



Pre-drilling background groundwater quality in the Deep River Triassic Basin of central North Carolina, USA



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ABSTRACT

Unconventional natural gas development via horizontal drilling and hydraulic fracturing has greatly increased the supply of natural gas in the United States. However, the practice presents concerns about the possibility for impacts on shallow groundwater aquifers. The Deep River Triassic Basin in central North Carolina is likely to contain natural gas that could be extracted via hydraulic fracturing in the future. Unlike other states where hydraulic fracturing has been employed, North Carolina has no history of commercial oil and gas extraction. In this study, we measured water chemistry, dissolved gases, and volatile organic compounds in 51 private drinking water well samples over the Deep River Triassic Basin. Our data document the background water quality of shallow aquifers in the Deep River Basin, which could provide an important baseline dataset if hydraulic fracturing occurs here in the future. We found only two of the 51 water wells sampled had dissolved CH₄ concentrations >0.1 mg/L, and no well had a methane concentration >0.5 mg/L. The $\delta^{13}\text{C}\text{-CH}_4$ of the two highest CH₄ concentration water wells (−69.5‰ and −61‰) suggest a biogenic CH₄ source and are distinct from the $\delta^{13}\text{C}\text{-CH}_4$ of two test gas wells drilled in the area (−54.41‰ and −45.11‰). Unlike other basins overlying shale gas formations in the US, we find no evidence for CH₄ migration into shallow groundwater in the Triassic basin. In addition, we found only seven VOCs in five water samples, with all levels below the US EPA's maximum contaminant levels. Ion and trace metal concentrations in most samples were also below US EPA primary drinking water standards, with the exception of two samples that exceed the standards for As. We modeled the depth of the upper surface of the Cummock Shale formation in the Deep River Basin using a kriging algorithm and found that its depth below the surface is shallow (0–~1500 m) relative to other shale formations that have been drilled commercially in the US, including the Marcellus in Pennsylvania and the Fayetteville in Arkansas. The relatively shallow shale, combined with the presence of multiple faults and diabase intrusions that characterize the geology of the area, may make the Deep River Triassic Basin more vulnerable to deep fluid connectivity to shallow aquifers.

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1. Introduction

The combination of horizontal drilling and hydraulic fracturing (HDHF) has dramatically increased the amount of natural gas and oil extracted in the United States and could soon become an important contributor to energy worldwide (Priddle, 2011). These technologies are used to extract hydrocarbons from organic-rich

shales and other tight formations that would otherwise be uneconomical to extract. Burning natural gas to produce electricity produces half as much CO₂ as does burning coal (Burnham et al., 2012) and with none of the sulfur dioxides and mercury compounds that are emitted from coal combustion. Although the potential exists for HDHF wells to emit large amounts of uncombusted CH₄ (Howarth et al., 2011), subsequent research has suggested that life-cycle CO₂ emissions from electricity generation using natural gas could be lower than those from coal (Allen et al., 2013; O'Sullivan and Paltsev, 2012; Jiang et al., 2011). The net long-term effect of abundant natural gas on the global power sector is

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complex, however, because the benefits of offsetting CO₂ emissions from coal-fired power are balanced against potential emission increases from lower-priced natural gas offsetting renewables with lower CO₂ emissions (Shearer et al., 2014).

Public concerns have been raised about the potential for hydraulic fracturing to contaminate shallow groundwater and surface water supplies (Vengosh et al., 2014). Recent work in the Marcellus Shale basin has demonstrated that water wells within 1 km of hydraulically fractured gas wells had statistically higher dissolved CH₄ and C₂H₆ concentrations on average than water wells farther away (Osborn et al., 2011; Jackson et al., 2013). The stratigraphic interval that is the source of stray gas and possible association with HDHF in some but not all cases remains debated (e.g. Molofsky et al. (2013)). While stray gas contamination has been documented in Pennsylvania, a similar study of private drinking water wells in the Fayetteville shale in Arkansas, USA found no evidence for shallow groundwater contamination from fugitive gas accompanying HDHF there (Warner et al., 2013). Moreover, gas well construction may be as important as geology, if not more so, in determining subsurface gas and fluid migration (Darrach et al., 2014). Importantly, the studies in both states were conducted after HDHF had already begun. In this paper, we seek to evaluate the potential for deep fluid connectivity in the Deep River Basin in North Carolina and to provide a baseline of water tests prior to likely oil and gas drilling in the region. This basin contains multiple faults and numerous diabase dikes, but it is not clear a priori whether these geologic features could enhance fluid connectivity at depth if HDHF occurs.

HDHF was legalized in North Carolina in August of 2012. The Deep River Basin in central North Carolina, USA, contains natural gas in the Cumnock Shale formation, which is the most likely shale play to be drilled using HDHF in the future. Unlike many other areas of the United States with unconventional gas reserves, North Carolina has little or no history of commercial oil and gas extraction. As such, it is important to collect background water quality data in advance of oil and gas drilling. These data will help document any changes in water chemistry if hydraulic fracturing occurs in the region.

In this study, we present data from 51 water samples collected from shallow private groundwater wells in the Deep River Basin overlying the Cumnock Shale. This study is a comprehensive effort to document the water chemistry in the Deep River Basin and includes analysis of the distribution of salts, metals, dissolved gases, volatile organic compounds, and isotopic ratios of CH₄ and Sr. This study provides a water quality database and some insights for the possible hydraulic connectivity between the shale formation and the overlying shallow drinking water aquifer. To further investigate the potential for subsurface fluid migration, we develop a depth model for the Cumnock Shale, with which we are able to identify the signature of fluids in the Cumnock Shale from the shallow, unconfined portion of the shale as containing higher dissolved CH₄ concentrations than those from the overlying Sanford Formation.

2. Materials and methods

2.1. Geologic setting

The majority of the samples were collected in Lee County, North Carolina, northwest of the town of Sanford, with some samples collected slightly to the north in southern Chatham County. The study area is located above the region of the Cumnock Shale most likely to be drilled for oil and gas first, based on past exploratory drilling and seismic studies (Reid et al., 2011). This area is characterized by gently rolling hills, with the Deep River bisecting the northern

portion of the study area (Fig. 1). The Cumnock Shale is of Triassic age (~230 million years old) and is contained within the Deep River rift basin. The Cumnock is underlain by the Pekin sandstone and overlain by the Sanford sandstone formations (see Fig. 2). The Deep River basin is divided into three sub-basins: the Sanford, Durham, and Wadesboro. The Durham and Sanford sub-basins are separated by the Colon cross-structure, a constriction of the basin caused by a faulted anticlinal structure (Reid and Milici, 2008). The Wadesboro sub-basin is similarly separated from the Sanford sub-basin by the Pekin cross-structure (Reid and Milici, 2008). The study area is located over the Sanford sub-basin. North Carolina contains another Triassic rift basin, the Dan River Basin, but that area is less likely than the Deep River Basin to contain economically extractable amounts of oil or natural gas (Milici et al., 2012).

The Cumnock Shale is the most likely target of initial gas drilling in North Carolina. The formation ranges in thickness from ~60 m in the north central area of the basin to 200 m near the Colon cross-structure (Reid and Milici, 2008), sloping downwards towards the southeast, with outcrops at the surface in the northwestern portion of the basin. The Cumnock contains a layer of coal that was mined in the early 1900s (with the location of former coal mines shown in Fig. 2). The depth of the Cumnock Shale has not been measured over its entire extent, but the model that we developed based on measured depths in boreholes and test wells (see Section 3.4 below) suggests that the Cumnock ranges in depth from 0 to ~1500 m over the study area. The depth to the metamorphic rock underlying the Pekin Formation at the base of the Deep River Triassic basin varies from 0 to ~1800 m over the study area.

The texture, thickness, and compositions of the three formations in the Sanford sub-basin vary transversely and longitudinally. The Cumnock is mostly a fine-grained shale in the northwestern portion of the sub-basin and grades into coarse-grained conglomeritic sandstone towards the southeast of the Triassic basin (Reinemund, 1955). Reid and Milici (2008) measured the organic content of the Cumnock to be 5.17% by mass (based on an average of 66 total samples from five drill holes), with an abundance of type III kerogen derived from plants. Diabase dikes intruded into the Deep River basin during the Late Triassic (Luttrell, 1989). These dikes range in thickness from centimeters to hundreds of meters and in length from meters to kilometers (Reid and Milici, 2008) and generally trend to the northwest, perpendicular to the major faults in the area (Fig. 2). The water wells in the Deep River Basin are generally low-yielding when confined to the tight sandstones of the Sanford Formation (Bain and Thomas, 1966). However, some wells in the study area, including at least one sampled for this study (as indicated in well construction records), are known to intersect diabase dikes and the Cumnock coal deposits (Reinemund, 1955). We were not able to make measurements of hydraulic head as part of this study, nor is the information available in the published literature or from the USGS. However, future studies of groundwater flow in the region would benefit from an effort to obtain such data.

