural deformation scenarios: (1) recent glaciation and isostatic rebound of shallow bedrock that was reported in the Appalachian and Michigan basins (Weaver et al., 1995); and (2) tectonic deformation that shaped particularly the Appalachian Basin (Lash and Engelder, 2011). These natural deformation events could explain the increased hydraulic connectivity and pathways that provide conduits for fluids and gas between the deeper production zones and shallow groundwater in the shallow geological formations overlying the Marcellus Shale in the Northern Appalachian Basin but apparently not in the study area in Arkansas.

Previous studies in the Marcellus Basin have suggested that the CH<sub>4</sub> leakage to shallow drinking water wells is most likely attributable to poor well integrity (Osborn et al., 2011a). Such human factors could also explain the lack of CH<sub>4</sub> contamination in Arkansas, possibly due to: (1) better wellbore integrity; and/or (2) a lack of conventional oil and gas development in north-central Arkansas prior to the shale gas extraction from the Fayetteville Formation (Kresse et al., 2012).

In conclusion, this study demonstrates the importance of basin- and site-specific investigations in an attempt to determine the possible effects of shale gas drilling and hydraulic fracturing on the quality of water resources. The study shows that possible groundwater impacts from shale-gas development differ between basins and variations in both local and regional geology could play major roles on hydraulic connectivity and subsurface contamination processes. Based on the results of this and previous studies (Osborn et al., 2011a; Warner et al., 2012), it is concluded that systematic monitoring of multiple geochemical and isotopic tracers is necessary for assessing possible groundwater contamination in areas associated with shale gas exploration as well as the possible hydraulic connectivity between shallow aquifers and deeper production zones.

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## Figure Captions

**Figure 1.** Study site location in north-central Arkansas. Unconventional shale-gas wells completed into the Fayetteville Shale are shown in black. Shallow groundwater samples were cataloged based on major element chemistry into four water categories: low-TDS (beige triangles), Ca-HCO<sub>3</sub> (blue circles), Na-HCO<sub>3</sub> (green squares), and Cl>20 mg/L (red diamonds).

**Figure 2a and b.** Map of sample locations and bedrock geology in the study area of north-central Arkansas. The majority of samples were collected from the Atoka (southern area) and Hale Formations (northern area). North-to-south geological cross-section in the study area (A-A' line is shown). Geological units gently dip to the south with the Atoka Formation outcropping in the southern portion of the study area. The underlying Fayetteville Shale shoals to the north.

**Figure 3a and b.** Comparison of results for duplicate samples submitted to a private laboratory (Isotech) by gas chromatography isotope ratio mass spectrometry (GC-IRMS) to those performed using a cavity-ring-down spectroscopy (CRDS) analyzer at Duke University for both dissolved CH<sub>4</sub> concentrations and  $\delta^{13}\text{C-CH}_4$ . Dissolved CH<sub>4</sub> concentrations from the two independent methods showed a good correlation ( $r^2=0.90$ ,  $p<1\times 10^{-15}$ ) with some variability at higher concentrations. The comparison of the  $\delta^{13}\text{C-CH}_4$  values obtained from the two analytical techniques showed a strong correlation ( $r^2=0.95$ ,  $p<1\times 10^{-15}$ ). The CRDS methodology showed some bias at lower  $\delta^{13}\text{C-CH}_4$  compared to the private laboratory. Note that this comparison includes samples from other study areas to cover a wide range of concentrations and  $\delta^{13}\text{C-CH}_4$  values.

**Figure 4.**  $\delta^{13}\text{C-DIC}$  (‰) and DIC (mg/L) in shallow groundwater samples. The average  $\delta^{13}\text{C-DIC}$  (-17‰ to -20‰) in the bulk groundwater indicates the majority of DIC is derived from weathering of silicate minerals that would approach -22‰. Methanogens in some of the Na-HCO<sub>3</sub> waters would leave DIC with elevated residual  $\delta^{13}\text{C-DIC}$  (green line).

**Figure 5a and b.**  $^{87}\text{Sr}/^{86}\text{Sr}$  versus Sr concentration ( $\mu\text{g/L}$ ) log scale and  $\delta^{11}\text{B}\text{‰}$  versus B concentration ( $\mu\text{g/L}$ ) in log scale. The lack of strong Sr and B isotopic relationships exclude possible mixing between the Fayetteville Shale water and the shallow groundwater. Instead the isotopic variations appear to be controlled by weathering and water-rock interaction.

**Figure 6.** Dissolved CH<sub>4</sub> concentrations (mg/L) in domestic wells plotted versus distance from the domestic wells to nearest natural gas well. Only one of 51 wells analyzed contained CH<sub>4</sub> at concentrations above the potential action level set by the Department of Interior (10 mg/L). There is no statistically significant difference in dissolved CH<sub>4</sub> concentrations from wells collected within 1 km of a gas well and those collected >1 km from a well. The highest dissolved CH<sub>4</sub> concentrations were detected in Na-HCO<sub>3</sub> water.

**Figure 7.** Histogram of  $\delta^{13}\text{C-CH}_4$  (‰) values of dissolved CH<sub>4</sub> plotted in comparison to published values for Fayetteville Shale produced gas  $\delta^{13}\text{C-CH}_4$  (‰) (Zumberge et al., 2012). Concentrations of the dissolved CH<sub>4</sub> in the studied shallow groundwater samples are indicated by color. The majority of samples, including all of those at higher CH<sub>4</sub> concentrations plot at more negative  $\delta^{13}\text{C-CH}_4$  values, indicating that a shallow biogenic origin likely contributes to the formation of CH<sub>4</sub>. The lone sample that overlaps with Fayetteville Shale values may represent migration of stray production gas, but at very low concentrations.

**Figure 8.** Dissolved CH<sub>4</sub> (mg/L) versus  $\delta^{13}\text{C-CH}_4$  (‰) (8a), Na (mg/L) (8b), and  $\delta^{13}\text{C-DIC}$  (‰) (8c) in shallow groundwater samples. The correlations observed between CH<sub>4</sub> and Na ( $r^2=0.46$ ) and DIC ( $r^2=0.79$ ) indicate that the highest CH<sub>4</sub> is found in Na-HCO<sub>3</sub> groundwater. At the higher DIC and CH<sub>4</sub> concentrations the depleted  $\delta^{13}\text{C-CH}_4$  indicates that methanogens likely contribute to the formation of CH<sub>4</sub>.  $\delta^{13}\text{C-DIC}$  versus  $\delta^{13}\text{C-CH}_4$  (‰) (8d) and DIC (mg/L) (8e) in shallow groundwater. The average

$\delta^{13}\text{C}$ -DIC (-17‰ to -20‰) in the bulk groundwater indicates the majority of DIC is derived from weathering of silicate minerals that would approach -22‰. Methanogens in some of the  $\text{Na-HCO}_3$  waters would leave DIC with elevated residual  $\delta^{13}\text{C}$ -DIC (green arrow).

**Figure 9.** The sum of Na, Ca and Mg (meq/L) versus dissolved inorganic C(DIC; meq/L) in shallow groundwater samples. Note that DIC balances the majority of the total cations in shallow groundwater samples across all water types.

**Figure 10.** The DIC, Ca and B concentrations versus Na in shallow groundwater samples.

**Figure 11.** The variations of major elements as normalized to  $\text{Cl}^-$  in shallow groundwater and the FS saline water. The composition of the FS water infers modified seawater through evaporation and halite precipitation (high Br/Cl ratio), water-rock interactions (enrichment of Na, Sr, Mg and Ca relative to the expected evaporated seawater curve), followed by dilution with meteoric water. Note that there is no apparent relationship between concentrations of constituents in shallow groundwater and the deeper FS waters. The negative correlation between Cl and DIC indicates that dilution is the main factor for the high DIC in the formation water. The positive correlation of Na/Cl and Ca/Cl with DIC concentration indicates that Na, Ca and DIC within the FS are likely sourced from carbonate dissolution combined with base-exchange reactions that have modified the original composition of the FS water.

**Figure 12.**  $\delta^{18}\text{O}$ ‰ versus  $\delta^2\text{H}$ ‰ values in shallow groundwater and the Fayetteville Shale brines. The relationship between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in shallow groundwater is consistent with the local meteoric water line (LMWL) while the Fayetteville Shale brines plot to the right of the LMWL and could reflect mixing between depleted  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  low-saline water and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ -enriched brines.

**Table 1.** Historical water quality results from the USGS National Water Information System database for Cleburne, Conway, Faulkner, Independence, Van Buren, and White Counties, Arkansas.

**Table 2.** Typical produced water TDS (mg/L) concentrations - Source USGS (Kimball, 2012).

**Supplementary data:- Table.** Geochemical results for samples collected from shallow aquifers and Fayetteville Shale produced waters and flowback fluids



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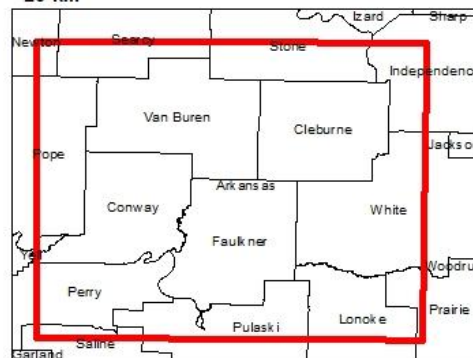
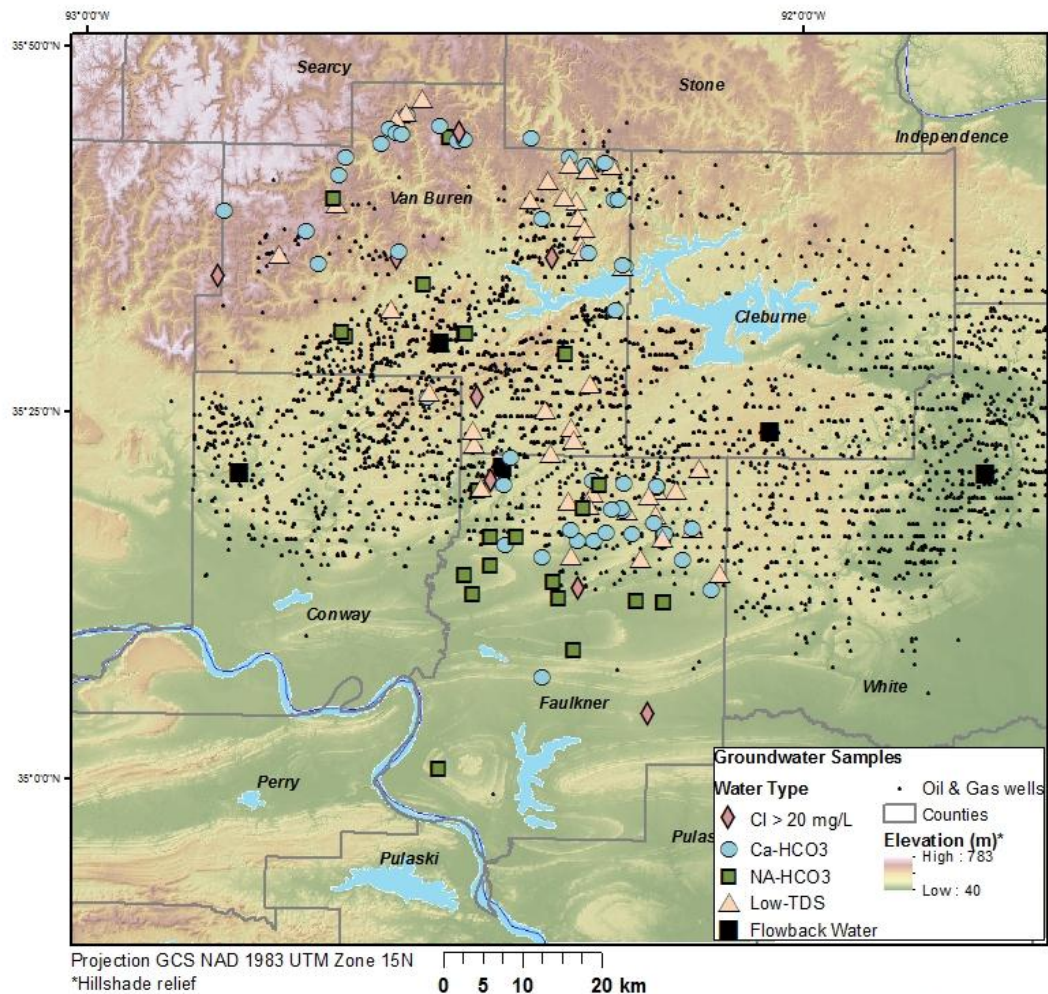


Figure 1.

