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A Comprehensive Analysis of Groundwater Quality in The Barnett Shale Region

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ABSTRACT

The exploration of unconventional shale energy reserves and the extensive use of hydraulic fracturing during well stimulation have raised concerns about the potential effects of unconventional oil and gas extraction (UOG) on the environment. Most accounts of groundwater contamination have focused primarily on the compositional analysis of dissolved gases to address whether UOG activities have had deleterious effects on overlying aquifers. Here, we present an analysis of 550 groundwater samples collected from private and public supply water wells drawing from aquifers overlying the Barnett shale formation of Texas. We detected multiple volatile organic carbon compounds throughout the region, including various alcohols, the BTEX family of compounds, and several chlorinated compounds. These data do not necessarily identify UOG activities as the source of contamination; however, they do provide a strong impetus for further monitoring and analysis of groundwater quality in this region as many of the compounds we detected are known to be associated with UOG techniques.

1. INTRODUCTION

The potential effects of unconventional oil and gas (UOG) drilling activities on groundwater quality have led to much concern despite a relative lack of scientific data. Recently, investigations in the Marcellus and Barnett shale formations in Pennsylvania and Texas found elevated levels of dissolved methane[1, 2] and heavy metals[3] in private water wells located near unconventional drilling sites. A number of extraction processes are utilized during unconventional shale exploration including directional drilling, shale acidization, and hydraulic fracturing, in which large quantities of water, proppants, and chemical additives are used to extract sequestered hydrocarbons. Additives used during hydraulic fracturing include viscosifiers, descaling agents, anti-corrosive compounds, lubricants, pH stabilizers, and other solvents that could be harmful if introduced into the environment.[4] Instances of chemical contamination can result from casing failures, which happen in approximately 3% of new gas well operations,[4] although recent findings indicate failure rates closer to 12% within the first year of operation.[5] Recent research has shown that hydraulic fracturing could potentially alter contaminant pathways to aquifers via increased advective transport and/or flow through existing fractures widened by UOG activities.[6, 7] Additionally, surface sources such as mishandled waste fluid and produced waters or spills of UOG fluids during stimulation or completion of wells may contaminate groundwater, and shallow water wells may be vulnerable to such contamination. [8]

One of the more active regions for UOG drilling is in north-central Texas where the Barnett shale formation supports approximately 20,000 UOG wells. This region includes a portion of the Dallas-Fort Worth metropolitan area and outlying areas, and groundwater is potentially vulnerable to contamination from various urban and rural sources. The Trinity and Woodbine aquifers overlying the Barnett shale formation have historically been described as good quality with low levels of heavy metals such as arsenic, selenium, strontium, and barium

and naturally elevated levels of total dissolved solids (TDS).[9] However, recent research on groundwater quality near Barnett shale UOG activities identified higher concentrations of heavy metals compared to historical data for this region.[3] For more detailed information regarding historical water quality in aquifers overlying the Barnett shale formation, we refer the reader to Fontenot et al. [3] Here, we present an updated analysis of groundwater quality in aquifers overlying the Barnett shale and adjacent areas of north-central Texas. The objectives of this study are to assess whether or not UOG activity may have had an impact on groundwater quality by screening for the presence of elevated natural constituents and contaminants potentially related to UOG activity, examining correlations among groundwater constituents, and to identify changes in groundwater quality since the previous study of Fontenot et al.[3] A total of 550 groundwater samples were screened for the presence of chemical compounds used in hydraulic fracturing, as well as for various metals and other dissolved ions. We detected elevated levels of 10 different metals and the presence of 19 different chemical compounds, including benzene, toluene, ethyl benzene and xylene (BTEX). These results constitute the largest analysis of groundwater quality in aquifers overlying a shale formation associated with UOG activities.

2. MATERIALS AND METHODS

2.1. Hydrogeology.

Groundwater samples (n=550) were collected from water wells that draw from the Trinity and Woodbine aquifers overlying the Barnett shale formation of Texas (Hereafter referred to as the “Barnett shale region”; Figure 1). The Texas Water Development Board classifies the Trinity and Woodbine aquifers as primary and secondary aquifers, respectively. Regionally, groundwater in the study area flows southeastward, although numerous groundwater production wells in the area create localized cones of depression in the water table potentiometric surface.