2.2. Well water sampling

We collected 51 water samples from private groundwater wells used for drinking water. Private wells were selected in collaboration with the United States Geologic Survey (North Carolina) office to represent the geographic area of the Sanford sub-basin as well as variations in depth and well construction methods. Well characteristics, including depth, were taken from well construction records provided by the Lee and Chatham County health departments. Where well records were not available, water well information was collected from tags left on the wellhead at the time of construction. Our well water samples were collected

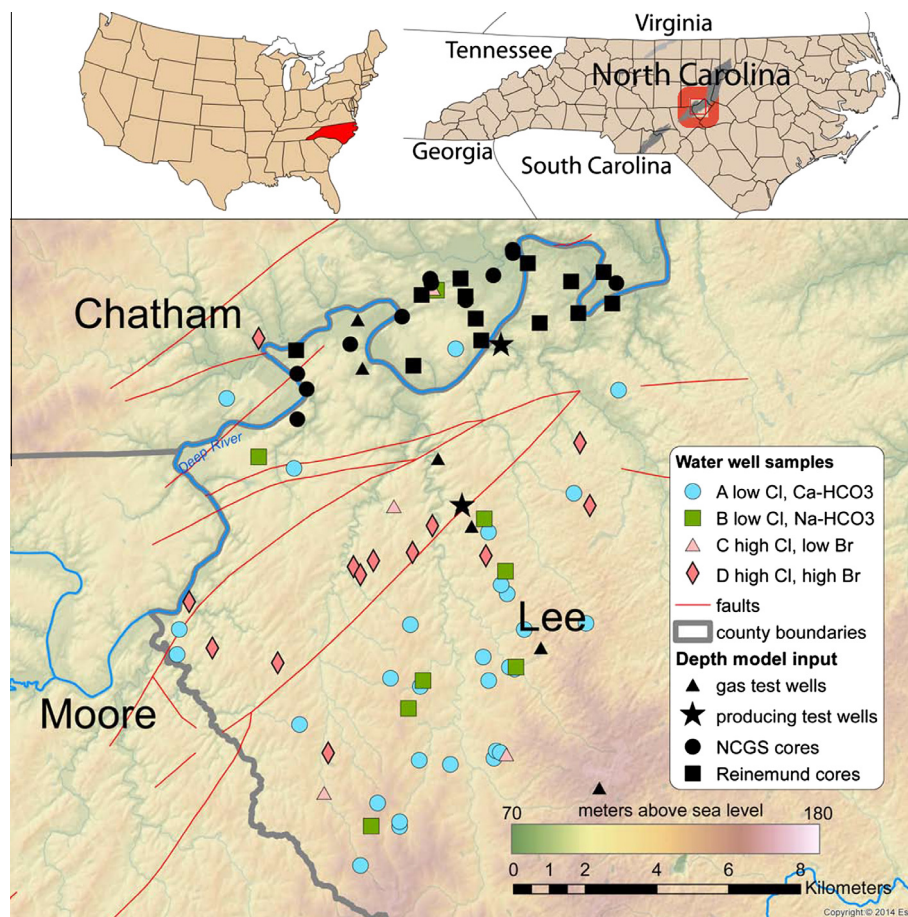


Fig. 1. Location of study area, well water samples, and surface elevation of study area. The Deep River Triassic Basin is highlighted in gray on the state map, with a red box (top right panel) around the inset (lower panel) of the study area that includes portions of Lee, Chatham, and Moore counties. Water well sampling locations are indicated, differentiated by water chemistry types (following Warner et al. (2012)): Ca–HCO₃ (“type A”, blue circles), Na–HCO₃ (“type B”, green squares), Cl > 20 mg/L with low Br (“type C”, pink triangles), and Cl > 20 mg/L with high Br (“type D”, red diamonds). Faults are indicated in red. Sources of data used in creating a depth model for the upper surface of the Cumnock Shale are indicated in black symbols, and described in the text. Elevation and fault data are from the NC Geologic Survey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between April and August 2012 in collaboration with USGS personnel. The data from the samples collected by the USGS during this sampling campaign can be found in Chapman et al. (2014).

Methods for collection of field parameters, such as pH, temperature, and specific conductance, followed standard USGS protocols (Wilde, 2006). Briefly, water wells were purged until field parameters (temperature, dissolved oxygen, electrical conductivity, and pH) stabilized, and all samples were collected upstream of pressure tanks or filtration devices. Samples analyzed for dissolved gases were collected in 1 L bottles, filled while submerged in sample water, following the instructions in Isotech Laboratories, Inc. (2014) and the methods in Osborn et al. (2011), Warner et al. (2013), and Jackson et al. (2013). Samples collected for trace element and major ion analyses were filtered (0.45 μm) upon collection into 100-ml plastic Nalgene bottles. Samples analyzed for volatile organic compounds were unfiltered and collected in pre-combusted U.S. EPA volatile organic assessment (VOA) vials without headspace. The vials were pre-acidified with 1 mL of 50% HCl (v/v) for preservation. All samples were preserved on ice in the field and subsequently refrigerated at the end of each day of sampling.

Concentrations of major ions, trace metals, and VOCs were analyzed at Duke University. Anion concentrations were determined by ion chromatography and cation concentrations by direct current plasma optical emission spectrometry (DCP-OES). Trace metal concentrations were determined by VG PlasmaQuad-3 inductively coupled plasma mass spectrometry (ICP-MS). Alkalinity was

determined by titration with HCl to pH 4.5. Dissolved CH₄ concentrations were determined by the USGS CFC lab for all samples (Hinkle et al., 2010). For a subset of samples, dissolved gases were analyzed by Isotech Laboratories for hydrocarbon concentrations and isotopic composition. All carbon isotopes were measured relative to Vienna Pee Dee Belemnite (VPDB). Values of δ¹⁸O and δ²H 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 the Duke Environmental Stable Isotope Laboratory (DEVIL) and are normalized to Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Standard Light Antarctic Precipitation (V-SLAP), respectively.

All isotopic and Sr concentrations were analyzed using isotope dilution under clean-lab practices in the Isotope Geochemistry Lab at the University of North Carolina, Chapel Hill. For each sample, approximately 30 g of sample was weighed and a ⁸⁴Sr spike was added. The sample was then dried and subsequently dissolved with 50 μg of 3.5 N HNO₃. The samples were passed through ion exchange columns using EiChrom SrSpec™ ion exchange resin. Strontium was isolated from other ions in the sample through rinses with 3.5 N HNO₃ and elution with water. The samples were then dried and loaded onto a rhenium filament and analyzed for Sr concentration and isotopic ratios on a Sector 54 thermal ionization mass spectrometer (TIMS). Samples were run in 3-cycle dynamic mode with an average ion beam intensity of 3 V ⁸⁸Sr with an