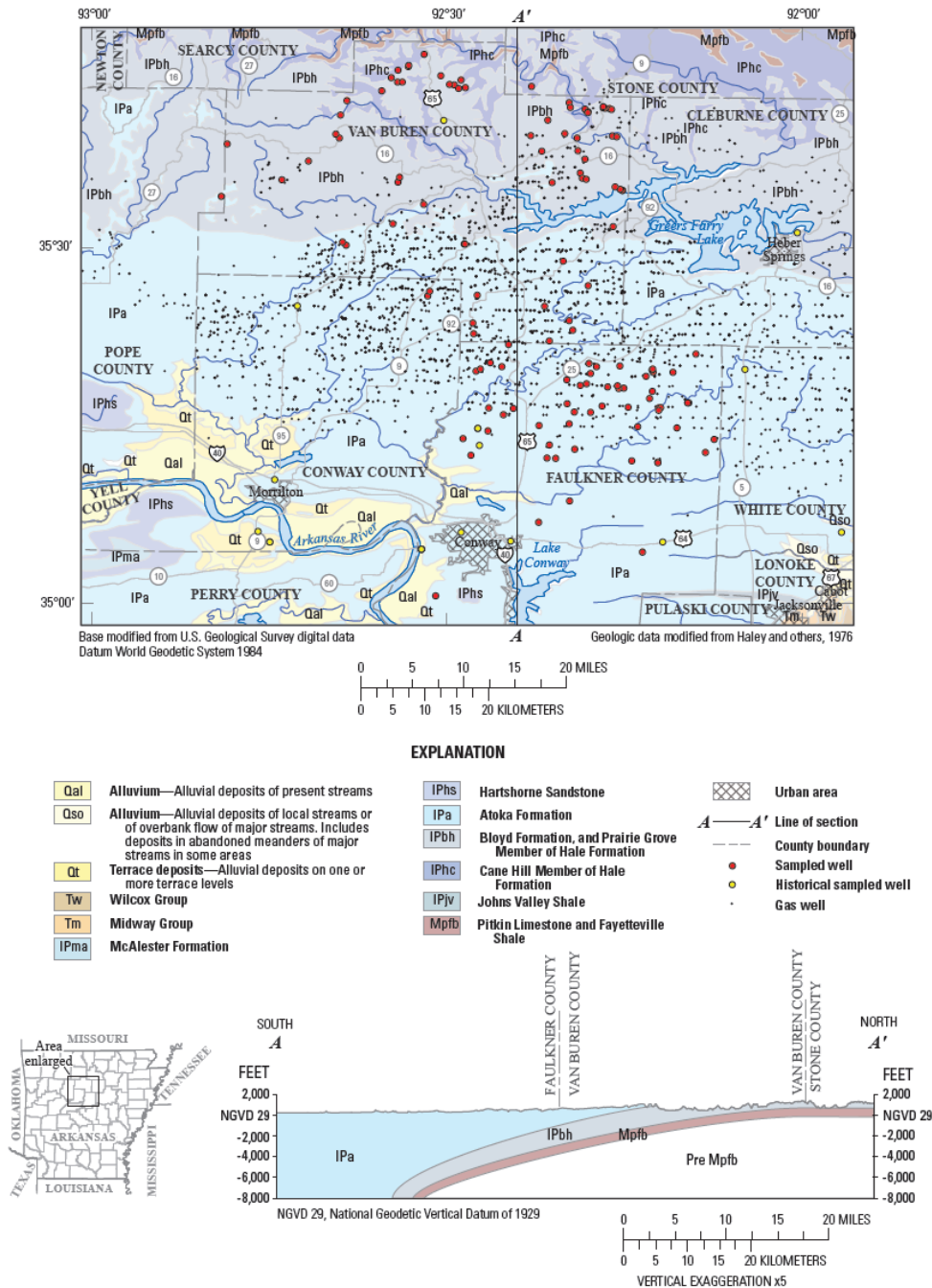


Figure 2.

Figure 2. Geology of the Fayetteville Shale study area with generalized geologic cross-section, north-central Arkansas.

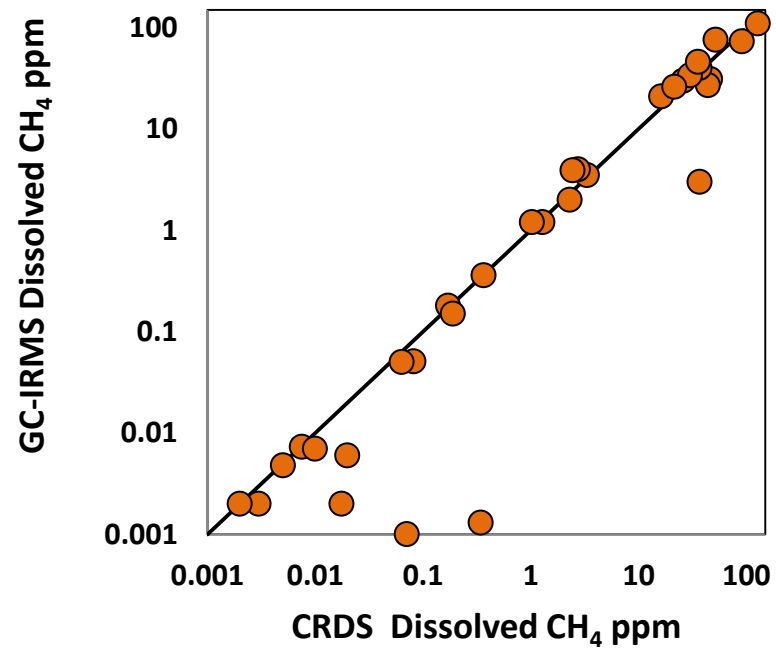
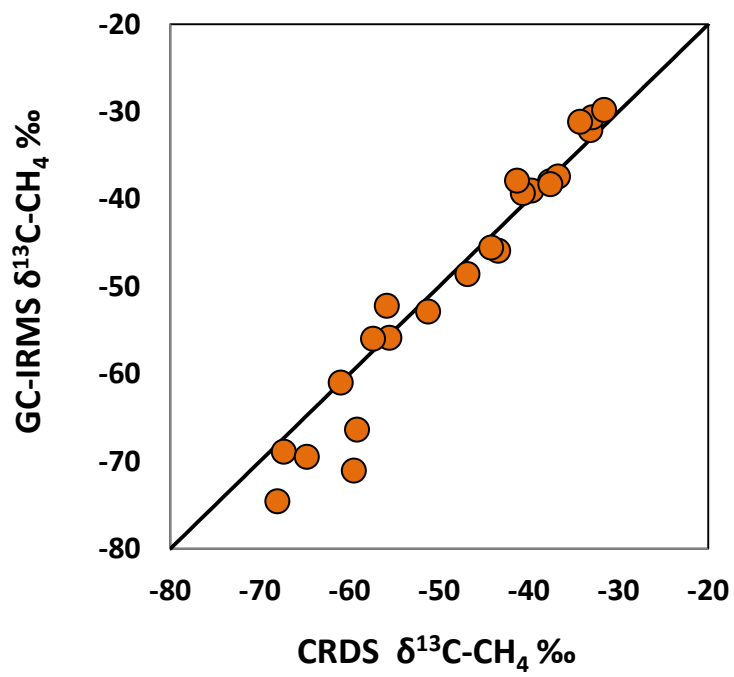


Figure 3a and 3b.

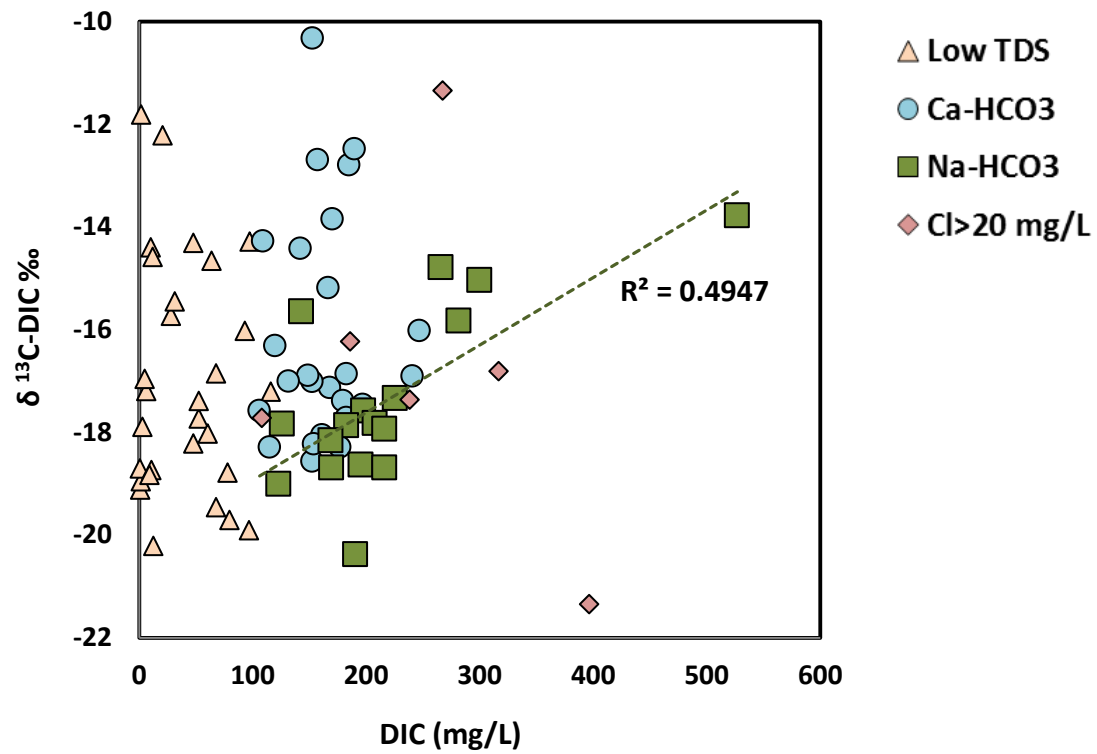


Figure 4.