Cretaceous sand formations of the Trinity Group outcrop in a north-trending band and dip underground to the east, where the aquifer becomes confined. The Trinity Group consists of three formations, from bottom to top: Twin Mountains, Glen Rose, and Paluxy. The Twin Mountains formation includes sand, shale, clay, and a basal gravel and conglomerate.[10] Major constituents of the Glen Rose formation, a confining unit, include limestone, marl, shale, and anhydrite. Mainly sand and shale make up the Paluxy Formation. The Glen Rose Formation is absent north of central Wise County; here, the Paluxy and Twin Mountains Formations merge together to form the Antlers Formation. Precipitation and seepage from reservoirs and streams recharge the unconfined Trinity outcrop zone.[11] Eastward, leakage through confining beds recharges the aquifer.[12] Annual recharge to the aquifer averages approximately 2.5 cm.[13]

The Woodbine Aquifer consists of ferruginous sand and sandstone interbedded with shale and clay of the Cretaceous Woodbine Formation. Discontinuous seams of lignite, gypsum, and volcanic ash are also present in the Woodbine Formation.[10] Overlying the Trinity Group and intervening strata, the Woodbine Formation also outcrops in the study area and dips eastward. Unconfined conditions occur in the outcrop zone, and artesian conditions prevail downdip.[11] Precipitation on the outcrop zone and seepage from lakes and streams recharge the aquifer. Average annual recharge to the aquifer is approximately 2 cm.[13]

2.2. Sample Collection.

Private water well samples (n=550) were collected from wells tapping the Trinity and Woodbine aquifers. Of the 550 samples, 350 came from private wells serving residential purposes, while 59 samples came from agricultural water wells, and 141 samples came from municipal or public water supply wells servicing communities throughout the Dallas-Fort Worth Metroplex. Approximately 83% of the samples were collected from wells tapping aquifers located above the Barnett shale formation, a feature populated by more than 20,000 UOG wells since the early 2000s. Samples were collected without prior knowledge of the

UOG activity in the area and all geospatial analyses were performed *ex post facto*. Samples were collected throughout Montague, Wise, Parker, Hood, Tarrant, Somervell, Johnson, Hill, Ellis, Dallas, Denton, Collin and Cooke counties (Figure 1). Water well depths ranged from 10-1200 m according to wellowners, and well depth tends to increase eastward in both aquifers, following the slope of the principal water-bearing formations into the subsurface. Sites were selected on the basis of well owner participation and our ability to collect unfiltered/untreated water that would be representative of the underlying aquifers, as described previously.[3] Measurements for basic water quality parameters such as temperature, dissolved oxygen (DO), conductivity, total dissolved solids (TDS), salinity, pH and oxidation-reduction potential (ORP) were performed with a YSI Professional Plus multi-parametric probe, and each water well was purged until measurements for these parameters had stabilized, indicating that samples were representative of fresh groundwater from the underlying aquifer. Two duplicate samples from each private water well were collected in photo-resistant HDPE bottles with no headspace. Samples for metals analysis were filtered and preserved with nitric acid to a pH less than 2 and stored at 4 ℃ until laboratory procedures could be performed. Samples for anion analysis were preserved with chloroform and frozen to reduce microbial degradation. All laboratory measurements were made within 14 days, except for the metal analysis, which was measured within 6 months of collection, per suggested holding times from the Environmental Protection Agency (EPA). [14] Method blanks and random analytical replicates were performed for each set of samples collected across multiple trips from December 2013 to August 2014 (See supporting information for exact sampling dates).

2.3. Analysis.

Chemical analyses included gas chromatography-mass spectrometry (GC-MS), headspace-gas chromatography (HS-GC), inductively coupled plasma - mass spectrometry and - optical emission spectroscopy (ICP-MS and ICP-OES), and ion chromatography (IC).

Specific organics were selected from a 2011 Congressional Report on hydraulic fracturing fluid ingredients[15] as well as frequently listed components of UOG fluids in the national hydraulic fracturing chemical registry (www.fracfocus.org).[16] These include metal ions, alcohols, aromatic compounds, aldehydes, amines, and others (See Supporting Information for a full list of screened species). Whenever possible, we evaluated constituents in the context of their respective Primary or Secondary Maximum Contaminant Limits (MCL), Health Advisory Levels, or other suggested levels as provided in the United States Environmental Protection Agency's (EPA) Drinking Water Standards.[17]

Information about UOG drilling activity in the region was obtained from www.fracfocus.org [16] and the Texas Railroad Commission,[18] the governing body for oil and gas drilling in the state of Texas. Geospatial analyses were conducted using ArcGIS 10.1. [19] Because we obtained measurements of water quality variables for nearly all sample wells, we evaluated the relationship between measures of water quality and both distance to nearest UOG well and depth of sample well using multiple regression and model selection based on adjusted R^2 values. We noted spurious positive relationships between distance to nearest UOG well and some water quality variables, and thus we elected to not use this predictor variable further (Table 1; see Results and Discussion below). We evaluated bivariate relationships for particular variables for which we had *a priori* reason to assume they may be related, and derived a composite variable for chloride, bromide, and nitrate using a principal components analysis (PCA) of these three variables based on the correlation matrix. Before all analyses, we log-transformed both distance measures and $\log_{10}$-transformed remaining variables to normalize distributions. To evaluate geographic patterns at a coarse scale, we used Pearson's chi-squared tests of independence for frequency of water well samples with either detection or EPA's Drinking Water Maximum Contaminant Limit (MCL) exceedances of selected compounds for each county with ≥ 40 total samples. This analysis allowed us to evaluate whether particular counties in north-central Texas exhibited higher or lower than expected frequencies of samples with particular compounds. All regression, correlation, and principal component analyses were performed in Systat 12.02 [20] and chi-squared tests were performed in the software program R.[21]