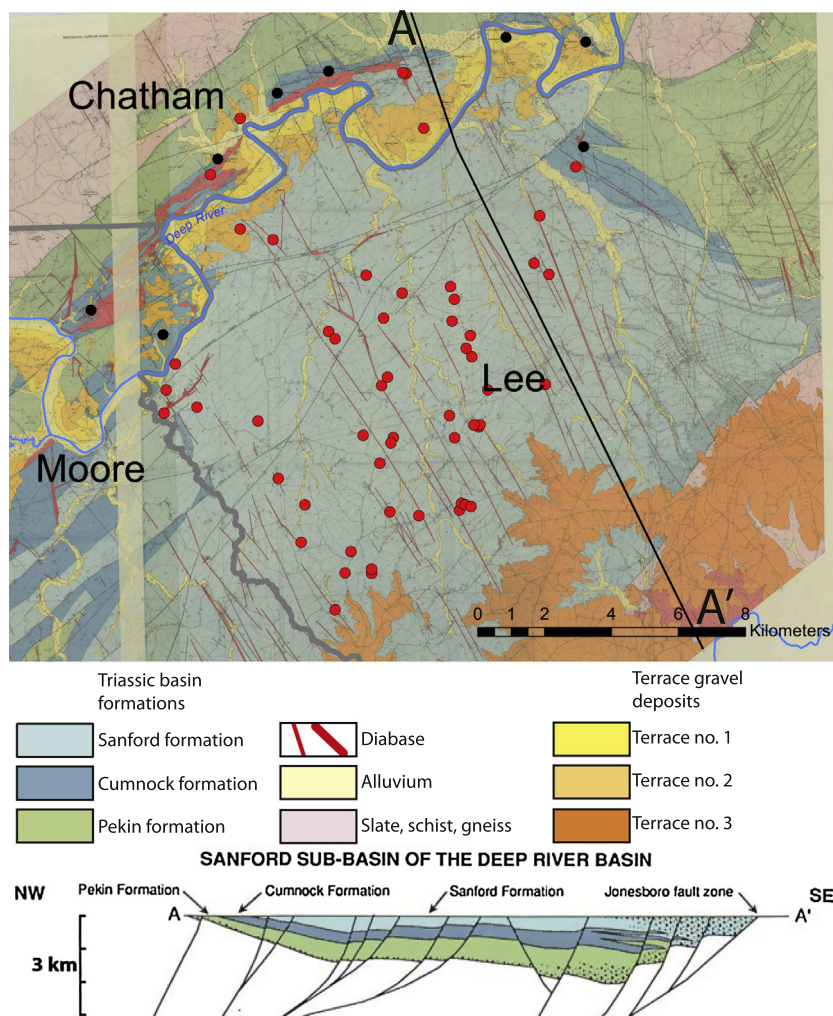


Fig. 2. Surface geology of study area, from Reinmund (1955), with water well sampling locations (red circles), location of former coal mines (black circles) (black text). Diabase dikes, shown in red, generally run NE to SW, with a large diabase outcrop in the NE of the study area near the border between Lee and Chatham counties. Geologic cross section from the North Carolina Department of Environment and Natural Resources (2012). The Cumnock Shale outcrops in the southwestern and northwestern portions of the study area (shown in darker blue) and gets deeper towards the southeast. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

exponential fractionation correction of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The resulting $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were corrected for the molarity of an ^{84}Sr spike added to the sample and re-corrected for fractionation. Replicate analyses of National Bureau of Standards (NBS) reference compound 987 yielded $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710258 (NBS reported value: 0.71034 ± 0.00026 , Moore et al. (1982)).

VOCs were quantified by gas chromatography with flame ionization detection (GC-FID) and standard reference compounds: 502.2 CAL 2000 Mega-Mix (No. 30431), 624 Calibration Mix #1 (No. 30020), 624 Calibration Mix #2 (No. 30021), 624 Calibration Mix #3 (No. 30022), all by Restek, Bellefonte, PA, USA. Compounds included in analysis are shown in the supplementary materials accompanying this article. For each water sample, 5-mL aliquots were manually injected with a glass micro-mate syringe (Cadence Science Inc., RI, USA) into a 5-mL Tekmar glass sparger on a Teledyne Tekmar Stratum Purge and Trap concentrator (Mason, OH, USA). The sample was purged for 4 min with ultra high purity helium, purified again using an RMSH2 purifier (Agilent Big Universal Trap Superior Helium Purifier) at a purge flow of 40 mL/min and dry purged for 1 min at 40 °C and 100 mL/min. The sample was then transferred onto an Agilent 7890A GC system with flame ionization detector (FID). The GC column was either an Agilent DB-624 (flow: 6 mL/min; temperature program: 40 °C,

2 min hold, ramp 4 °C/min–150 °C, then ramp 8 °C/min–200 °C) or a Restek-502.2 (flow: 20 mL/min; temperature program: 40 °C, 6 min hold, ramp 6 °C/min–200 °C). Both are long columns containing hydrophobic, thick stationary phases designed to maximize resolution for volatile hydrocarbons, and calibration standards were used to independently confirm retention times on each column. The compound identities were reconfirmed by GC-MS measurements on an Agilent 7890A GC system with MS 5975C with Chemstation Software.

2.3. Historical gas well records

Boreholes and test wells (32) were drilled in the sampling region over the past 50 years to evaluate the potential for oil and gas development. We used information from these wells and from other sources to estimate the depth between the land surface and the top of the Cumnock Shale to create a depth model for the upper boundary of the Cumnock Shale (see Section 2.4). Two test wells, both drilled in 1998, produced elevated pressure from natural gas and were then capped shortly after drilling. These wells remained capped and closed until gas samples from these two test wells were collected by the NC Geologic Survey in 2009 and analyzed for gas composition by Isotech Laboratories (Reid et al., 2011).

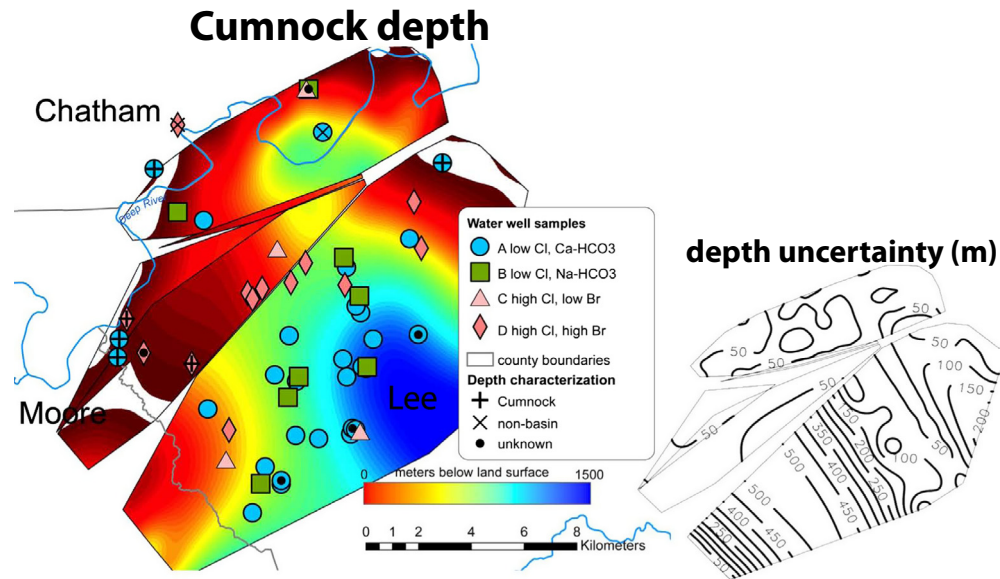


Fig. 3. Inferred depth of Cumnock Formation within the study area, based on data sources pictured in Fig. 1 and described in the text. The shale ranges in depth from near surface (red) to 1500+ m (blue). Discontinuous changes in shale depth occur at faults. Each zone bounded by faults was modeled independently using ordinary kriging with a cubic semivariance function. Shape and color of symbols represent water chemistry of sampled water wells and follow Fig. 1. The depth model was used to identify which water wells intersect the Cumnock (black cross, $n = 6$) and which water wells do not. Wells in terrace gravel deposits were classified as “non-basin” (black x, $n = 2$). Wells without depth data are labeled “unknown” (black dot, $n = 5$). Wells without overlain symbols are of known depth and do not intersect the Cumnock. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.4. Depth model

As the Cumnock is relatively shallow in the northern and western portion of the study area, some of the water wells sampled in this study intersect and draw water from both the Cumnock and the overlying Sanford formations. In order to identify which water wells in our study might represent the geochemical signature of fluids from the Cumnock Shale, we reconstructed the depth of the shale. Although the water wells in this study draw from the unconfined portion of the Cumnock Shale, which is influenced by meteoric recharge, we used our depth reconstruction to search for a distinct chemical signature of water derived from fractures in the shallow portion of the Cumnock Shale. This information could be useful in tracking potential future fluid migration associated with HDHF or predicting the composition of fluids that return to the surface after HDHF (produced water) in the Cumnock Shale.

The depth from land surface to the top of the Cumnock Shale was recorded in well logs of 19 test wells (Melinda Chapman, United States Geological Survey (Raleigh, NC), personal communication). Reinemund (1955) also documented depth from land surface to upper shale boundary in 13 deep wells in the northwestern portion of the study area. Our depth estimate was constrained at these 32 points and along known boundaries of Cumnock surface outcrops (Fig. 2). The model was further constrained along two depth transects presented in Reinemund (1955) (Fig. 1). Since the depth to shale changes discontinuously at fault boundaries, each area bounded by faults was modeled independently.

Using these data, the depth of the surface of the shale was estimated via an ordinary kriging approach (Ahmadi and Sedghamiz, 2008). A cubic semivariogram was employed to minimize the uncertainty over the relatively large and sparsely documented area of the depth surface (Nikroo et al., 2010). The parameters of the semivariogram were determined by an iterative least squares fit. The resulting kriged surface is shown in Fig. 3 and varies from 0 in the northwest of the study area to 1500 m in the southwest. The standard deviation of the kriged depth estimate is shown in Fig. 3 and ranges from <100 m in the northern portion of the study area, with the highest density of depth measurements, to >500 m

in the south-central portion of the study area, where there are no measured shale depths to constrain the model.