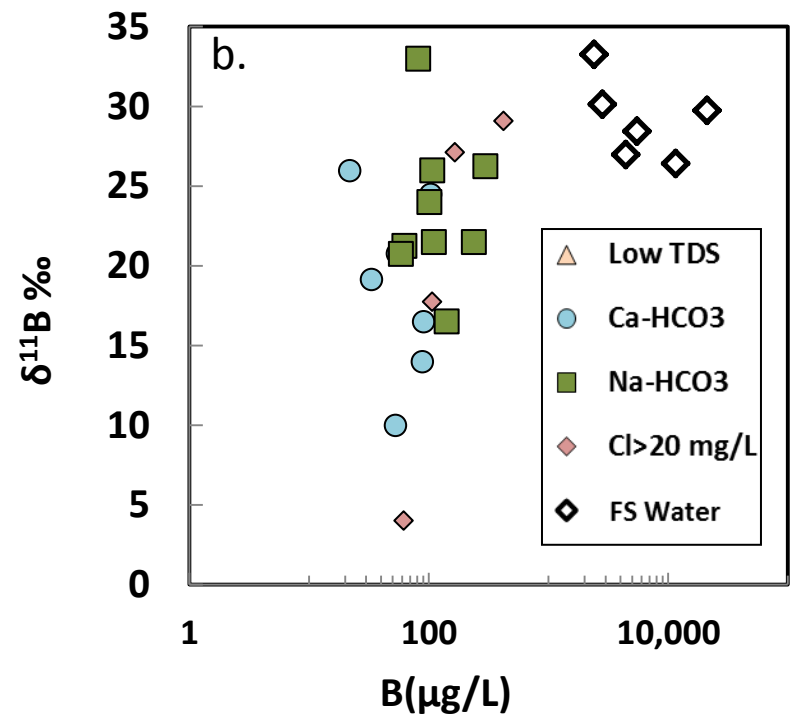
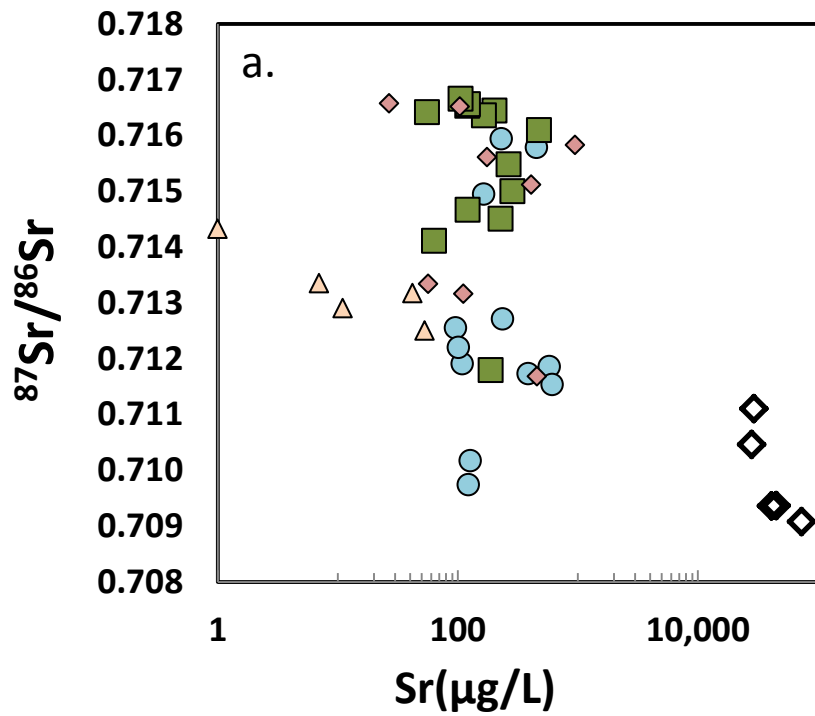


Figure 5a and 5b.

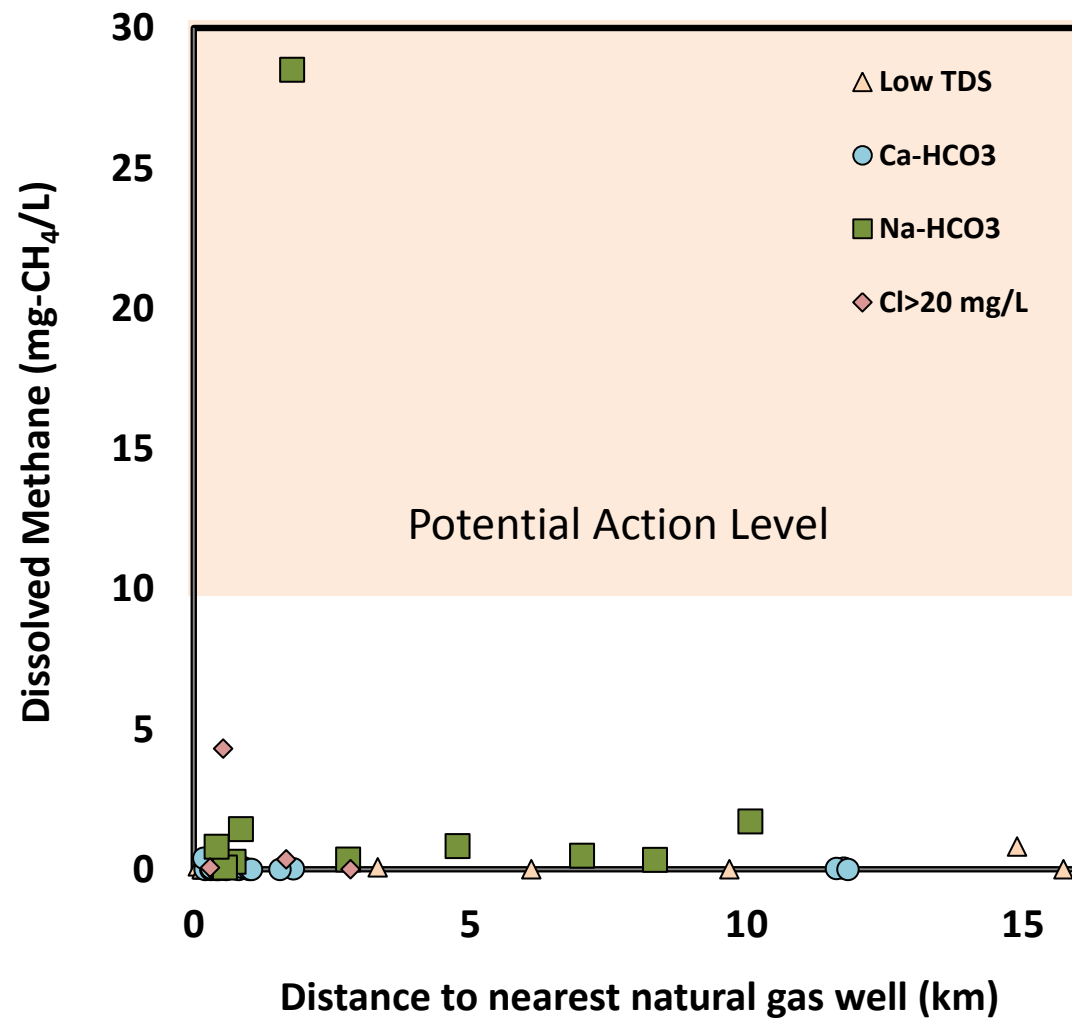


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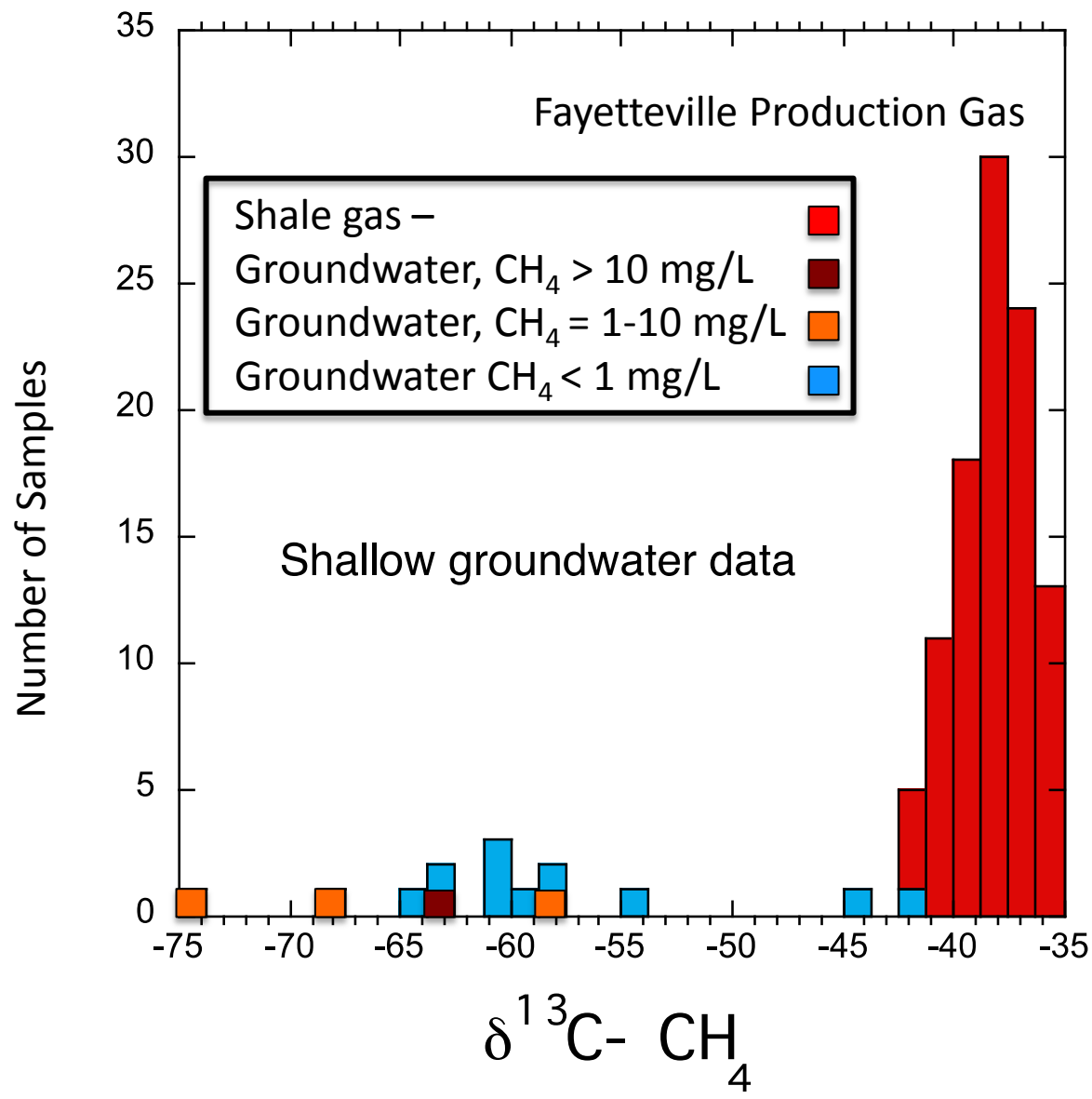