3. RESULTS AND DISCUSSION

A total of 550 groundwater samples was collected from private and public water supply wells throughout the Barnett shale region. Sampled water wells ranged from 90 m away from the nearest UOG well in areas of active UOG extraction to 47,220 m away from the nearest UOG well in areas outside of the Barnett shale, with a median and mean distance of 807 and 2,315 m respectively. The large difference between median and mean values reflects the influence of extreme outliers at the higher end of this range. Of the 550 samples, 339 (61.6%) were collected from water wells within 1 km of the nearest UOG well, which likely reflects the increased willingness of well owners to participate in this research in more heavily drilled areas. Unfortunately, this opportunistic and necessarily biased sampling hindered our ability to make meaningful inferences regarding levels of contamination as a function of distance from nearest UOG well for several reasons: (1) the expectation of no detection of a given contaminant for a given sample well assumes uniform and substantial sampling across a gradient of distances from UOG wells, but the distribution of well samples as a function of distance from UOG well was strongly right-skewed; (2) the radius of 1 km for the majority of our groundwater samples is not an adequate distance to detect meaningful statistical patterns of contaminant diffusion from the site of UOG wells; and (3) distance to nearest UOG well is positively correlated with depth of groundwater well ($r = 0.36$, $p < 0.0001$) (SI Figure 1), a potential confounding variable (see water quality results below). Water wells in the eastern part of the study area tend to be both farther away from UOG wells (because the Barnett shale formation is westward) and deeper (because the aquifers deepen eastward); thus, explaining observation (3) above. We observed some weak, positive correlations between UOG wells and some analytes, but interpret these results as spurious for the reasons mentioned above in conjunction with the following additional considerations: (1) positive relationships between analyte concentrations and distance from UOG well have no reasonable causal basis, but are readily explained by the correlation with depth of sample

well, (2) explanatory power of the correlations using distance from UOG well was consistently lower than for correlations with depth of well, suggesting that between these collinear factors, it is more parsimonious to assume that relationships with distance from UOG well are confounded.

3.1. Water Quality

Multiple regression analyses of basic water quality parameters as a function of distance from nearest UOG well (distance) and depth of groundwater well sample (depth) revealed that depth is a substantially better predictor of overall water quality than is distance, albeit most relationships were weak (Table 1). In general, TDS concentrations tend to increase eastward in the study area, as groundwater moves along the principal water-bearing formations of the Trinity and Woodbine aquifers. With travel, increased residence (contact) time facilitates more dissolution of aquifer constituents. For example, sodium, chloride, sulfate, and various other constituents tend to increase eastward, as does water well depth. All variables showed a positive relationship with depth except for dissolved oxygen, which showed a negative relationship with depth. Dissolved oxygen levels tend to be higher in shallower, unconfined areas of the aquifer where groundwater mixes with gases in the vadose zone. Values for pH exhibited a nonlinear relationship with depth, with low values in shallow wells, high values at intermediate depths, and a slight trend toward neutral pH for the deepest wells. Values for pH also tend to be lower in the unconfined outcrop zones, where slightly acidic rainwater recharges the aquifers. Model selection indicated that for many variables, an additive or interaction model best explained the total variance in the dataset; however, the low R^2adj values for models including only UOG distance for each of these response variables, and the collinearity between depth and UOG distance, suggest that the inclusion of distance in these models is spurious. Basic water quality analyses revealed the consistent occurrence of elevated TDS throughout the 13 counties sampled. Of the 550 samples, 344 exceeded the Secondary MCL of 500 mg/L suggested by the EPA. TDS values ranged from 68.5 to 3328

mg/L with an average slightly above the MCL (630.3 mg/L). Measurements also showed pH values ranging from 5.3 to 9.4 with a mean value of 8.1. Collectively, 254 samples were outside of the range of 6.5-8.5 suggested by the EPA MCL, with 15 samples having pH measurements below 6.5 and 239 samples having pH measurements above 8.5. Elevated TDS and pH measurements are not unusual for the Trinity and Woodbine aquifers, as similar results have been reported previously.[3, 22]