3. Results and discussion

3.1. Geochemical and depth characterization

Shallow groundwater samples were divided into four water categories based on major water chemistry (following the framework of Warner et al. (2013, 2012)). Samples with <20 mg/L of Cl were divided based on whether they were dominated by Ca (defined as “type A”, $n = 29$) or Na (“type B”, $n = 8$) waters. The Ca–HCO₃ water type dominates the data set and represents a typical interaction with calcium carbonate minerals in shallow aquifers. The difference between Ca–HCO₃ and Na–HCO₃ water types could indicate different aquifer rock types and/or a longer residence time in groundwater through a longer flow path and exchange with clay minerals (Kresse et al., 2012; Warner et al., 2013). Samples with >20 mg/L of Cl were divided based on Br/Cl ratios: those with Br/Cl < 0.0015 (“type C”, $n = 3$) and those with Br/Cl > 0.0015 (“type D”, $n = 13$). The elevated [Cl] with low Br/Cl represented by type C waters could be indicative of anthropogenic surface contamination, such as leaching from septic fields or application of salt on roadways as a deicing agent. In contrast, the elevated Cl and Br in type D waters are consistent with the Br/Cl ratio of evaporated seawater (Fig. 4, McCaffrey et al., 1987). The presence of saline groundwater with a Br/Cl ratio above that of seawater has been interpreted as an indicator for mixing with deep saline water in other areas (Warner et al., 2012). Although the 20 mg/L Cl threshold employed by Warner was motivated by the distribution of Cl concentrations in historical groundwater records of northeastern Pennsylvania, it is employed here because there is, to our knowledge, no pre-existing Cl concentration data for the Triassic Basin upon which to revise this threshold to the Triassic Basin aquifer.

Water wells were also classified based on the depth of their screened interval in relation to the reconstructed Cumnock Shale

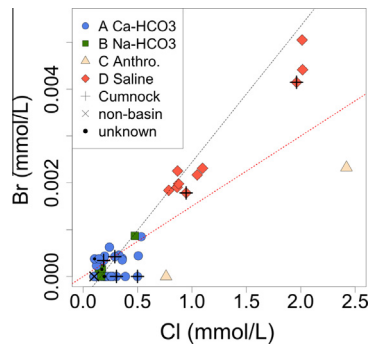


Fig. 4. Br and Cl concentrations measured in shallow groundwater samples. Br and Cl were positively related ($R^2 = 0.78$). Considering all samples except those with anomalously low Br to Cl ratio (“type C”, $n = 3$), the slope of the line of best fit is 0.0029 (dotted, gray), higher than that of the seawater evaporation line (0.00015, dotted, red) (Kendall and Coplen, 2001). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

depth (Fig. 3). Wells that intersected the upper boundary were classified as “Cumnock wells” ($n = 6$). All Cumnock wells were either within Cumnock outcrops or were cased through the predicted depth of the overlying Sanford Formation. Wells that did not intersect the top surface of the Cumnock were classified as “Sanford wells” ($n = 38$). Wells that were outside of the Triassic basin were classified as “non-basin wells” ($n = 2$). Wells without available depth information were labeled as “unknown” ($n = 5$).

3.2. Water quality

Ca^{2+} and Na^+ were the dominant cations in all samples, with no sample having more than 0.4 MEQ % Mg (Fig. 5). HCO_3^- was the dominant anion in most of our well water samples. SO_4^{2-} was the dominant anion in only three samples, with more than 0.35 MEQ %. These samples were also high in Cl and low in Br, further suggesting that water defined as type C originated from anthropogenic contamination (Office of Water, 1999).

Variations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the water samples were consistent with the Local Meteoric Water Line (LMWL) (Kendall and Coplen, 2001) (Fig. 6), which suggests that the groundwater in this region originated from modern precipitation and that subsequent changes in water chemistry were caused by water–rock interactions. Mixing with saline fluids confined within the Cumnock Shale could cause salinization of the fresh meteoric water and increase the $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Yet in order to change the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of shallow groundwater, a large fraction (potentially greater than 20% (Warner et al., 2012)) of saline water is required. The chemistry

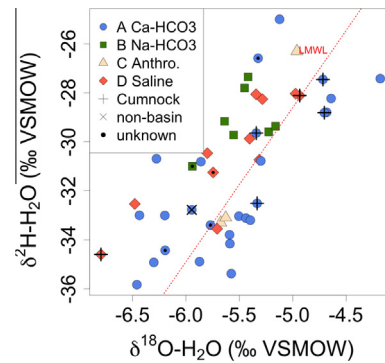


Fig. 6. Isotopes of oxygen and hydrogen in water samples follow the local meteoric water line (LMWL), suggesting a relatively recent meteoric source and short residence time underground.

and stable isotope composition of the study groundwater indicate that the shallow aquifers are replenished by active recharge of modern meteoric water and the groundwater is modified into distinctive water types in the area, such as the Na– HCO_3 water (type B), an apparent anthropogenically contaminated water (type C), and groundwater possibly mixed with saline water (type D). The Cumnock wells identified in this study are relatively shallow and draw from the unconfined zone of the shale and did not show evidence of a strongly saline signature. We conclude that, in the unconfined and shallow area of the Cumnock Shale, the groundwater is dominated by meteoric water.

Distributions of some of the inorganic constituents are illustrated in Fig. 7. Of the 51 water wells measured in this study, only two exceeded primary drinking water standards and 21 exceeded US federal or NC state drinking water standards for at least one element, all shown in Fig. 7. The US Environmental Protection Agency (EPA) establishes legally enforceable primary water quality standards to limit the levels of contaminants in public drinking water (however, these standards are not enforceable in private drinking water wells). Only two wells exceeded a US EPA primary water quality standard, both for As. Unlike primary water quality standards, US EPA’s secondary water quality standards are not legally enforceable and regulate contaminants that may cause aesthetic effects, such as taste, odor, or color. Of the 21 samples exceeding water quality standards, 16 exceeded the EPA secondary standard for Mn of 0.05 mg/L. The one sample that exceeded the EPA secondary standard for Cl (250 mg/L) was a notable outlier, with almost 3 times the Cl of any other sample in this study. This type C sample near the center of our study area had notably high concentrations of a number of other elements, including Li, Na, Mg,

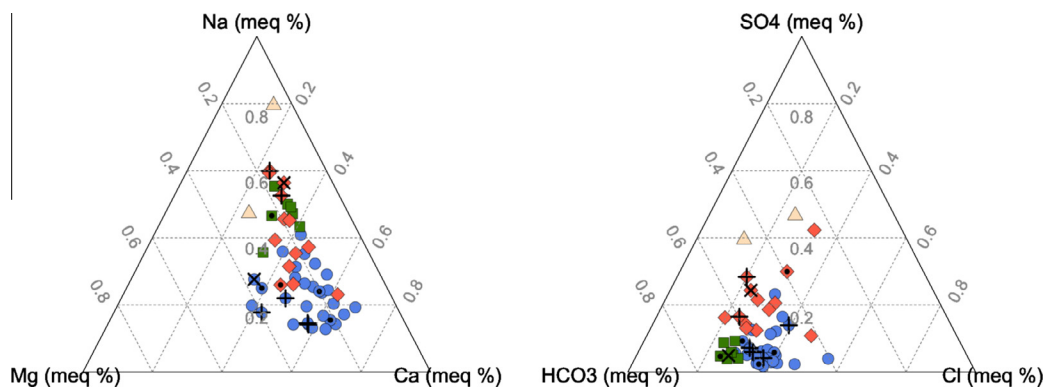


Fig. 5. Major cations (left panel) and anions (right panel). Symbols follow those in Fig. 3.