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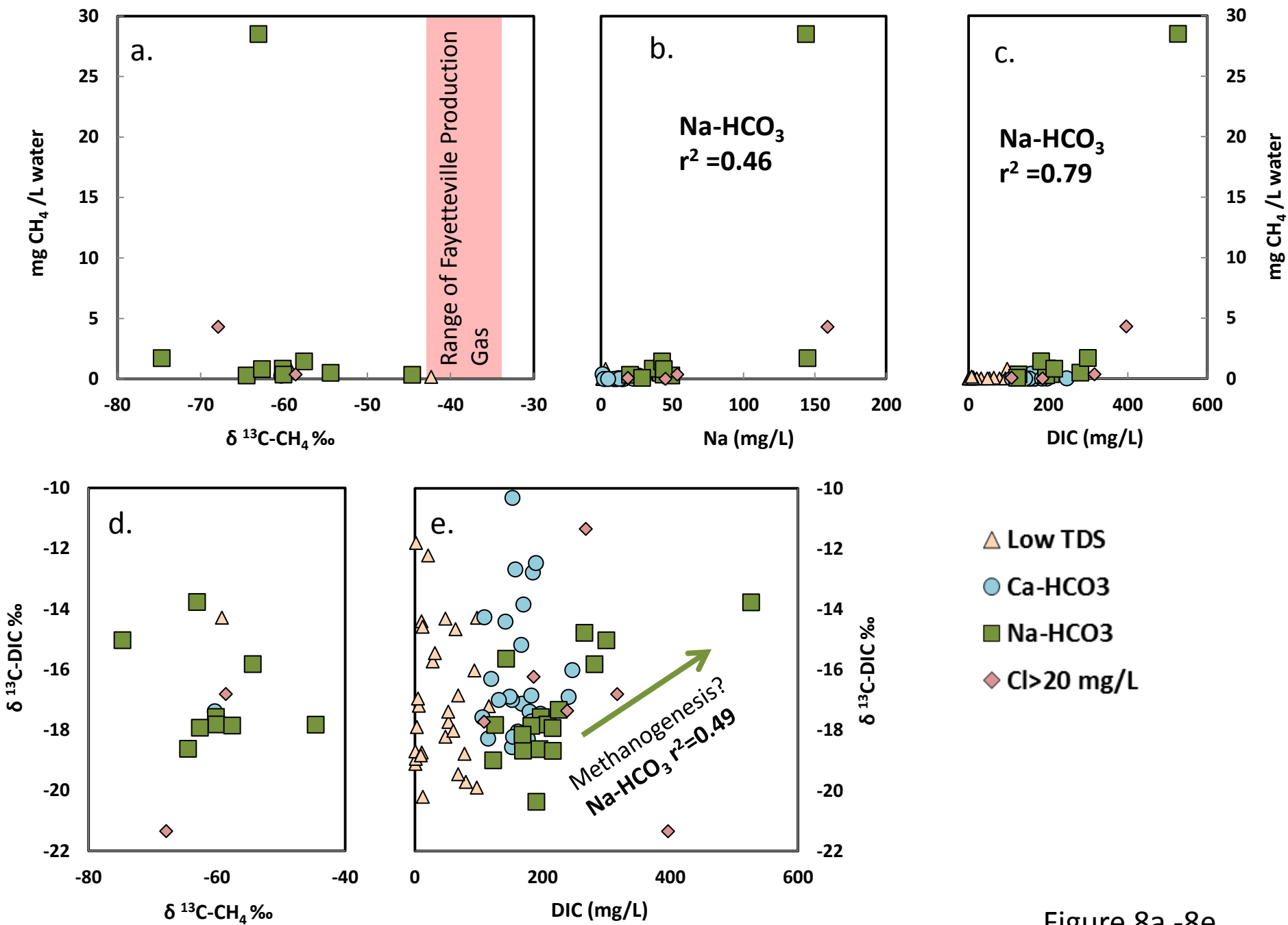


Figure 8a -8e.



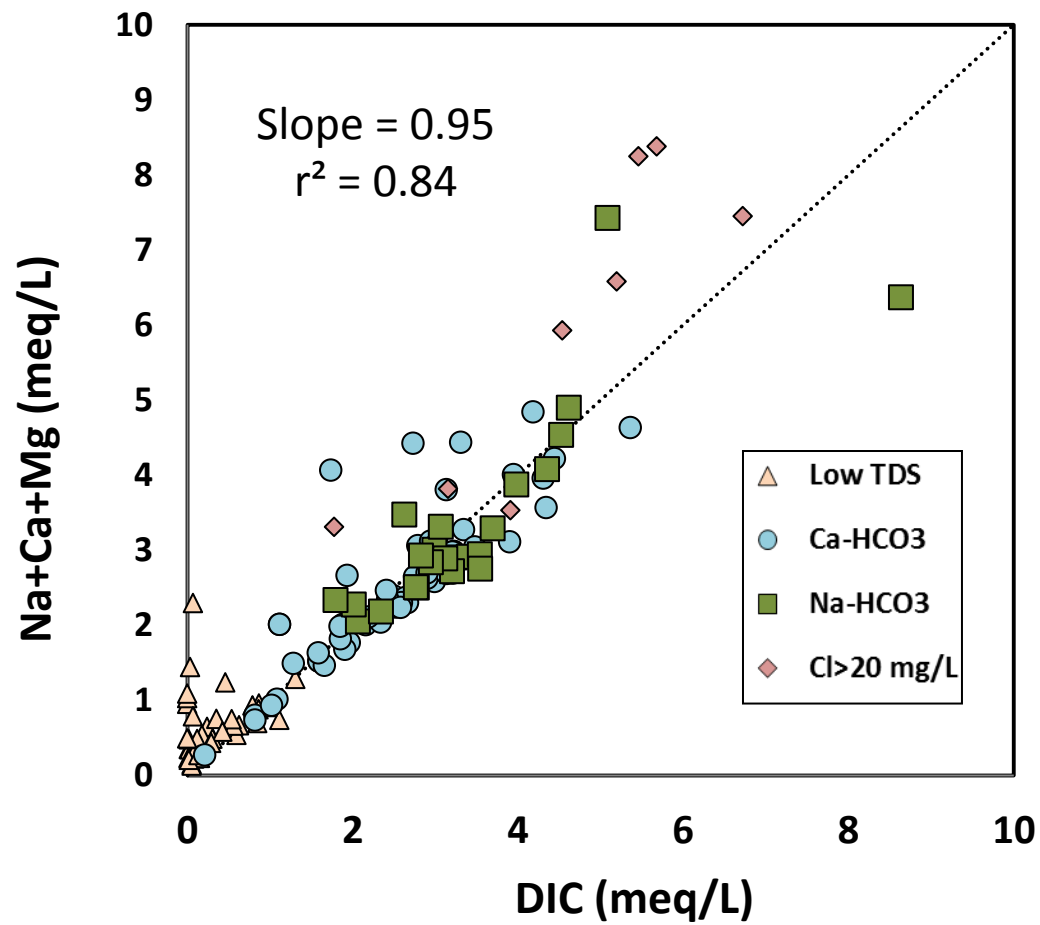


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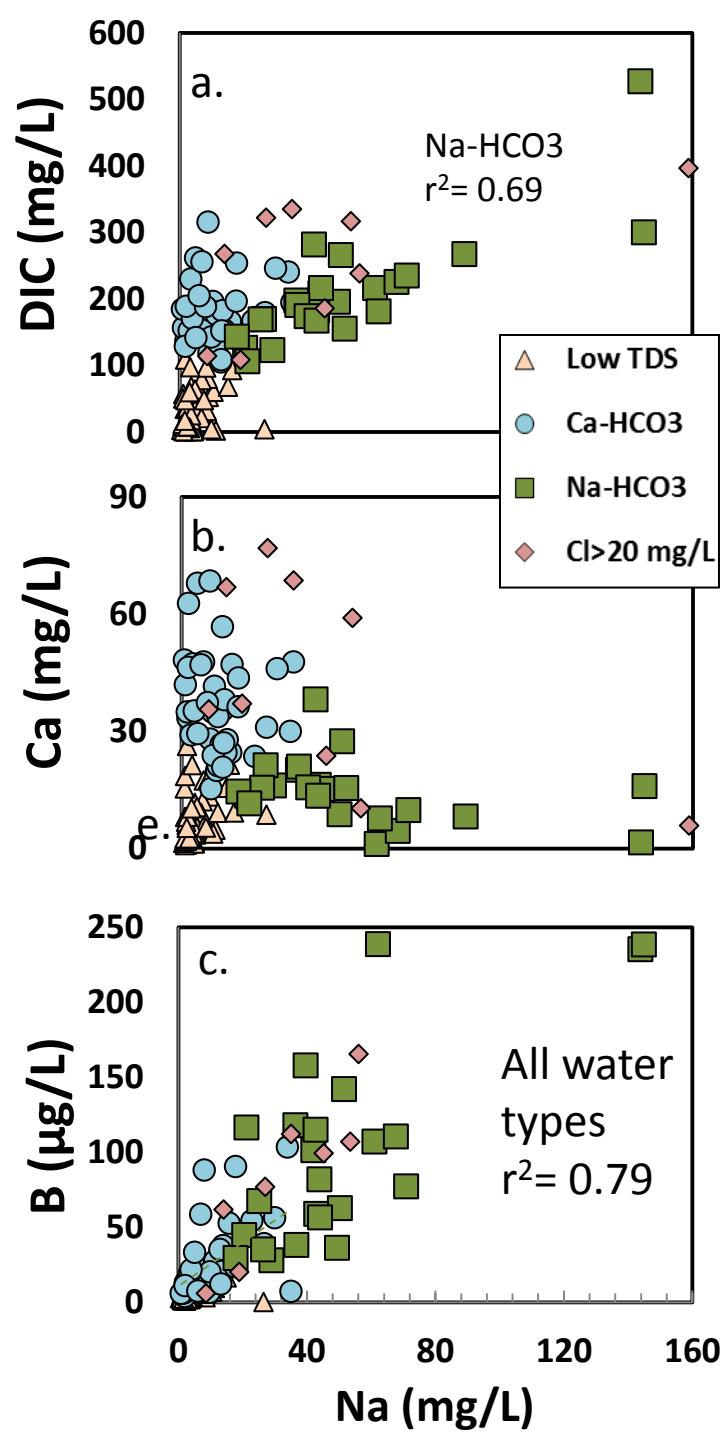


Figure 10a, 10b, 10c.