3.2. Anions in Groundwater

Subsequent analyses using ion chromatography (IC) were performed to assess the prevalence of selected water quality anions in the Trinity and Woodbine aquifers. Nitrate and fluoride were measured to characterize the relative effect of agricultural surface activities on the underlying groundwater. Nitrate was detected in 223 of the 550 samples, and 2 samples were found to be elevated above the 44.3 mg/L MCL, with a maximum value of 55.7 mg/L. As a whole, nitrate values were higher (median = 0.95 mg/L) than those previously reported in the Trinity and Woodbine aquifers, each with median values of 0.4 mg/L.[22] High levels of nitrate in shallow groundwater often stem from agricultural processes, such as the use of fertilizer and organic manures, as well as septic systems and decaying vegetation. Nitrate values tend to be higher in the outcrop zones of the aquifers, where they are more vulnerable to contaminants originating from the land surface. Generally, the outcrop zone of the Trinity aquifer is more rural than that of the Woodbine aquifer, and agricultural activity in the Trinity outcrop zone may account for higher median nitrate values observed in that aquifer. Fluoride was found to be elevated above its 4 mg/L MCL in 2 wells with a median value of 0.3 mg/L, less than previous measurements collected in the 2000s (0.7 and 1.3 mg/L for the Trinity and the Woodbine aquifers, respectively).[22] Elevated fluoride levels may originate from phosphate fertilizers and mineral constituents in the aquifers, especially in the Woodbine aquifer.[23, 24] For example, fluoride is known to occur at relatively high levels in parts of the Woodbine aquifer,[24] a plausible source being volcanic ash deposits.

An overall prevalence of nitrate and the lack of covariation between nitrate and fluoride (r = -0.05) suggest that they may be coming from different sources, such as agricultural sources for nitrate and natural sources for fluoride. Sulfate levels (median value of 52.8 mg/L) were below those discovered in previous measurements; 79 and 114 mg/L for the Trinity and Woodbine aquifers in samples collected in the 2000s.[22] Chloride levels were also found to be consistent with historical measurements with a median value of 25.4 mg/L compared to 35 and 36.3 mg/L discovered in samples previously collected from the Trinity and Woodbine aquifers, respectively.[22] However, chloride was found to be elevated above the 250 mg/L MCL threshold in 21 wells with a maximum value of 3373.8 mg/L, a value over 3 times greater than previously observed.[22]

Formation water in general contains elevated concentrations of chloride, bromide, sodium, and sulfate.[25] Of these ions, bromide has recently been used when attempting to identify formation water intrusion with the aquifer because of its naturally low abundance and conservative behavior in groundwater. High levels of chloride and bromide can be an indication of anthropogenic contamination, one possibility being UOG activity,[26] a result of groundwater mixing with produced water from the shale formation.[25] Bromide was detected in 170 water wells ranging from 0.03 to 6.4 mg/L (Supporting Information Descriptive Statistics Table). Previous groundwater monitoring efforts within a few of the counties sampled in this study showed bromide concentrations up to approximately 3.5 mg/L, with an outlier of 8.4 mg/L; however, bromide was not detected in the majority of samples.[26, 27]

Overall, bromide showed a moderately high positive correlation with chloride when both compounds occurred together (r = 0.32, p < 0.0001), with a particularly strong log-linear trend along a ratio within the ~100–150 range (Figure 2). Additionally, a composite variable derived from a PCA of chloride, bromide, and nitrate (all three compounds were strongly positively correlated with the first principal component axis, which had an eigenvalue of 1.351 and explained 45.1% of the total variance in this combination of variables) was negatively

correlated with depth of groundwater well (r = -0.34, p = 0.002), suggesting a surface source may contribute to observed concentrations of these contaminants (SI Figure 2). It should be noted that denitrification and reducing conditions at higher depths could also lead to this correlation.