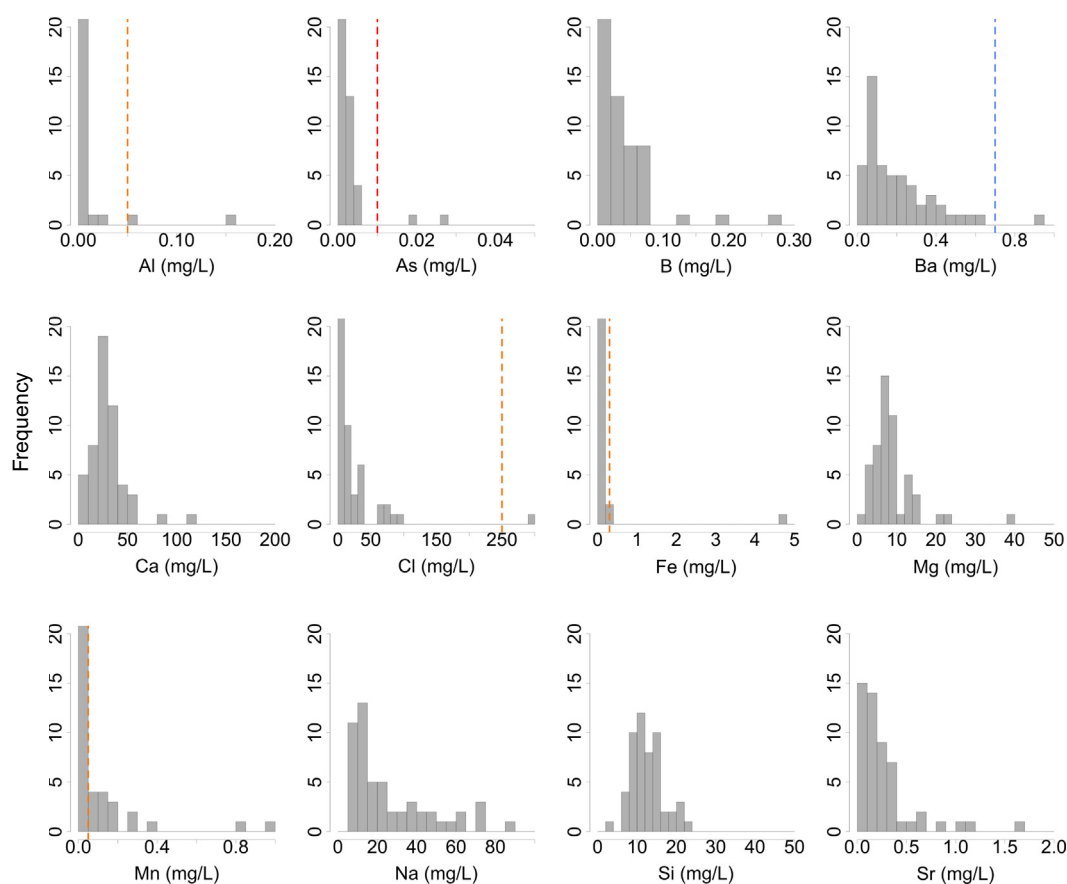


Fig. 7. Distribution of concentrations of a subset of elements measured in this study. Water quality standards are shown as dotted lines: US EPA primary standards in red (As only), US EPA secondary standards in orange (Al, Cl, Fe, and Mn), and NC primary standards in blue (Ba only). For panels with no water quality standards shown, there are either no existing water quality standards for that element (Ca, Mg, Na, Si, Sr) or all federal and state water quality standards exceed the range of values we measured (B). Few concentrations exceeded any federal or state water quality standards. Only two detections exceeded a national primary drinking water standard, both for As. More wells in this study exceeded the Mn secondary standard of 50 $\mu\text{g/L}$ than any other drinking water standard. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Cl, Ca, Mn, Br, and Sr, possibly due to local anthropogenic contamination.

There are eight former coal mines in the study area, mostly located towards the north and west parts of the basin where the Cumnock outcrops (Fig. 2). We expected water–rock interactions with the coal to produce elevated Na, Al, Zn, Pb, Fe, and SO_4 in water samples taken near former coal mines (Cravotta, 2008a,b). However, we found no systematic trend towards Na- HCO_3 type B waters or elevated SO_4 in the northern part of the study area. It is possible that former coal mines influence water quality (e.g., elevated Mn concentrations), but at a local scale and not basin-wide. Additional sampling within the coal-mined areas could help determine any potential influence on water-quality.

It is also possible that faults in the region could influence groundwater chemistry. However, the relatively low number of samples in each water type category, as well as the limited number of faults in our study area, limits our ability to draw statistically significant conclusions.

The Sr isotopic composition, $^{87}\text{Sr}/^{86}\text{Sr}$, varied from 0.706660 to 0.712880 (Fig. 8) and showed no significant difference between the different water chemistry groups or the locations of wells in different geological formations. Sr isotope ratios also showed no correlation with major element concentrations, including B/Cl ratios. However, 7 of the 8 lowest Sr isotope ratios were measured in groundwater samples from the northern portion of the study area near the Deep River. One possible source for this preferentially low Sr isotopic ratio in the northern portion of the study is

groundwater interactions with the large number and volume of diabase intrusions in this area. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the diabase in the Deep River Basin are between 0.7044 and 0.7072 (Pegram, 1990). Thus, Sr input from these diabase formations could lower the Sr isotopic ratios in groundwater that has interacted with diabase rocks. However, although there are numerous diabase dikes in the northern portion of our study area, these dikes occur in other parts of our study area as well. Moreover, the diabase rocks in the Deep River Basin are dominated by olivine tholeiite, with 8.80 to 15.14% MgO (Pegram, 1990), but we see no correlation between Sr isotopic composition and Mg concentration in groundwater samples (Fig. 8). However, the Mg present in the diabase rocks could be immobilized in Mg-rich phases, making it less mobile than Sr. Thus, a lack of correlation between Sr and Mg in our samples does not definitively exclude interaction between our samples and diabase dikes.

Surface water input is another possible source of the relatively lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater from the northern portion of our study area. Rainwater in the Deep River area has an average Sr concentration of approximately 0.002 mg/L and isotopic composition of 0.709364 (Tanner, 2014). Thus, mixing with surface water could produce groundwater samples with relatively low [Sr] and $^{87}\text{Sr}/^{86}\text{Sr}$. However, we did not find any correlation between [Sr] and $^{87}\text{Sr}/^{86}\text{Sr}$ and see no evidence for a mixing line with a surface water end member (Fig. 8, top right panel). Moreover, no other elements show evidence of enhanced surface water interaction in the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ samples. Thus, determining the source of the

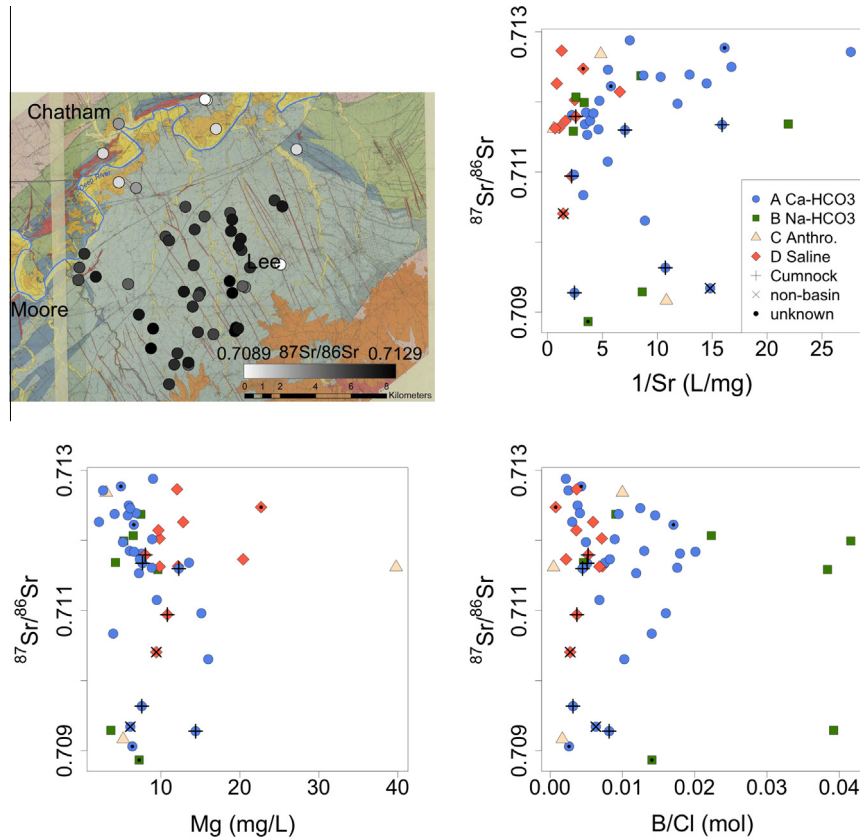


Fig. 8. All water samples with $^{87}\text{Sr}/^{86}\text{Sr} < 0.710$ except for one occurred in the northern portion of the study area (top left panel). One possible explanation for this distribution is the large concentration of diabase dikes in the northwest of the study area. However, Sr isotopes showed little correlation with Mg (lower left panel), which would be expected from interactions with dikes rich in olivine tholeiite. Infiltration of low $^{87}\text{Sr}/^{86}\text{Sr}$ surface water near the Deep River in the northern portion of the study area could also cause the low Sr isotopic ratios observed in groundwater samples. However, ions other than Sr did not show evidence for extensive surface water infiltration, and Sr isotopes showed little correlation with most ions (Sr and B shown in right two panels). Based on our data, it is difficult to determine the mechanism controlling the geographic distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ in the Deep River Basin.

geographic pattern of Sr isotopic composition that we observed would likely require further study.

3.3. Methane

We detected dissolved CH_4 (>0.001 mg/L) in 25 of the 51 samples analyzed (Fig. 9). Of the 25 samples with detectable CH_4 , only two had dissolved CH_4 concentration >0.1 mg/L: 0.24 and 0.48 mg/L, sufficient for isotopic analysis, with both from Cumnock wells. Cumnock water samples had statistically higher CH_4 concentrations on average (mean: 0.1309) than samples from either the Sanford Formation (mean: 0.0086; $P < 0.01$) or from outside the Triassic basin (mean: 0.0071; $P < 0.01$). Overall, the CH_4 concentrations in background drinking water samples in NC were much lower than those measured in shallow aquifers overlying the Marcellus shale (Heisig and Scott, 2013), somewhat lower than those measured above the Fayetteville shale (Warner et al., 2013), and well below the 10 mg/L action level recommended by the US Department of the Interior (Eltzschlager et al., 2001).