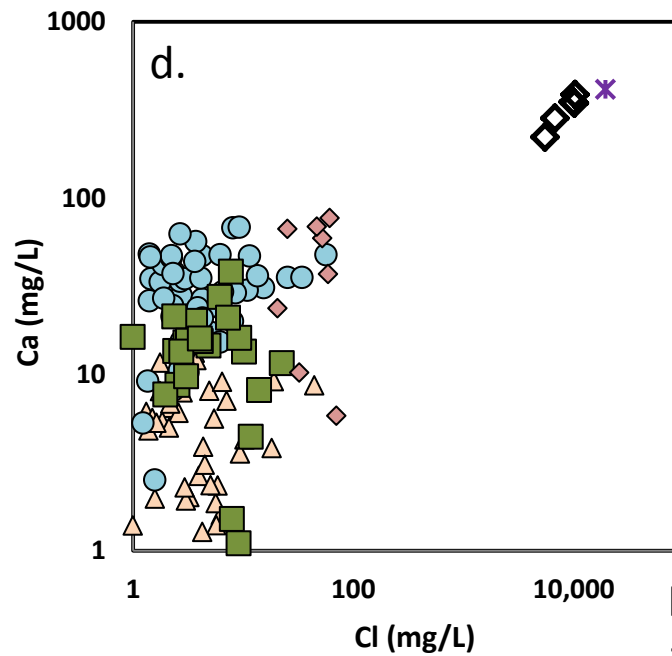
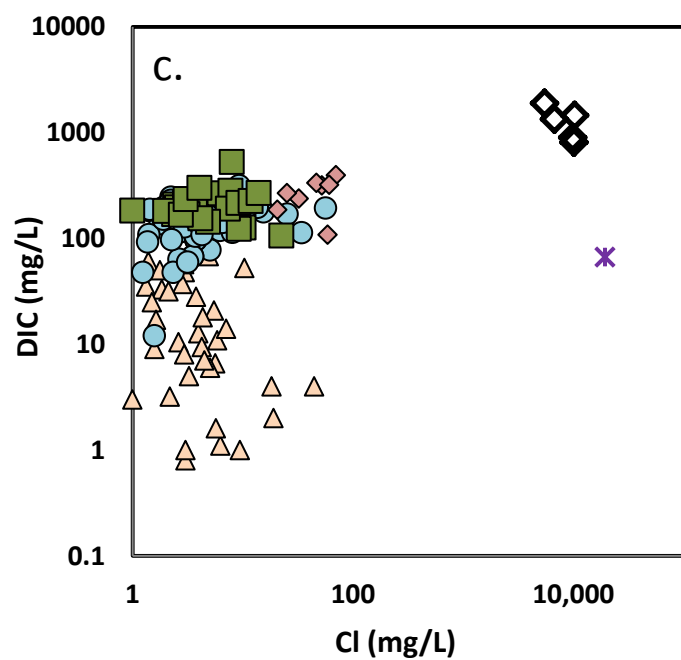
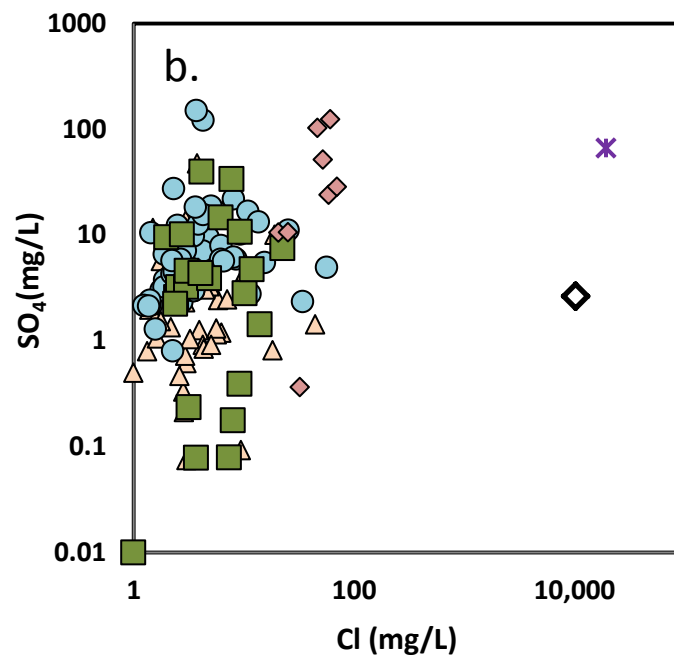
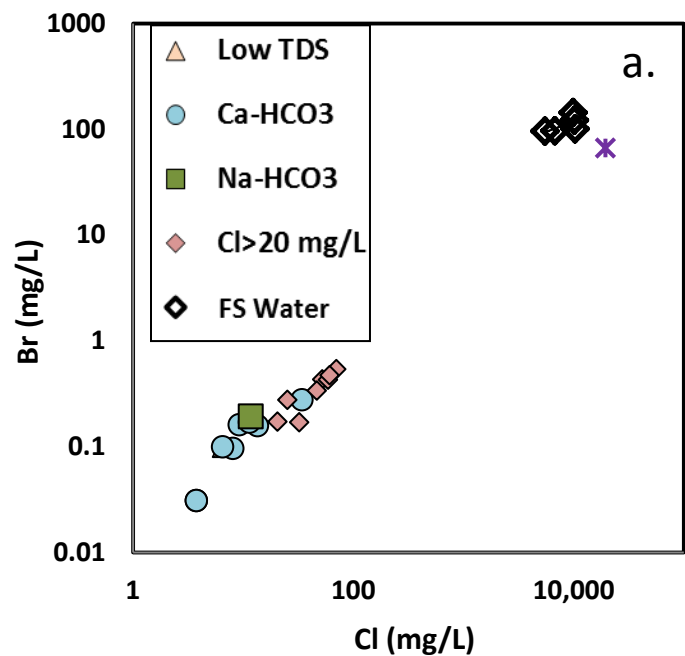


Figure 11a-11d.

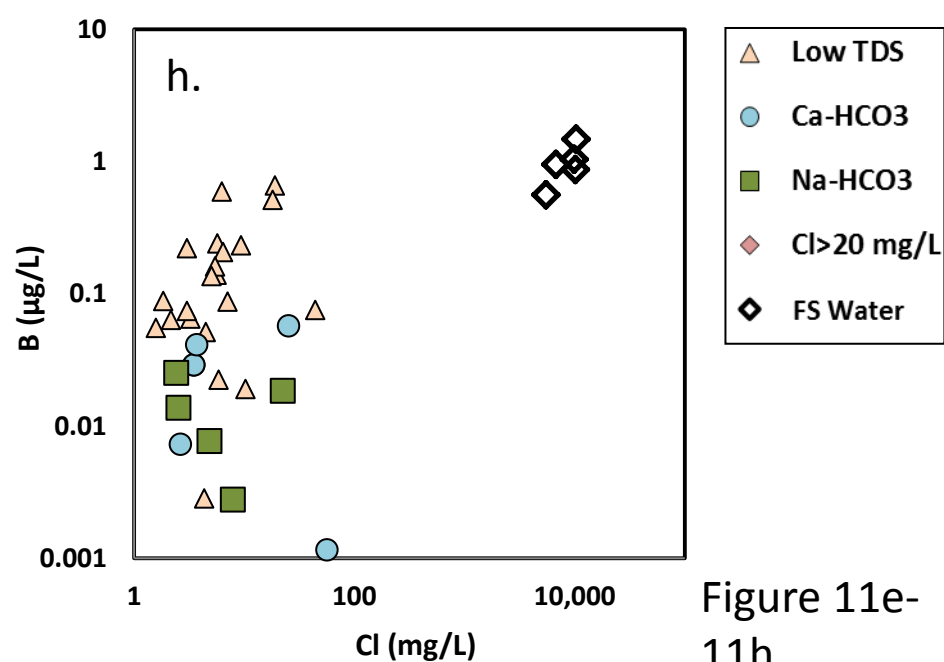
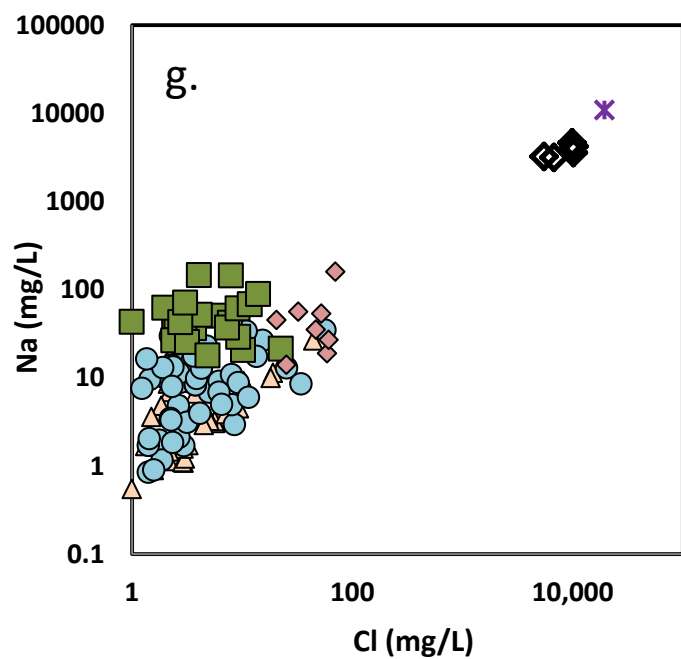
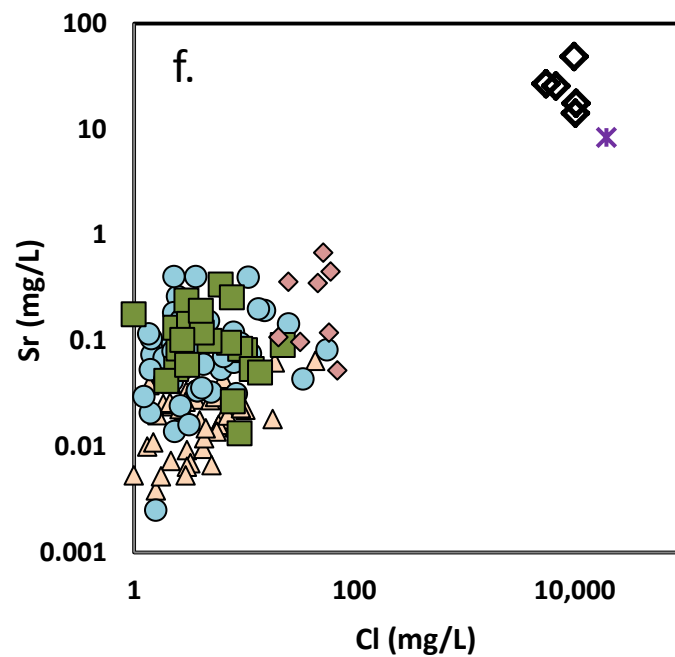
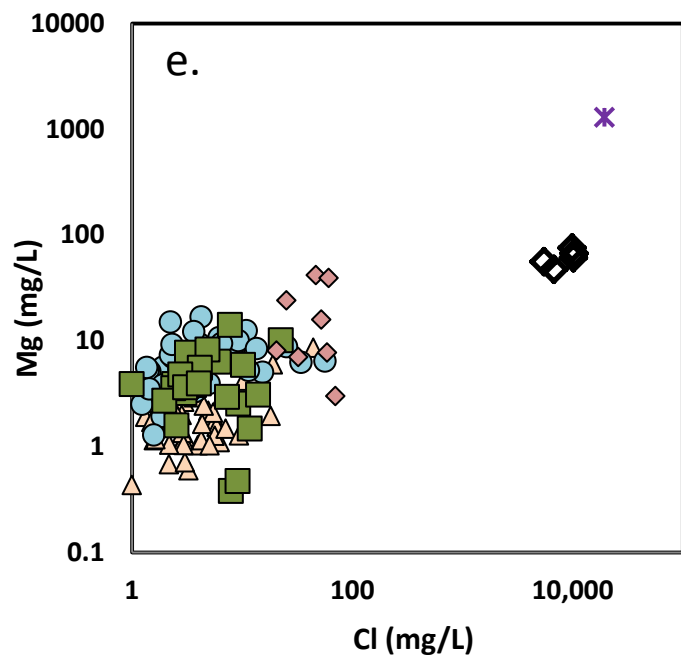


Figure 11e-11h.