Calculating the chloride/bromide mass ratio of groundwater samples can be useful for sourcing contamination or mixing of sources.[28] Previous investigators used chloride/bromide ratios to identify potential sources of groundwater contamination.[29] Based upon several published studies, chloride/bromide ratios generally range from 50-150 in atmospheric precipitation, 300-600 in domestic sewage, 1000-10,000 in dissolved evaporites, and 100-200 in unimpaired, shallow groundwater.[30] In oilfield brine (formation water), chloride/bromide ratios vary widely, but typically fall between 100 and 300. This ratio can also be achieved by mixing unimpaired groundwater with groundwater impaired by evaporites. Mixing of groundwater from multiple sources leads to intermediate ratios of these conservative ions. Of the 550 samples, 170 (30.9%) had detectable amounts of bromide. The median chloride/bromide ratio of all samples with detectable bromide was 239, with a minimum of 3 and a maximum of 1465. Of the 170 wells with bromide, 97 wells (57.1%) had a chloride/bromide ratio between 100 and 300. Of the 550 well samples, 17.6% had a chloride/bromide ratio between 100 and 300. A localized area in southern Parker County showed the highest chloride/bromide ratios, ranging from 725 to 1465. These relatively high ratios may reflect dissolution of evaporites present in the aquifers or confining formations. A less likely, though plausible explanation is saline surface water (e.g. waters impacted by road salt[31]) mixing with relatively shallow groundwater in or near the Trinity aquifer's outcrop zone. Only eight samples had a chloride/bromide ratio less than 10. In previous studies, such extremely low ratios have been attributed to mixing of groundwater with runoff impacted by brominated gasoline additives.[32, 33] Five of the eight samples with chloride/bromide ratios below 10 are located adjacent to a state highway or interstate.

3.3. Metals Analysis

ICP-MS and ICP-OES analyses were used to evaluate the concentrations of 15 different metal ions that are good indicators of groundwater condition. Of the 550 collected samples, 10 were found to have arsenic levels above the 10 µg/L MCL threshold, with a maximum value of 114 µg/L. Similarly, strontium was found to be elevated above the 4.0 mg/L MCL threshold in 9 wells with a maximum detection of 8.9 mg/L. Selenium was detected more frequently than in previous investigations [3] (detected in 507 of the 550 samples), but in much lower concentrations than the MCL. A prior analysis of 100 private wells in the Barnett shale by Fontenot et al. revealed higher levels of arsenic, barium, selenium, and strontium than seen in this study.[3] Fontenot et al. suggested that these naturally occurring groundwater constituents could concentrate in iron-oxide rust/scale formations that can build up in water wells, which could then be liberated by mechanical perturbances of private water wells such as those generated by nearby UOG activities.[3] While this remains a plausible explanation for the elevated concentrations of heavy metals observed by Fontenot et al.,[3] decreased drilling activity and a likely decrease in mechanical disturbances in 2014 compared to 2011 (1,902 permits issued in 2013-14 versus 4,136 in 2010-2011), may explain the decreased levels of dissolved metals compared to previous measurements. [34]

These ions can also originate from natural sources such as the mineral constituents of the aquifers. Changes in oxygen-reduction potential can also change valence states, which may liberate or bind some of these species. As such, some fluctuation is expected to occur naturally, as well as be induced by changes in water levels and redox conditions caused by pumping. Compared to the previous measurements collected by Fontenot et al.[3], ORP values suggested a more oxidative environment with a median value of 80.7mV compared to a previous median value of 28.6. Coupled with an increase in pH from 7.69 to 8.30, the current conditions are less favorable for dissolved metals compared to the conditions observed in 2011. Additionally, the samples in Fontenot et al.[3] were not acidified and filtered as they were

sampling for total metals not dissolved metals as in the current study. However, it should be noted that this difference in sampling protocol likely cannot account for the large variations in metals concentrations between the two studies as total metals analysis usually leads to a more conservative concentration estimate than dissolved metals analysis.

Beryllium, iron, and molybdenum were also elevated in 75, 87, and 187 of the groundwater samples, respectively, with a higher than expected frequency of MCL exceedances in Montague County based on chi-squared tests (Table 2). Beryllium exceedances (0.004 mg/L MCL) were also detected at a higher than expected frequency in Parker and Tarrant counties; whereas iron exceedances (0.3 mg/L MCL) levels were also higher than expected in Cooke and Johnson counties, and molybdenum exceedances (0.04 mg/L MCL) were more frequent in Parker and Wise counties (Table 2). The significance of these three ions remains to be determined, as there is no historical precedent for reference. Other metal ions found in excess of their respective MCL values include barium (1 sample), chromium (1 sample), copper (1 sample), nickel (16 samples), and zinc (1 sample).

3.4. Gas Chromatography Analyses

GC-MS and HS-GC analyses revealed the most striking results of this study. Of the 39 volatile and semi-volatile compounds that were screened, 13 compounds were detected at least once. In particular, methanol and/or ethanol were detected in 35 and 240 wells respectively with average concentrations of 0.5 and 3.2 mg/L and maximum concentrations of 44.6 and 394.2 mg/L, respectively. Methanol and ethanol both are used extensively in unconventional drilling as anti-corrosive agents and gelling agents (www.fracfocus.org);[16] however, these two alcohols can also be produced *in situ*. Methanol can be produced through the digestion of methane by methanotrophic bacteria,[35] whereas ethanol can be produced organically by thermophilic bacteria,[36] albeit typically in much smaller concentrations than was observed here. Both methanol and ethanol were found in 19 wells from Denton, Parker, and Montague counties, in localized areas similar to the areas exhibiting high bromide. These two