There are multiple lines of evidence suggesting that the CH_4 in the two highest- CH_4 water samples was formed biologically. Both the $\delta^{13}\text{C}$ of CH_4 and the ratio of CH_4 to higher chain hydrocarbons, such as C_2H_6 and C_3H_8 , can be used to differentiate CH_4 formed biologically from thermogenic CH_4 (Schoell, 1980). Biological CH_4 production, such as anaerobic fermentation and bacterial carbonate reduction, generally give rise to CH_4 that is depleted in ^{13}C , with $\delta^{13}\text{C}-\text{CH}_4$ between -80‰ and -60‰ (Whiticar, 1999). Thermogenic CH_4 formation typically results in less fractionation

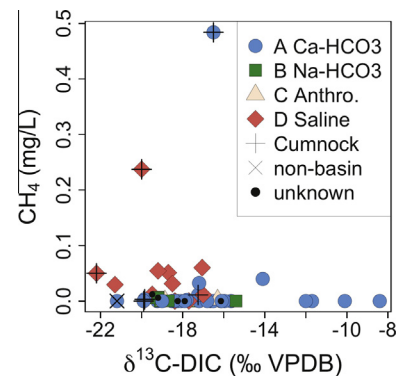


Fig. 9. CH_4 concentration and $\delta^{13}\text{C}-\text{DIC}$ of shallow groundwater samples. All but two water samples had $[\text{CH}_4] < 0.1$ mg/L. Type D samples, with $\text{Cl} > 20$ mg/L and elevated Br, had statistically higher $[\text{CH}_4]$ than other types of samples. There is no evidence for fractionation associated with thermogenic CH_4 modification, and the $\delta^{13}\text{C}-\text{DIC}$ of source organic matter is typically $\sim -22\text{‰}$ (Aravena et al., 1992).

of the end product, with $\delta^{13}\text{C}-\text{CH}_4$ of produced CH_4 greater than -40‰ (Schoell, 1980). Higher chain hydrocarbons such as C_2H_6 and C_3H_8 are commonly formed along with CH_4 during thermogenic CH_4 production, but CH_4 is the only hydrocarbon produced in measurable quantities by biological reactions on land (Schoell, 1980).

The $\delta^{13}\text{C}-\text{CH}_4$ values measured from the two highest- CH_4 water well samples were -69.5‰ and -61‰ , both suggesting a

biological CH₄ source (Fig. 10 and Table 1). No higher-chain hydrocarbons were detected in either of the highest-CH₄ water samples (detection limit 0.1 mg/L), also indicative of a biological CH₄ source. These $\delta^{13}\text{C}-\text{CH}_4$ and the predominance of CH₄ are in contrast to those measured directly from two test gas wells drilled in the region. Previous CH₄ samples from these two test gas wells had $\delta^{13}\text{C}$ of -45.11‰ and -54.41‰ (Reid et al., 2011), indicative of a thermogenic and possibly mixed thermogenic and biogenic source. C₂H₆ and C₃H₈ were detected in both of the gas well samples (Table 1), but not in the highest-concentration CH₄ drinking water samples, further suggesting a biogenic source for the CH₄ detected in these water samples. Consequently, our data indicate that there is no evidence of natural thermogenic CH₄ migration from the Cumnock Shale into overlying aquifers at present. This is in contrast to the natural CH₄ migration into shallow groundwater documented in other areas overlying shale formations, such as northeastern Pennsylvania, USA (Warner et al., 2012).

Bulk water chemistry types were correlated with CH₄ concentrations in our water samples, where type D waters (with high Cl and Br) had elevated CH₄ levels. The co-occurrence of slightly saline water and CH₄ suggests a flow of CH₄-rich groundwater from deep sources, as was observed in groundwater overlying the Marcellus shale in northeastern Pennsylvania (Darrach et al., 2014; Vengosh et al., 2014). Here, the CH₄ concentration was too low in all but the two highest-CH₄ water samples to analyze the

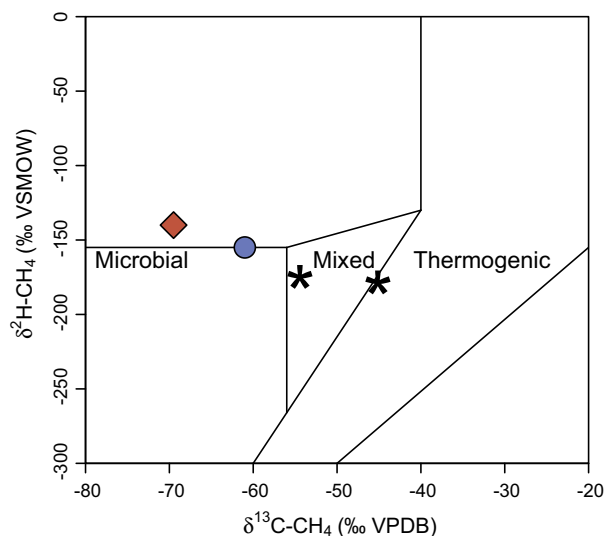


Fig. 10. $\delta^{13}\text{C}-\text{CH}_4$ and $\delta^2\text{H}-\text{CH}_4$ of two well water samples with $[\text{CH}_4] > 0.1 \text{ mg/L}$ (red diamond and blue circle, indicating type D and type A waters respectively; both highest-CH₄ samples are from the Cumnock Formation) and two test gas wells drilled into the Cumnock shale within the study area. Classification regions follow Schoell and others (Schoell, 1980; Whiticar, 1999; Jackson et al., 2013). CH₄ in water well samples appears to be produced microbially and not due to migration of thermogenic CH₄ from the Cumnock formation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$\delta^{13}\text{C}-\text{CH}_4$ and C₂H₆ concentrations to determine the source of hydrocarbons. As such, it is not possible to determine whether the detected CH₄ observed in type D waters is due to mixing with deeper saline water containing thermogenic CH₄ or more shallow biogenic CH₄. The mixed thermogenic-biogenic composition of the two production gas wells in the Cumnock could reflect the early stage of maturation of the natural gas relative to natural gas from other shale formations with more thermogenic signatures (i.e. $\delta^{13}\text{C}-\text{CH}_4 > -50\text{‰}$), such as the Marcellus Shale (Osborn et al., 2011). Further sampling is necessary to establish the isotopic fingerprint of the Cumnock Shale, which could help identify fugitive gas contamination in the study area if it occurs in the future.

Although $\delta^{13}\text{C}-\text{CH}_4$ data are not available for water samples with CH₄ < 0.1 mg/L, the C isotopes of dissolved inorganic carbon (DIC) can provide some indirect insight into the mechanisms governing CH₄ formation (Fig. 9). The two primary sources of DIC in most groundwater environments are dissociation of CO₂ from the decay of organic matter in the soil during the recharge process, with a $\delta^{13}\text{C}$ of approximately -23‰ (Aravena et al., 1992), and C from the dissolution of marine carbonate rocks, with $\delta^{13}\text{C}$ of around 0‰ (Clark and Fritz, 1997). In our data, the mean $\delta^{13}\text{C}-\text{DIC}$ of samples with detectable CH₄ (-18.43‰) was slightly more negative than that of samples without detectable CH₄ (-16.52‰ , $P < 0.05$). Average $\delta^{13}\text{C}-\text{DIC}$ was also significantly different between water types ($P < 0.05$), with type D waters having the lowest group mean value of -18.9 mg/L ($P < 0.1$, ANOVA post hoc test with Bonferroni adjustment). The fractionation associated with CO₂ production during methanogenesis would enrich the $\delta^{13}\text{C}$ of the remaining pool of DIC (Aravena et al., 2003), whereas methanotrophy in anaerobic layers would deplete the $\delta^{13}\text{C}$ of the DIC pool (Templeton et al., 2006). Fractionation associated with methane transport is likely negligible (Fuex, 1980). The $\delta^{13}\text{C}-\text{DIC}$ of the shallow groundwater samples in our study was close to -23‰ , which suggests that most of the DIC was derived from degradation of organic matter and likely rules out possible fractionation associated with CH₄ modification.

Na-HCO₃ type B water samples did not exhibit higher CH₄ concentrations on average than Ca-HCO₃ type A water samples. In studies of water samples from other shale basins (Warner et al., 2013; Molofsky et al., 2013), the longer residence time of Na-HCO₃ waters relative to Ca-HCO₃ generally gives rise to statistically significant enhancements in CH₄ concentration in Na-HCO₃ waters relative to Ca-HCO₃ waters. The lack of CH₄ enrichment in type B waters is further evidence for a lack of widespread CH₄ migration from the Cumnock Shale into overlying aquifers.