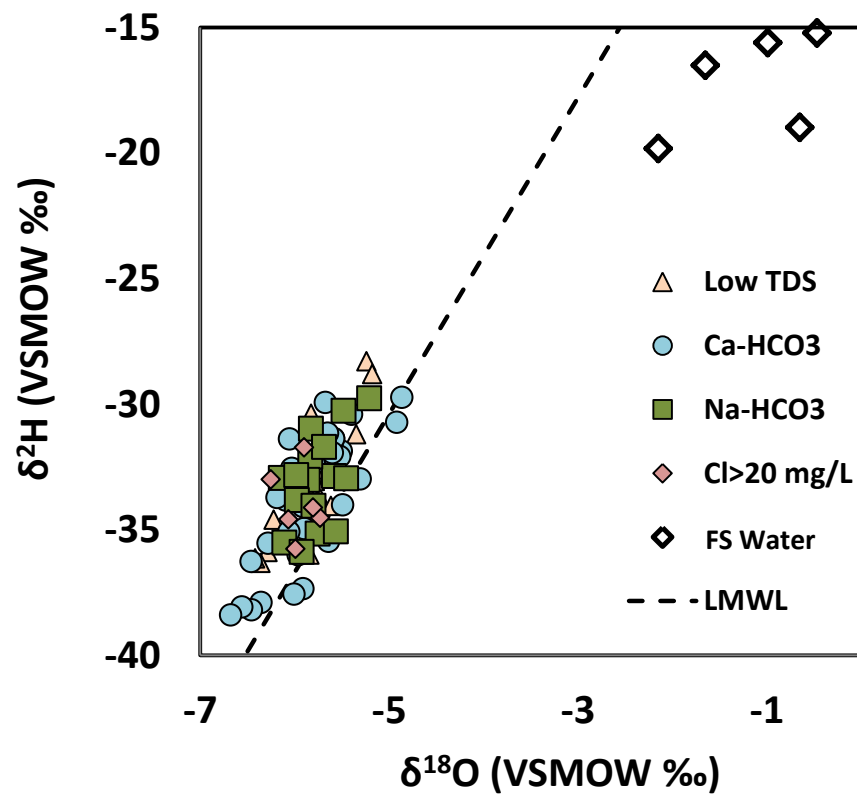


Figure 12.

Table 1. Shallow groundwater, flowback, and produced water results.

Sample	Type	Temp	pH	Cond	Well Depth (ft)	Cl (mg/L)	Br (mg/L)	NO <sub>3</sub> -N (mg/L)	SO <sub>4</sub> (mg/L)	Total Alkalinity (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Na (mg/L)	Fe (mg/L)	Ba (mg/L)	Mn (mg/L)	Si (mg/L)	Li ppb	B ppb	<sup>87</sup> Sr/ <sup>86</sup> Sr	δ <sup>11</sup> B ‰	δ <sup>3</sup> H ‰	δ <sup>18</sup> O ‰	δ <sup>13</sup> C‰- DIC	TDS Calculated (mg/L)	He	H <sub>2</sub>
ASG-001	Cl>20mg/L	17.74	7.09	705		52	0.43	nd	52	317	59	16	0.68	54	0.1	0.2	0.1	9.5	24	107	0.715832	17.7	-31.7	-5.9	-16.8	388		
ASG-002	Cl>20mg/L	16.54	6.34	403		59	0.43	nd	24	108	37	8	0.12	19	3.0	0.1	0.3	14.6	22	20	0.715612		-34.5	-5.7	-17.7	200		
ASG-003	Cl>20mg/L	18.14	7.2	448		32	0.17	1.69	0	239	10	7	0.10	56	0.2	0.1	0.1	8.6	5	165	0.716516	27.1	-34.1	-5.8	-17.4	223		
ASG-004	Cl>20mg/L	16.4	7.06	798	90	47	0.34	0.3	102	335	69	42	0.35	35	0.5	0.1	0.1	8.8	9	112	0.715117					459		
ASG-005	Cl>20mg/L	18.8	8.63	851	100	70	0.54	nd	29	397	6	3	0.05	159	0.5	0.0	0.1	6.6	14	420	0.716577	29.1	-34.6	-6.1	-21.4	461	na	na
ASG-006	Cl>20mg/L	16.2	6.74	371	140	21	0.17	0.4	11	186	24	8	0.11	45	0.5	0.0	0.1	9.5	7	99	0.713162		-35.8	-6.0	-16.2	199	na	na
ASG-007	Cl>20mg/L	16.1	7.03	909	60	61	0.47	0.3	124	322	77	39	0.45	27	0.1	0.1	0.1	6.5	3	77	0.713338					487		
ASG-008	Cl>20mg/L	16.3	6.65	307	130	34	0.28	0.2	2	114	36	6	0.04	9	0.5	0.0	0.1	6.1	2	6					143			
ASG-009	Cl>20mg/L	17.3	7.23	617	120	25	0.28	0.3	11	268	67	24	0.36	14	0.1	0.3	0.0	7.4	3	62	0.711683	4.0	-33.0	-6.3	-11.3	272		
ASG-010	Ca-HCO <sub>3</sub>	16.75	6.3	346		25	nd	nd	11	170	35	9	0.14	13	1.1	0.1	0.2	12.4	12	20			-36.0	-6.0	-13.8	177		
ASG-011	Ca-HCO <sub>3</sub>	18.17	6.47	281		5	nd	nd	10	168	24	6	0.15	23	0.2	0.1	0.1	17.1	19	54	0.715943	20.8	-33.8	-6.1	-17.1	149		
ASG-012	Ca-HCO <sub>3</sub>	17.41	6.93	334		15	nd	nd	6	179	31	5	0.19	27	0.5	0.1	0.2	10.8	14	39			-35.5	-5.6	-17.4	172		
ASG-013	Ca-HCO <sub>3</sub>	15.29	6.44	246		2	nd	nd	5	152	25	5	0.13	15	0.6	0.1	0.1	13.6	12	33	0.716227	19.1	-32.3	-5.7	-18.6	127		
ASG-014	Ca-HCO <sub>3</sub>	17.17	7.13	260		2	nd	nd	12	152	28	5	0.26	14	0.1	0.2	0.1	11.3	12	31			-31.8	-5.7	-17.0	136		
ASG-015	Ca-HCO <sub>3</sub>	16.92	6.65	264		3	nd	nd	6	161	28	7	0.07	9	0.1	0.1	0.2	13.9	14	13			-32.2	-5.6	-18.0	132		
ASG-016	Ca-HCO <sub>3</sub>	16.51	6.6	255		4	nd	nd	7	149	27	5	0.11	12	1.0	0.1	0.2	13.8	12	28	0.715200		-33.8	-6.0	-16.9	128		
ASG-017	Ca-HCO <sub>3</sub>	16.59	6.28	505		4	nd	1.17	122	166	47	17	0.12	16	1.8	0.1	0.2	16.0	33	53	0.714950	10.0	-29.7	-4.9	-15.2	288		
ASG-018	Ca-HCO <sub>3</sub>	16.86	6.4	212		6	nd	nd	8	120	15	7	0.05	9	2.6	0.1	0.4	13.1	13	24			-37.3	-5.9	-16.3	105		
ASG-019	Ca-HCO <sub>3</sub>	17.09	6.18	240		8	nd	nd	22	115	20	7	0.12	11	1.7	0.1	0.1	12.2	13	22	0.714504		-37.6	-6.0	-18.3	124		
ASG-020	Ca-HCO <sub>3</sub>	14.94	6.46	229		3	nd	nd	10	131	21	6	0.07	11	0.8	0.1	0.1	12.8	11	28			-32.0	-5.6	-17.0	116		
ASG-021	Ca-HCO <sub>3</sub>	17.13	6.62	250		2	nd	nd	5	154	25	5	0.18	14	0.3	0.1	0.1	14.0	12	38			-30.4	-5.4	-18.2	126		
ASG-022	Ca-HCO <sub>3</sub>	16.06	7.09	314		2	nd	nd	4	197	42	6	0.08	10	0.1	0.1	0.0	11.0	4	8	0.712553		-33.0	-5.3	-17.5	160		
ASG-023	Ca-HCO <sub>3</sub>	16.18	7.08	285		1	nd	nd	2	182	35	5	0.07	10	0.3	0.1	0.1	10.5	4	7			-31.4	-6.1	-17.7	143		
ASG-024	Ca-HCO <sub>3</sub>	17.24	6.23	466		4	nd	0.05	151	106	57	8	0.15	13	0.9	0.1	1.0	14.1	20	14			-31.1	-5.7	-17.6	284		
ASG-025	Ca-HCO <sub>3</sub>	17.27	6.87	284		3	nd	0.05	4	177	34	5	0.16	11	0.0	0.1	0.0	14.3	13	13	0.714099		-35.0	-5.9	-18.3	144		
ASG-026	Ca-HCO <sub>3</sub>	16.89	6.36	428		11	nd	1.66	17	241	30	13	0.40	34	0.3	0.1	0.1	8.9	16	104	0.715791	24.5	-32.1	-5.5	-16.9	222		
ASG-027	Ca-HCO <sub>3</sub>	16.21	6.5	302		2	nd	0.01	6	182	38	7	0.13	13	0.0	0.1	0.1	15.2	12	20			-34.0	-5.5	-16.9	156		
ASG-028	Ca-HCO <sub>3</sub>	15.7	6.82	224		2	nd	0.1	3	138	33	3	0.05	2	0.0	0.1	0.1	7.3	3	4						111		
ASG-029	Ca-HCO <sub>3</sub>	15.7	7.26	260		2	nd	0.2	3	157	42	2	0.07	1	0.1	0.0	0.0	3.2	0	6			-37.9	-6.4	-12.7	127	na	na
ASG-030	Ca-HCO <sub>3</sub>	26.2	7.77	278	130	9	nd	1.2	6	153	29	9	0.03	3	0.0	0.0	0.0	1.6	0	10			-30.7	-4.9	-10.3	130	na	na
ASG-031	Ca-HCO <sub>3</sub>	15.7	6.84	486	25	8	nd	nd	6	262	68	7	0.06	5	0.2	0.0	0.6	5.2	1	9						223		
ASG-032	Ca-HCO <sub>3</sub>	15.6	6.62	222	30	3	nd	0.5	7	129	35	4	0.06	2	0.5	0.0	0.1	5.3	1	6						114		
ASG-033	Ca-HCO <sub>3</sub>	15.5	7.35	402	100	3	nd	0.5	6	185	63	7	0.11	2	0.0	0.0	0.0	4.6	3	13	0.709742		-35.1	-6.1	-12.8	171	na	na
ASG-034	Ca-HCO <sub>3</sub>	17.2	6.93	520		9	nd	0.5	10	316	68	10	0.10	9	0.0	0.1	0.0	4.8	2	17	0.711914					262		
ASG-035	Ca-HCO <sub>3</sub>	19.5	6.51	263	130	4	nd	0.5	13	143	24	9	0.08	10	0.7	0.1	0.2	13.7	10	20						129		
ASG-036	Ca-HCO <sub>3</sub>	19.8	6.81	367		13	nd	0.5	13	197	36	8	0.20	18	0.0	0.1	0.3	8.5	7	24	0.712717					186		
ASG-037	Ca-HCO <sub>3</sub>	16.6	6.86	477	125	56	nd	0.1	5	195	48	6	0.08	35	0.5	0.1	0.2	5.2	3	7						246		
ASG-038	Ca-HCO <sub>3</sub>	16.9	6.92	220	40	4	nd	0.0	16	109	21	5	0.06	13	0.9	0.0	0.4	6.8	3	35			-31.9	-5.6	-14.3	112	na	na
ASG-039	Ca-HCO <sub>3</sub>	17.1	6.84	298	65	1	nd	1.1	2	185	48	3	0.05	1	0.0	0.0	0.0	3.7	0	6						147		
ASG-040	Ca-HCO <sub>3</sub>	16.4	7.1	255	65	2	nd	0.1	7	152	27	4	0.04	13	0.3	0.0	0.3	14.8	6	12						127		
ASG-041	Ca-HCO <sub>3</sub>	16.1	7.17	466	30	2	nd	0.5	4	247	46	15	0.10	30	1.5	0.0	0.1	9.0	2	56	0.712206		-35.5	-6.3	-16.0	219	na	na
ASG-042	Ca-HCO <sub>3</sub>	16.7	6.95	370	160	2	nd	0.9	6	230	47	7	0.04	3	0.0	0.0	0.0	4.0	0	19						179		
ASG-043	Ca-HCO <sub>3</sub>	16.3	6.91	288	60	4	nd	0.1	4	171	35	9	0.04	4	0.5	0.0	0.1	6.1	5	22		26.0				140		
ASG-044	Ca-HCO <sub>3</sub>	16	7.32	418	60	6	nd	0.1	6	256	48	11	0.33	7	0.2	0.3	0.2	6.5	2	59	0.711734					203		
ASG-045	Ca-HCO <sub>3</sub>	24.8	7.39	318		1	nd	0.1	11	189	46	4	0.11	2	0.5	0.1	0.0	4.5	1	11	0.710176		-38.1	-6.6	-12.5	157		
ASG-046	Ca-HCO <sub>3</sub>	16.7	7.24	446	43	4	nd	0.1	18	254	44	12	0.40	18	0.2	0.1	0.2	7.4	3	91	0.711862	16.5				221		
ASG-047	Ca-HCO <sub>3</sub>	15.5	7.5	358	100	2	nd	2.4	27	189	37	9	0.41	8	0.0	0.1	0.0	4.5	2	88	0.711539	14.0				177		
ASG-048	Ca-HCO <sub>3</sub>	14.8	6.73	264	45	7	0.10	0.7	6	142	29	9	0.07	5	1.1	0.1	0.2	8.7	3	33			-33.7	-6.2	-14.4	126	na	na
ASG-049	Ca-HCO <sub>3</sub>	18.3	7.08	367	150	11	0.17	0.6	3	205	47	5	0.08	6	0.1	0.1	0.1	5.3	1	7						173		
ASG-050	Na-HCO <sub>3</sub>	16.46	6.55	232		10	nd	0.01	3	126	13	6	0.08	21	1.1	0.0	0.1	11.2	7	45	0.716597		-32.9	-5.6	-17.8	115		
ASG-051	Na-HCO <sub>3</sub>	18.18	8.64	824		8	nd	2.83	0	527	2	0	0.03	144	0.0	0.0	0.0	4.5	27	235			-33.2	-5.9	-13.8	412		
ASG-052	Na-HCO <sub>3</sub>	17.53	7.28	444		6	nd	1.49	15	266	27	6	0.34	50	0.2	0.1	0.0	9.7	15	63	0.716092	21.2	-33.0	-5.5	-14.8	235		
ASG-053	Na-HCO <sub>3</sub>	17.57	6.7	539		8	nd	1.93	34	282	38	14	0.26	42	0.9	0.1	0.1	8.5	14	101	0.714999	24.0	-35.2	-5.8	-15.8	274		
ASG-054	Na-HCO <sub>3</sub>	17.1	7.39	304		4	nd	nd	0	198	20	4	0.16	36	0.1	0.0	0.0	10.7										