alcohols have been detected previously in this region, but at that time, no conclusions could be made about their origin.[3] Propargyl alcohol and isopropyl alcohol were also detected in 155 and 8 water wells, respectively, with maximum concentrations of 26.4 and 9.4 mg/L, respectively. Moreover, when present together, ethanol levels were correlated with propargyl alcohol levels (r = 0.53, p < 0.0001), but not with methanol levels (r =-0.13, p = 0.517). The source of these alcohols remains to be determined; however, methanol, ethanol, and propargyl alcohol were all detected at a greater percentage within the Barnett shale (89, 92, and 90%, respectively) than the percentage of total samples collected within the producing region (83.1%). In particular, ethanol was detected at a higher frequency than expected in Montague, Parker, Tarrant, and Wise counties based on chi-squared analysis; whereas propargyl alcohol was found at a higher incidence in samples from Johnson, Parker, Tarrant and Wise counties (Table 2). These counties comprise the most productive sub-region of the Barnett shale; 18,559 UOG well stimulation events were recorded here since the year 2000, and collectively, these species constitute a specific sub-set of compounds commonly used in unconventional well stimulation per the 2011 Congressional Report on hydraulic fracturing.[15] Of the four alcohol species that were detected throughout the study, only methanol showed a negative correlation with well depth (r = -0.39, p = 0.034), suggesting the source of the methanol originated from the surface, as could result from the mishandling of waste solutions and/or fluid spills. The correlations between well depth and ethanol and propargyl alcohol were not significant (p > 0.05), and there were insufficient detections of isopropyl alcohol to perform a correlative analysis with well depth.

Dichloromethane (DCM) was detected in 122 samples, with 121 of these detections exceeding the suggested MCL of 0.005 mg/L, and 93% of the detections coming from samples collected within the Barnett shale region. DCM had a mean concentration of 0.08 mg/L across the dataset, with a maximum concentration of 2.9 mg/L. The source of this industrial solvent remains to be determined; however, DCM has been detected in a previous

study of groundwater quality in the Permian Basin, a region in western Texas that has recently seen increased UOG activity (Hildenbrand et al., in review). DCM has also been implicated in air quality contamination events associated with unconventional drilling in Colorado[37] and UOG flowback water.[38] There is no known natural occurrence of DCM except through the microbial degradation of chlorinated solvents with higher degrees of chlorination like chloroform.[39] This explanation is plausible and could apply to the data set given that chloroform was also detected in 330 of the collected samples, and in 41 of the 122 samples where DCM was detected. Consistent with this explanation, a scatterplot of DCM levels as a function of chloroform levels (when both compounds were present in a sample) revealed two discrete clusters of samples with distinct, inverse ratios of these compounds (Figure 3). For one cluster of samples, the ratio of DCM/chloroform was ~62:1, whereas in the other, the dominant compound was chloroform with a DCM/chloroform ratio of ~1:32. These striking clusters may be the signatures of two widespread and temporally distinct types of contamination events. The cluster with the higher DCM/chloroform ratio may represent an older contamination event, in which microbial degradation of chloroform had progressed farther than in the more recent event, which accordingly exhibits less degradation of chloroform to DCM. Regardless, the consistent, but distinct, ratios of these compounds for samples constituting those clusters is striking. Alternatively, DCM may also have been introduced from an exogenous source. DCM is a commonly used degreasing agent,[40] and raw use of large volumes of concentrated DCM at the well pad could present a possible pathway for contaminating nearby surface water and shallow groundwater. A breach of flowback waste pits, whether from overflow or faulty linings, can also introduce DCM and many other species into the surface environment.[41] A spill of the solvent solution would account for DCM being present without other chlorinated species. Additionally, trichloroethylene (TCE) was detected in 14 samples at very low levels ranging from 0 to 0.04 mg/L, and was detected exclusively from samples collected within the Barnett shale region.