Elevation has been suggested as an additional controlling factor for CH₄ concentration in groundwater in the Marcellus Shale region of Pennsylvania (Molofsky et al., 2013). However, our study area has little variation in surface elevation ($\sim 70\text{--}180 \text{ m}$ above sea level), and elevation was not well correlated to CH₄ concentration ($R^2 = 0.052$). Furthermore, elevation does not appear to strongly influence water chemistry, as sample types (A–D) are not statistically distinguishable as a function of surface elevation using ANOVA.

Table 1

Hydrocarbon concentration and isotopes for methane (C1), ethane (C2), and propane (C3) in two highest-CH₄ concentration well water samples and two test gas wells in the study area. Dash symbol (“–”) indicates concentration below detection limit for isotopic analysis.

Sample	C1/C+	$\delta^{13}\text{C}-\text{C1}$	$\delta^2\text{H}-\text{C1}$	$\delta^{13}\text{C}-\text{C2}$	$\delta^2\text{H}-\text{C2}$	$\delta^{13}\text{C}-\text{C3}$	$\delta^2\text{H}-\text{C3}$
<i>Water wells</i>							
NCL-08	–	–69.5	–140	–	–	–	–
NCL-17	–	–61.0	–155	–	–	–	–
<i>Gas wells</i>							
Simpson # 1	19.82	–54.41	–174.8	–34.60	–151.4	–29.66	–120.6
Butler #3	9.04	–45.11	–178.5	–36.81	–175.8	–31.61	–121.3

3.4. Volatile organic compounds

VOC loads in shallow groundwater were generally low and do not appear to be correlated with geologic formation or water type (see supplementary materials). We detected select VOCs (e.g. chloroform, toluene, and ethylbenzene) above detection limits (with quantification limits $\leq 10 \mu\text{g/L}$ for all compounds detected) in 5 of 51 samples, but none exceeded EPA maximum contaminant levels.

The halogenated VOCs detected have known industrial sources; for example, chlorinated ethanes from the breakdown of trichloroethylene; 1,3-dichlorobenzene as an intermediate of the chemical industry; ethylbenzene and toluene as petroleum components; and chlorinated compounds used as solvents (except chloroform, which can be formed naturally, but not at milligram per liter concentrations). Further, the detected compounds are not typically present in agricultural chemicals that could be in use in the rural study area, such as pesticides and fertilizers. We were not able to locate other common potential industrial sources, such as army bases or dry-cleaning businesses, within our study area (using Google Maps), except for the presence of an automotive repair shop. We postulate that the VOCs observed in this well were most likely the result of a yet-identified local anthropogenic source.

Although the levels of halogenated solvents we detected were low, their frequency of detection in our groundwater samples (5 out of 51) in an area with relatively little industrial activity highlights two issues that could arise if hydraulic fracturing were to occur in the region. First, the number of sources of such compounds makes unambiguous source apportionment difficult for those chemical species, unless their concentrations rose substantially. Second, their presence highlights the need for pre-drilling testing of each residential drinking water well to establish a baseline for any future testing after drilling. Without such a baseline database, their presence could erroneously be attributed to oil and gas drilling unless other chemical or isotopic tracers of HDHF could be established.

4. Conclusions

We have presented a comprehensive evaluation of the water chemistry and dissolved gas in the Sanford sub-basin of central North Carolina. Our data and those presented by Chapman et al. (2014) from samples collected during the same sampling campaign are the first, to our knowledge, to document the groundwater characteristics in the region.

Of the 51 sampled private drinking water wells, we found the majority did not exceed federal or state drinking water quality standards. Only two wells exceeded a US EPA primary drinking water standard, both for arsenic. Of the 51 wells sampled in this study, 16 exceeded the US EPA secondary drinking water standard for Mn, with two wells simultaneously exceeding the secondary standard for Fe and one well for Cl. These results are similar to those in Chapman et al. (2014), who found that 35% of their samples exceeded the drinking water standard for Mn. Volatile organic compounds were largely absent from shallow groundwater in the area. This is to be expected, as this area has no history of heavy industry or other source of organic compound contamination. However, a few groundwater samples contained detectable concentrations of select VOCs and the presence of VOCs alone likely cannot be used as an indicator of contamination from HDHF, even in rural areas.

We have used data from research wells and test gas wells to reconstruct the depth of the surface of the Cumnock Shale (Fig. 3). The upper surface of the Cumnock Shale is distributed between the ground surface and ~ 1500 m below the ground

surface within our study area, which is much shallower than the depth of other shale deposits, such as the Marcellus Shale in Pennsylvania or the Fayetteville Shale in Arkansas. Using this depth model, we identified water wells that likely intersect or approach the shallow portion of the Cumnock Shale. However, we were not able to identify a distinctive chemical signature shared by the water derived from these wells.

We found relatively low dissolved CH_4 , with only two samples having CH_4 concentrations above 0.1 mg/L . Based on the low $\delta^{13}\text{C}-\text{CH}_4$, these two samples appear to be from biogenic sources and are not consistent with the isotopic and higher-chain hydrocarbon signature of natural gas observed in test wells from the Cumnock Shale. Similarly, Chapman et al. (2014) found very low levels of dissolved CH_4 in groundwater samples from the Sanford sub-basin. We found no evidence for migration of thermogenic CH_4 from the Cumnock Shale into shallow aquifers over geologic time. This current lack of CH_4 in groundwater could serve as an important baseline value and comparison if HDHF occurs in this area in the future.

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References

- Ahmadi, S., Sedghamiz, A., 2008. Application and evaluation of kriging and cokriging methods on groundwater depth mapping. *Environ. Monit. Assess.* 138 (1–3), 357–368. <http://dx.doi.org/10.1007/s10661-007-9803-2>.
- Allen, D.T., Torres, V.M., Thomas, J., Sullivan, D.W., Harrison, M., Hendler, A., Herndon, S.C., Kolb, C.E., Fraser, M.P., Hill, A.D., Lamb, B.K., Miskimins, J., Sawyer, R.F., Seinfeld, J.H., 2013. Measurements of methane emissions at natural gas production sites in the United States. *Proc. Nat. Acad. Sci.* <http://dx.doi.org/10.1073/pnas.1304880110>, <<http://www.pnas.org/content/early/2013/09/10/1304880110.abstract>>.
- Aravena, R., Harrison, S., Barker, J., Abercrombie, H., Rudolph, D., 2003. Origin of methane in the Elk Valley coalfield, southeastern British Columbia, Canada. *Chem. Geol.* 195, 219–227 (Isotopic records of microbially mediated processes). <<http://www.sciencedirect.com/science/article/pii/S0009254102003960>>.
- Aravena, R., Schiff, S., Trumbore, S., Dillon, P., Elgood, R., 1992. Evaluating dissolved inorganic carbon cycling in a forested lake watershed using carbon isotopes. *Radiocarbon* 34 (3), 636–645. <<https://journals.uair.arizona.edu/index.php/radiocarbon/article/view/1514>>.
- Bain, G.L., Thomas, J.D., 1966. *Geology and Ground-Water in the Durham Area*, North Carolina. Tech. Rep., North Carolina Department of Water and Air Resources.
- Burnham, A., Han, J., Clark, C.E., Wang, M., Dunn, J.B., Palou-Rivera, I., 2012. Life-cycle greenhouse gas emissions of shale gas, natural gas, coal, and petroleum. *Environ. Sci. Technol.* 46 (2), 619–627. <<http://pubs.acs.org/doi/abs/10.1021/es201942m>>.
- Chapman, M.J., Gurley, L.N., Fitzgerald, S.A., November 2014. Baseline Well Inventory and Groundwater-Quality Data from a Potential Shale Gas Resource Area in Parts of Lee and Chatham Counties, North Carolina, October 2011–August 2012. Data Series 861, U.S. Geological Survey.
- Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*, first ed. CRC Press.
- Cravotta, C.A., 2008a. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: constituent quantities and correlations. *Appl. Geochem.* 23 (2), 166–202 (sulfide Oxidation – Sulfide Oxidation: Insights from Experimental, Theoretical, Stable Isotope, and Predictive Studies in the Field and Laboratory). <<http://www.sciencedirect.com/science/article/pii/S0883292707002776>>.
- Cravotta, C.A., 2008b. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: geochemical controls on constituent concentrations. *Appl. Geochem.* 23 (2), 203–226 (sulfide Oxidation – Sulfide Oxidation: Insights from Experimental, Theoretical, Stable Isotope, and Predictive Studies in the Field and Laboratory). <<http://www.sciencedirect.com/science/article/pii/S0883292707002788>>.