Bold and italics indicate analysis was completed using CRDS.

Ar	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO	C <sub>1</sub>	C1/C2	δ <sup>2</sup> H-C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub>	iC <sub>4</sub>	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	C <sub>6</sub> +	Specific	BTU	Dissolved CH <sub>4</sub> cc/L	Dissolved CH <sub>4</sub> mg/L	Helium dilution	Distance to NG well (km)	Distance to Stream (km)	Dissolved CH <sub>4</sub> mg/L	Land Surface Elevation (m)	# of NG wells within 1 km	δ <sup>13</sup> CH <sub>4</sub> ‰	<sup>228</sup> Ra (pCi/L)	<sup>226</sup> Ra (pCi/L)	
																			0.350 0.057			1.67 0.29 17.70 0.94	0.37 0.47 0.39 0.14	0.350 0.057	92 149 98 236	1 11 0 3	-59		
1.40	3.15	0.25	74.94	nd	20.23	730.32	-181	0.0277	nd	nd	nd	nd	nd	nd	nd	0.895	205	6.50	4.30	0.68	0.54	0.73	4.30	215	6	-68			
1.33	18.91	10.33	69.43	nd	nd			nd	nd	nd	nd	nd	nd	nd	nd	1.056	0	< 0.0005	0.000	0.69	2.84 1.28 6.65 9.78 11.76	0.21 0.62 0.16 0.67 0.40		483 363 359 404 137	0 0 0 0 0				
																					0.042 0.016 0.267 0.000 0.000 0.000 0.068 0.000 0.000 0.000 0.045 0.003		0.042 0.016 0.267	143 142 113 202 236 129 154 145 190 183 190 189 186 140 178 129 166 331	0 6 1 7 2 1 0 1 3 3 6 0 0 2 0	-60			
1.38	20.37	3.09	73.25	0.035	1.88			nd	nd	nd	nd	nd	nd	nd	nd	1.01	19	0.6	0.4	0.68	0.18	0.63	0.4	347	0				
1.4	28.57	0.95	69.01	0.054	0.012			nd	nd	nd	nd	nd	nd	nd	nd	1.017	0	0.0035	0.0023	0.70	0.43 0.91 1.09 0.45 0.79 0.67 3.57 4.10	0.40 0.48 0.24 0.14 0.11 0.71 0.25 0.18	0.0023	351 357 341 335 360 216 173 321	0 3 2 4 3 1 0 0				
1.52	12.93	3.75	81.78	0.024	nd			nd	nd	nd	nd	nd	nd	nd	nd	1.012	0	< 0.0005	0.000	0.72	0.45 0.79 0.67 3.57 4.10	0.14 0.11 0.71 0.25 0.18		341 335 360 216 173 321	2 4 3 1 0 0				
1.57	3.64	3.84	90.88	0.010	0.0621			nd	nd	nd	nd	nd	nd	nd	nd	1	1	0.019	0.012	0.69	0.57 1.18 0.17	0.11 0.08 0.29	0.012	163 208 255	5 0 6				
1.53	4.14	7.04	87.15	nd	0.141			nd	nd	nd	nd	nd	nd	nd	nd	1.018	1	0.042	0.028	0.67	11.63 1.58 15.24 15.00 13.00 8.89 8.52	0.12 0.38 0.29 0.33 0.07 0.33 0.12	0.028	253 439 451 424 394 374 361	0 0 0 0 0 0 0				
1.57	3.38	8.53	86.51	nd	0.007			nd	nd	nd	nd	nd	nd	nd	nd	1.025	0	0.002	0.0013	0.7	11.84 0.41 8.35 1.79 1.39	0.78 0.29 0.14 0.09 0.12	0.0013	405 253 95 120 100	0 4 0 0 1				
																					7.03 4.78 2.80 0.72 0.86 0.57 0.42	0.11 0.12 0.40 0.80 0.42 0.53 0.10	0.480 0.822 0.344 0.261 1.429 0.057 0.800	88 106 142 172 142 128 220	0 0 1 5 2 7 4	-45 -63			
																					0.26 0.24 4.30 4.65 3.86 25.75 0.38	0.02 0.14 0.10 0.08 0.05 0.52 0.36		190 116 99 98 92 171 221	6 1 2 2 0 0 3	-54 -60 -64 -58			

																				0.21	0.32		193	6	
																				0.26	0.33		191	6	
																				0.68	0.07		174	1	
																				0.22	0.85		156	3	
																				0.52	0.16		223	6	
																				6.48	0.90		468	0	
1.29	3.31	1.87	85.49	nd	8.04	-339	nd	nd	nd	nd	nd	nd	nd	nd	0.954	81	2.5	1.7	0.66	10.08	0.41	1.7	410	0	-75
																				0.08	0.45	0.098	136	6	
																				0.79	0.50		214	3	
																				0.95	0.73		234	3	
																				0.43	0.50		200	2	
																				0.51	0.47	0.012	207	3	
																				0.43	0.19		230	8	
																				1.05	0.22		144	0	
																				0.74	0.13		198	7	
																				0.33	0.52		164	2	
																				0.00	0.36		189	1	
																				0.47	0.10		196	3	
																				0.39	0.08		118	1	
																				1.48	0.06		116	2	
																				0.75	0.08		135	1	
																				0.38	0.09		113	2	
																				1.56	0.13		162	0	
																				0.79	0.10		178	2	
																				2.46	0.27		392	2	
																				2.26	0.00		192	0	
1.29	18.15	14.63	65.91	0.016	nd		nd	nd	nd	nd	nd	nd	nd	nd	1.078	0	< 0.0005	0.0001	0.68	0.17	0.04		352	2	
																				0.30	0.45		342	1	
																				0.25	0.14		330	4	
																				0.48	0.28		240	2	
																				0.85	0.45		266	4	
1.33	15.85	7.81	74.99	0.019	nd		nd	nd	nd	nd	nd	nd	nd	nd	1.038	0	< 0.0005	0.0001	0.69	0.17	0.19		256	4	
																				3.33	0.49		158	0	
1.46	11.02	12.54	74.95	0.026	nd		nd	nd	nd	nd	nd	nd	nd	nd	1.058	0	< 0.0005	0.0001	0.72	0.15	0.57		264	4	
1.33	6.33	13.92	78.38	0.027	0.0094		nd	nd	nd	nd	nd	nd	nd	nd	1.058	0	0.0028	0.0019	0.69	0.68	0.79	0.0019	236	13	
																				0.22	0.48		215	4	
																				0.46	0.21		217	4	
1.35	8.71	15.46	74.46	0.025	nd		nd	nd	nd	nd	nd	nd	nd	nd	1.07	0	< 0.0005	0.0001	0.70	0.33	0.06		123	12	
																				0.20	0.33		345	6	
																				0.33	0.07		251	9	
																				0.43	0.57		182	6	
																				0.22	0.45		176	3	
																				0.47	0.42		265	2	
																				0.44	0.07		495	5	
																				6.18	0.39		472	0	
																				15.75	1.15		442	0	
																				16.34	0.40		449	0	
																				15.76	0.47		440	0	
																				0.59	0.31		208	6	
																				0.91	0.45		156	1	
																				0.23	0.15		196	0	
																				0.58	0.21		117	1	
																				1.21	0.28		179	0	
1.43	0.73	13.09	84.43	0.009	0.316		nd	nd	nd	nd	nd	nd	nd	nd	1.045	3	0.100	0.0690	0.68	3.33	0.22	0.069	153	0	
1.44	3.59	12.85	82.1	0.011	0.0049		nd	nd	nd	nd	nd	nd	nd	nd	1.049	0	0.0015	0.0010	0.67	6.11	0.26	0.001	521	0	
																				9.46	0.25		277	0	
																				1.01	0.12		426	0	
1.28	18.14	12.67	67.9	nd	0.0064		nd	nd	nd	nd	nd	nd	nd	nd	1.067	0	0.0019	0.0013	0.67	15.74	0.26	0.0013	451	0	
1.36	9.73	11.65	73.45	nd	3.81	-339	nd	nd	nd	nd	nd	nd	nd	nd	1.035	39	1.2	0.8100	0.66	14.90	0.33	0.81	441	0	-59
1.56	3.52	8.74	86.16	nd	0.0166		nd	nd	nd	nd	nd	nd	nd	nd	1.027	0	0.0049	0.0033	0.67	9.70	0.18	0.0033	402	0	
1.47	0.07	8.39	89.40	nd	0.67	-122	nd	nd	nd	nd	nd	nd	nd	nd	1.02		0.22	0.1500				-122.00			-42

Table 2. Historical water quality results from the USGS National Water Information System database for Cleburne, Conway, Faulkner, Independence, Van Buren, and White Counties, Arkansas.