Collectively, a possible co-migration of dichloromethane, chloroform, and trichloroethylene is consistent with the previous detection of these chlorinated compounds in flowback water from unconventional drilling operations.[42]

At least one of the BTEX (benzene, toluene, ethylbenzene and xylene) class of compounds was detected in 381 of 550 collected samples, and 10 wells had detectable amounts of all four BTEX compounds. These compounds collectively can be found in hydrocarbon fuels, whether raw, processed, or waste, and some individually as industrial solvents or as intermediates in the chemical industry. Benzene was detected in 34 wells, 91% of which were detected from samples collected within the Barnett shale region. Benzene concentrations exceeded the MCL guideline of 0.005 mg/L in all 34 of the detections and reached a maximum concentration of 0.09 mg/L. Toluene, ethylbenzene, and three xylene isomers were also found to be prevalent throughout the Trinity and Woodbine aquifers, being detected in 240, 22, and 240 wells respectively, although at trace concentrations well below their individual MCL values. Interestingly, 83% of samples within Montague County (55 of 66) contained a BTEX compound. This area houses underground injection wells for drilling waste disposal across north-central Texas and Oklahoma, thus it is exposed to the largest volume of produced waters in the region through either trucked or injected water, which must be disposed of with great care.[41] Furthermore, this area is also vulnerable to contamination because it occupies the unconfined outcrop zone of the Trinity aquifer. Of the four BTEX compounds, toluene was the only constituent to have a significant relationship with respect to well depth (r = -0.20, p = 0.003). This observation is consistent with that of methanol and well depth, suggesting that the source of these two constituents originated from the surface.

No research has been reported on organics leaching from underground injection wells, but salt contamination has been identified in association with injection wells and plugged oil and gas wells in southeast Texas.[43] Compared to equivalent studies, the abundance of BTEX compounds in the Barnett shale region is consistent with the characterization of produced

water. Previous findings have detected various BTEX compounds in fracturing influents (mixed fluids before injection) across 22 drilling sites of the Marcellus and Barnett shales. The concentration and occurrence of these BTEX compounds increased in samples collected after multiple days of flowback because of the influent's extended contact with the shale formation.[42] Cyclohexane was also detected in 221 of the 550 collected samples with a maximum concentration of 1.3 mg/L. Interestingly, 75% of the cyclohexane detections were observed in samples collected within the Barnett shale, below the percentage of water samples collected within the shale region (83%). However, based on chi-squared analysis cyclohexane was detected at higher than expected frequencies in Cooke, Denton, Johnson and Hood counties, all of which are highly productive areas with respect to UOG extraction, with the exception of Cooke County (645 UOG stimulation events since the year 2000; Table 2).

Collectively, these data constitute one of the largest studies of groundwater quality in a shale formation associated with UOG activities. The detection of numerous volatile organic compounds in aquifers above the Barnett shale does not necessarily implicate unconventional UOG extraction as the source of contamination; however, it does provide an impetus for further monitoring and analysis of groundwater quality in this region.

ASSOCIATED CONTENT

Supporting Information

Additional materials and methods, figures, tables, and the complete water quality data set referenced in the text. This information is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

[†] These authors contributed equally to this work. Author contributions: ZLH, DDC, BEF, JMM, CPS and KAS designed research; ZLH, DDC, JTT, and CER recruited volunteer study participants and collected samples; SK, CPS, DJH, AFK, CER, JBT, BEF, JMM, PH, and JLW conducted analytical chemistry analyses, hydrogeology descriptions, geospatial analyses, statistical analyses, and performed quality checks and verification of all data collected; BEF, JMM, ZLH, DDC, and JLW analyzed data and provided conclusions for statistical analyses and geospatial relationships; TB and HR analyzed UOG drilling localities and common industrial practices; AFK, CPS, PH, TB, HR, CER and JLW provided comments, conclusions, and corrections on earlier versions of the manuscript; ZLH, BEF, DDC, JMM, PH and KAS wrote the paper.

Notes

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The authors declare no competing financial interest.