- Darrah, T.H., Vengosh, A., Jackson, R.B., Warner, N.R., Poreda, R.J., 2014. Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. *Proc. Nat. Acad. Sci.* 111 (39), 14076–14081, <<http://www.pnas.org/content/111/39/14076.abstract>>.
- Eltischlager, K.K., Hawkins, J.W., Ehler, W.C., Baldassare, F.J., September 2001. Technical Measures for the Investigation and Mitigation of Fugitive Methane Hazards in Areas of Coal Mining. Tech. Rep., U.S. Department of the Interior Office of Surface Mining.
- Fuex, A., 1980. Experimental evidence against an appreciable isotopic fractionation of methane during migration. *Phys. Chem. Earth* 12 (0), 725–732, <<http://www.sciencedirect.com/science/article/pii/0079194679901538>>.
- Heisig, P.M., Scott, T.-M., 2013. Occurrence of Methane in Groundwater of South-Central New York State, 2012–Systematic Evaluation of a Glaciated Region by Hydrogeologic Setting. Scientific Investigation Report 2013-5190, U.S. Geological Survey.
- Hinkle, S.R., Shapiro, S.D., Plummer, L.N., Busenberg, E., Widman, P.K., Casile, G.C., Wayland, J.E., 2010. Estimates of Tracer-Based Piston-Flow Ages of Groundwater from Selected Sites: National Water Quality Assessment Program, 1992–2005. Scientific Investigation Report 2010-5229, U.S. Geological Survey.
- Howarth, R., Santoro, R., Ingraffea, A., 2011. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change* 106 (4), 679–690. <http://dx.doi.org/10.1007/s10584-011-0061-5>.
- Isotech Laboratories, Inc., 2014. Collection of Ground Water Samples from Domestic and Municipal Water Wells for Dissolved Gas Analysis Using Gas Bottles. Online.
- Jackson, R.B., Vengosh, A., Darrah, T.H., Warner, N.R., Down, A., Poreda, R.J., Osborn, S.G., Zhao, K., Karr, J.D., 2013. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Proc. Nat. Acad. Sci.* 110, 11250–11255, <<http://www.pnas.org/content/early/2013/06/19/1221635110.abstract>>.
- Jiang, M., Griffin, W.M., Hendrickson, C., Jaramillo, P., VanBriesen, J., Venkatesh, A., 2011. Life cycle greenhouse gas emissions of Marcellus shale gas. *Environ. Res. Lett.* 6 (3), 034014, <<http://stacks.iop.org/1748-9326/6/i=3/a=034014>>.
- Kendall, C., Coplen, T.B., 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol. Process.* 15 (7), 1363–1393, <<http://dx.doi.org/10.1002/hyp.217>>.
- Kresse, T.M., Warner, N.R., Hays, P.D., Down, A., Vengosh, A., Jackson, R.B., 2012. Shallow Groundwater Quality and Geochemistry in the Fayetteville Shale Gas-Production Area, North-Central Arkansas, 2011. Scientific investigation report 2012-5273, U.S. Geological Survey.
- Luttrell, G.W., 1989. Stratigraphic Nomenclature of the Newark Supergroup of Eastern North America. *Bulletin* 1572, U.S. Geological Survey.
- McCaffrey, M.A., Lazar, B., Holland, H.D., 1987. The evaporation path of seawater and the coprecipitation of Br⁻ and K⁺ with halite. *J. Sediment. Res.* 57 (5), 928–937, <<http://jgsedres.sepmonline.org/content/57/5/928.abstract>>.
- Milici, R.C., Coleman, J.L., Rowan, E.L., Cook, T.A., Charpentier, R.R., Kirschbaum, M.A., Klett, T.R., Pollastro, R.M., Schenk, C., 2012. Assessment of undiscovered oil and gas resources of the East Coast Mesozoic Basins of the Piedmont, Blue Ridge Thrust Belt, Atlantic Coastal Plain, and New England Provinces, 2011. Fact Sheet 2012-3075, U.S. Geological Survey.
- Molofsky, L.J., Connor, J.A., Wylie, A.S., Wagner, T., Farhat, S.K., 2013. Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Groundwater* 51 (3), 333–349. <http://dx.doi.org/10.1111/gwat.12056>.
- Moore, L.J., Murphy, T.J., Barnes, I.L., Paulsen, P.J., 1982. Absolute isotopic abundance ratios and atomic weight of a reference sample of strontium. *J. Res. Natl. Bureau Stand.* 87 (1), 1–8.
- Nikroo, L., Kompani-Zare, M., Sepaskhah, A., Fallah Shamsi, S., 2010. Groundwater depth and elevation interpolation by kriging methods in Mohr Basin of Fars province in Iran. *Environ. Monit. Assess.* 166 (1–4), 387–407. <http://dx.doi.org/10.1007/s10661-009-1010-x>.
- North Carolina Department of Environment and Natural Resources, March 2012. North Carolina Oil and Gas Study Under Session Law 2011-276. Tech. Rep., North Carolina Department of Environment and Natural Resources.
- Office of Water, January 1999. Health Effects from Exposure to High Levels of Sulfate in Drinking Water Study. Tech. Rep. 815-R-99-001, U.S. Environmental Protection Agency.
- Osborn, S.G., Vengosh, A., Warner, N.R., Jackson, R.B., 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Nat. Acad. Sci.* 108 (20), 8172–8176, <<http://www.pnas.org/content/108/20/8172.abstract>>.
- O'Sullivan, F., Paltsev, S., 2012. Shale gas production: potential versus actual greenhouse gas emissions. *Environ. Res. Lett.* 7 (4), 044030, <stacks.iop.org/ERL/7/044030>.
- Pegram, W.J., 1990. Development of continental lithospheric mantle as reflected in the chemistry of the Mesozoic Appalachian Tholeiites, USA. *Earth Planet. Sci. Lett.* 97 (3–4), 316–331, <<http://www.sciencedirect.com/science/article/pii/0012821X90900494>>.
- Priddle, R., 2011. World Energy Outlook 2011. Special report, International Energy Agency, 9 rue de la Federation, 75739 Paris Cedex 15, France.
- Reid, J.C., Milici, R.C., 2008. Hydrocarbon Source Rocks in the Deep River and Dan River Triassic Basins, North Carolina. Open-File Report 2008-1108, U.S. Geological Survey.
- Reid, J.C., Taylor, J.B., Olsen, P.E., Patterson, O.F.I., March 26 2011. Natural Gas Potential of the Sanford Sub-Basin, Deep River Basin, North Carolina. Search and Discovery AAPG Eastern Meeting (10366).
- Reinemund, J.A., 1955. Geology of the Deep River Coal Field, North Carolina. Professional Paper 246, U.S. Geological Survey.
- Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* 44 (5), 649–661, <<http://www.sciencedirect.com/science/article/pii/0016703780901556>>.
- Shearer, C., Bistline, J., Inman, M., Davis, S.J., 2014. The effect of natural gas supply on us renewable energy and CO₂ emissions. *Environ. Res. Lett.* 9 (9), 094008, <<http://stacks.iop.org/1748-9326/9/i=9/a=094008>>.
- Tanner, M., 2014. The Sr budget of the Croatan National Forest. Senior thesis, University of North Carolina, Chapel Hill.
- Templeton, A.S., Chu, K.-H., Alvarez-Cohen, L., Conrad, M.E., 2006. Variable carbon isotope fractionation expressed by aerobic CH₄-oxidizing bacteria. *Geochim. Cosmochim. Acta* 70 (7), 1739–1752, <<http://www.sciencedirect.com/science/article/pii/S0016703705009373>>.
- Vengosh, A., Jackson, R.B., Warner, N., Darrah, T.H., Kondash, A., 2014. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* 48, 8334–8348, <http://dx.doi.org/10.1021/es405118y>. <<http://pubs.acs.org/doi/abs/10.1021/es405118y>>.
- Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., Vengosh, A., 2012. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc. Natl. Acad. Sci.* 109 (30), 11961–11966, <<http://www.pnas.org/content/109/30/11961.abstract>>.
- Warner, N.R., Kresse, T.M., Hays, P.D., Down, A., Karr, J.D., Jackson, R.B., Vengosh, A., 2013. Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas. *Appl. Geochem.* 35, 207–220, <<http://www.sciencedirect.com/science/article/pii/S0883292713001133>>.
- Whitcar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* 161 (1–3), 291–314, <<http://www.sciencedirect.com/science/article/pii/S0009254199000923>>.
- Wilde, F.D. (Ed.), 2006. U.S. Geological Survey Techniques of Water-Resources Investigations, 2nd ed., vol. 9. U.S. Geological Survey. (Chapter A4: Collection of water samples) <<http://pubs.water.usgs.gov/twri9A4/>>.