Latitude	Longitude	Date sample collected	Sample start time	pH	Specific conductance (μS/cm)	Temperature (°C)	Depth of well (feet)	Total Dissolved Solids (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Bicarbonate (mg/L)	Chloride (mg/L)	Silica (mg/L)	Sulfate (mg/L)	Nitrate (mg/L as nitrogen)	Iron (μg/L)	Manganese (μg/L)
351352	914018	9/28/1954	--	6.9	213	--	217	142	21	4.8	17	129	3	14	0.8	0.34	30	--
351352	914018	2/5/1955	--	7.4	223	11	217	121	21	3.8	18	124	3.5	9.4	1.6	1.8	0	--
351352	914018	4/18/1955	--	6.9	213	11	217	120	19	5.7	18	126	3.2	12	0.8	0.16	100	--
350509	924502	1/25/1959	--	7.5	236	--	127	--	--	--	--	--	--	--	--	--	--	--
350509	924502	8/25/1959	--	6.9	602	--	127	--	--	--	63	40	146	--	6.2	1.8	--	--
350604	924602	1/13/1959	--	8.1	366	--	43.1	--	--	--	--	--	62	--	--	--	--	--
353123	920028	9/16/1960	--	6.3	311	16.5	74.9	228	33	10	4.7	20	2.8	10	111	0.23	0	--
351026	924438	9/15/1960	--	7.2	371	18.5	33	24	19	8.3	38	110	32	5.7	22	3.4	0	--
352510	924242	9/26/1960	--	6	243	--	50.8	126	8.4	2.8	21	28	24	6.3	22	2.5	0	--
345704	922429	9/26/1960	--	6.8	1210	18	128	790	65	34	145	284	180	5.8	122	0.11	70	--
350510	921150	9/16/1960	--	6.8	1360	17	45.3	1040	51	83	72	88	378	9.1	12	0	0	--
350515	922440	9/16/1960	--	6.3	573	18	22.4	435	21	24	51	33	96	8.6	100	0.16	0	--
350600	922852	1/23/1951	--	8	631	15.5	--	--	--	--	--	374	2.5	--	18	--	10	--
350432	923214	1/25/1965	--	7.4	422	--	155	263	28	11	48	233	20	22	8.8	0	--	100
350432	923214	10/1/1971	--	6.6	736	21.9	155	411	52	32	53	332	64	12	15	0.11	--	20
350432	923214	3/2/1976	1000	6.9	--	--	155	--	41	18	48	251	31	18	13	--	1400	240
350432	923214	3/2/1976	1005	--	--	--	155	--	44	21	52	301	33	21	24	--	120	140
351447	922727	9/26/1960	--	6.7	263	19.5	19.1	192	23	11	15	150	3.2	20	6.4	0.05	80	--
351447	922727	9/30/1953	--	8.1	475	21	19.1	--	--	--	--	270	15	--	20	0.203	--	--
351322	922719	7/24/1997	1000	6.7	378	20.8	416	136	21	5.9	12	--	2.1	29	16	< 0.007	6300	600
353323	932618	9/16/1960	--	8	1840	16.5	84.9	1450	95	211	53	980	100	5.6	255	0	0	--
350600	915643	4/15/1955	--	6.8	159	17	42	159	9.7	7.5	9.6	80	6.2	17	5.2	0.14	0	--
351237	914531	6/21/1955	--	8.2	351	16	11	--	39	8.7	26	210	6	--	5	0.18	10	--
351947	920453	9/26/1960	--	6.3	154	20	160	7	7.9	4.3	9.4	44	9.5	13	5.6	0.68	0	--
352847	913056	5/19/1964	--	5.9	32	15.5	--	27	107	0.3	2	6	4.5	12	1.2	0.294	--	10
354055	923020	8/29/1968	--	6.6	202	19	--	121	15	9.1	13	121	1.6	15	4.2	0.11	--	170
352114	913253	9/1/1983	1415	--	62	19	64	--	--	--	--	--	8.8	--	--	--	--	--
352114	913352	9/1/1983	1530	--	430	17	--	--	--	--	--	--	28	--	--	--	--	--
352020	913248	9/1/1983	1340	--	895	20.5	318	--	--	--	--	--	33	--	--	--	--	--
351934	913521	9/1/1983	--	--	440	18	65	--	--	--	--	--	18	--	--	--	--	--
351849	913836	8/30/1983	1245	--	735	22	90	--	--	--	--	--	110	--	--	--	--	--
351843	913914	8/31/1983	0830	--	930	17	35	--	--	--	--	--	140	--	--	--	--	--
351822	913834	8/30/1983	1330	--	1260	20	80	--	--	--	--	--	260	--	--	--	--	--
351725	913358	8/31/1983	1350	--	277	17	60	--	--	--	--	--	49	--	--	--	--	--
351636	913822	9/20/1983	1515	6.8	390	18	--	217	34	9.5	34	--	5.4	25	3.4	--	860	70
351606	914232	9/6/1955	--	6.6	158	18.5	141	108	11	6.5	12	86	5	--	3.4	0.43	0	--
352508	913130	9/2/1983	1330	--	610	17	66	--	--	--	--	--	38	--	--	--	--	--
352414	912949	9/2/1983	--	--	297	19	60	--	--	--	--	--	7	--	--	--	--	--
352351	913107	9/2/1983	0900	--	420	18	100	--	--	--	--	--	9.3	--	--	--	--	--
352229	913040	9/2/1983	1020	--	280	17	85	--	--	--	--	--	70	--	--	--	--	--
352256	913124	9/2/1983	0945	--	180	18	154	--	--	--	--	--	19	--	--	--	--	--
352207	913337	9/2/1983	0745	--	598	22	72	--	--	--	--	--	140	--	--	--	--	--
352146	913250	9/1/1983	1500	--	540	19.5	176	--	--	--	--	--	12	--	--	--	--	--

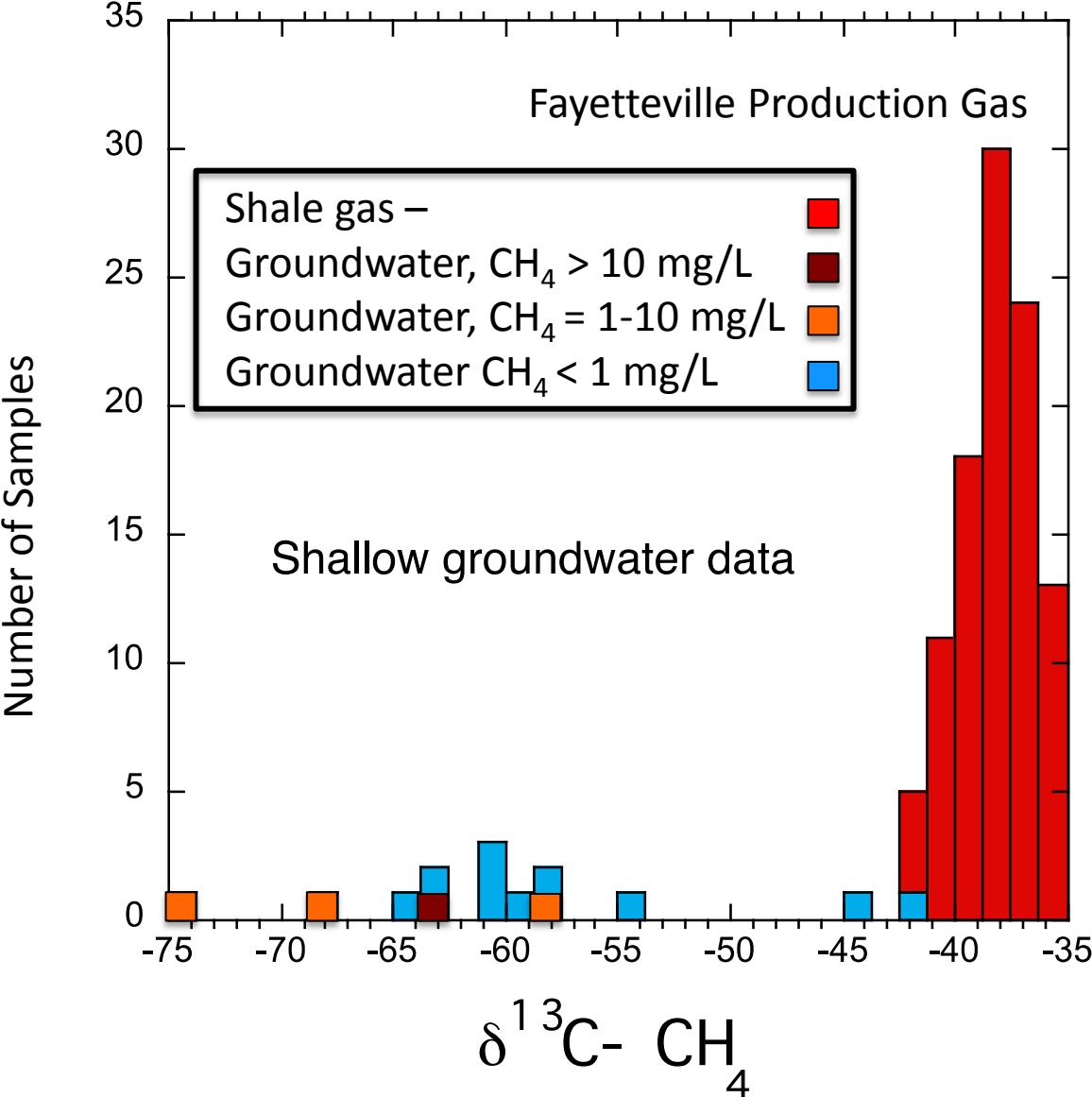
Table 3. Typical Produced Water TDS (mg/L) Concentrations.

	TDS (mg/L)	DIC (mg/L)
<b>Fayetteville Shale</b>	<b>25,000</b>	1300 <sup>a</sup>
Barnett Shale	60,000	610*
Woodford Shale	110,000	
Haynesville Shale	120,000	
Permian Basin	140,000	
Marcellus Shale	180,000	140*

a - this study

\* EPA workshop on hydraulic fracturing -[http://www.epa.gov/hfstudy/12\\_Hayes\\_-\\_Marcellus\\_Flowback\\_Reuse\\_508.pdf](http://www.epa.gov/hfstudy/12_Hayes_-_Marcellus_Flowback_Reuse_508.pdf)

Source, Kimball, 2012 citation of USGS produced water database- available at <http://energy.cr.usgs.gov/prov/prodwat/data.htm>





**Highlights**

- No evidence for shallow groundwater contamination in Fayetteville Shale, Arkansas;
- Methane in groundwater is low and likely associated with shallow aquifer processes;
- No relationship between methane and salinity in groundwater and shale-gas wells;
- $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  suggest biogenic origin for dissolved methane;
- Water- aquifer rock interaction controls majority of water chemistry.