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FIGURES AND TABLES

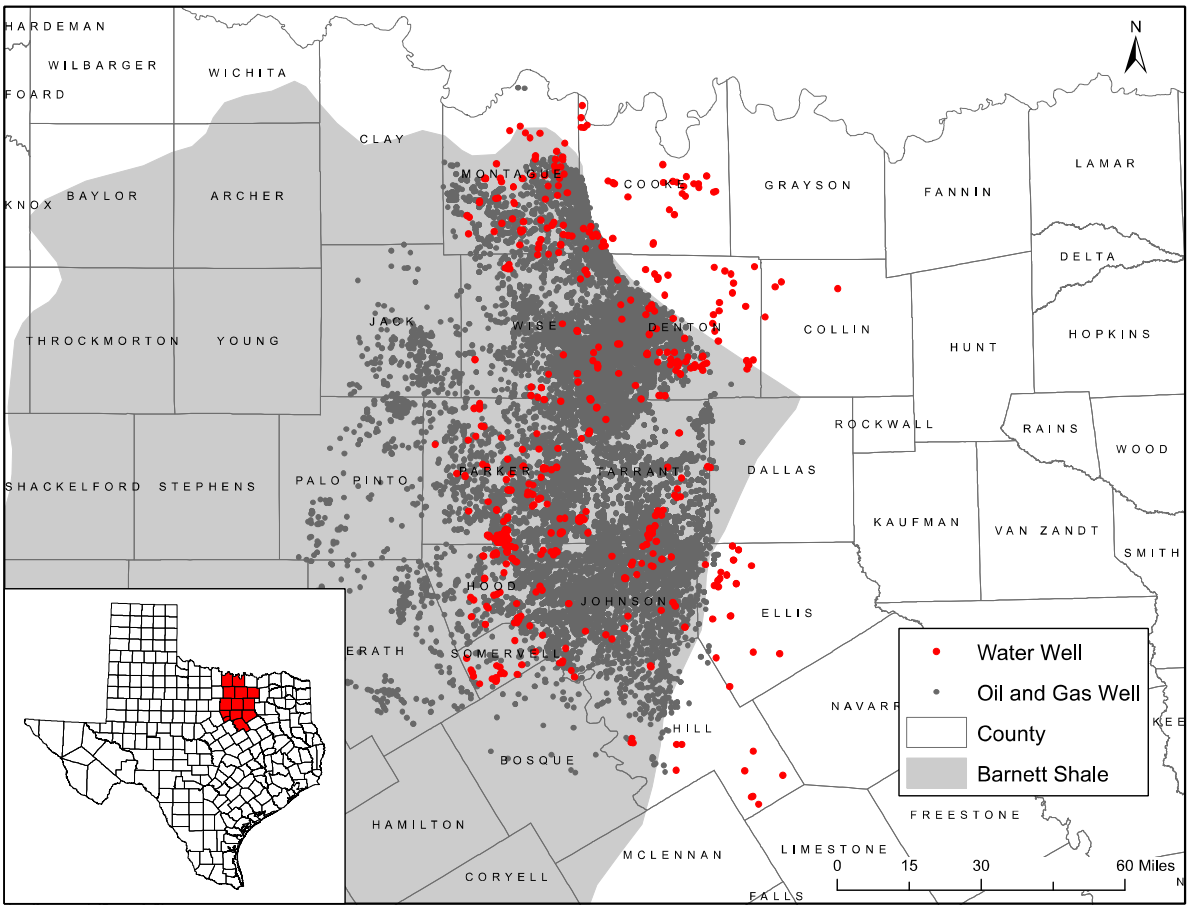

Figure 1. Sampled water wells (red) in relation to UOG wells (dark grey) throughout the Barnett shale region (grey).

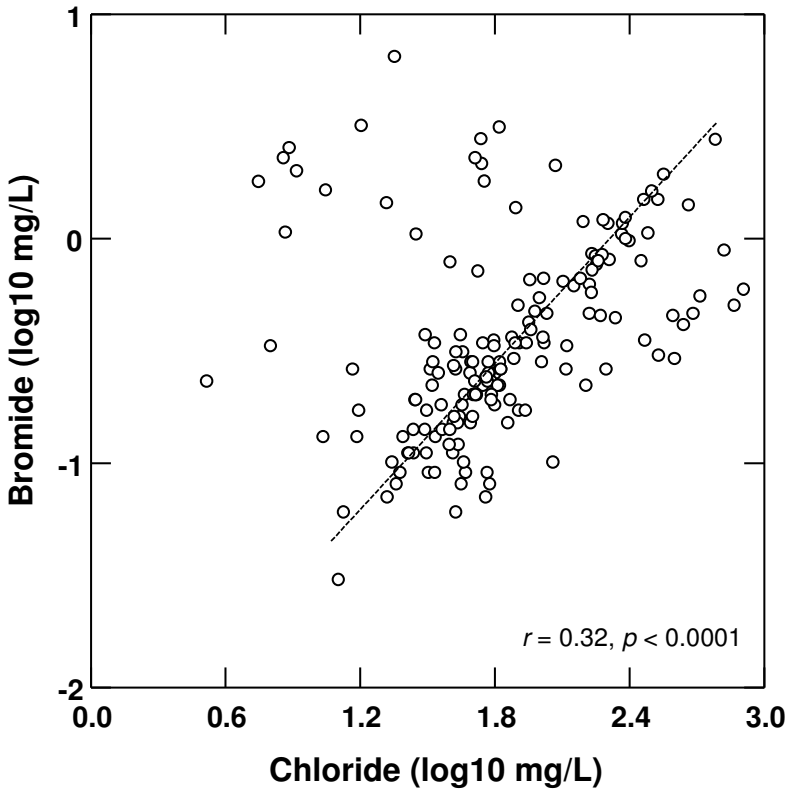

Figure 2. Bromide concentrations relative to chloride concentrations for samples with detectable levels of bromide (*n*=170). The dashed line is for visual purposes only, and indicates a log-linear trend apparent in a subset of samples.

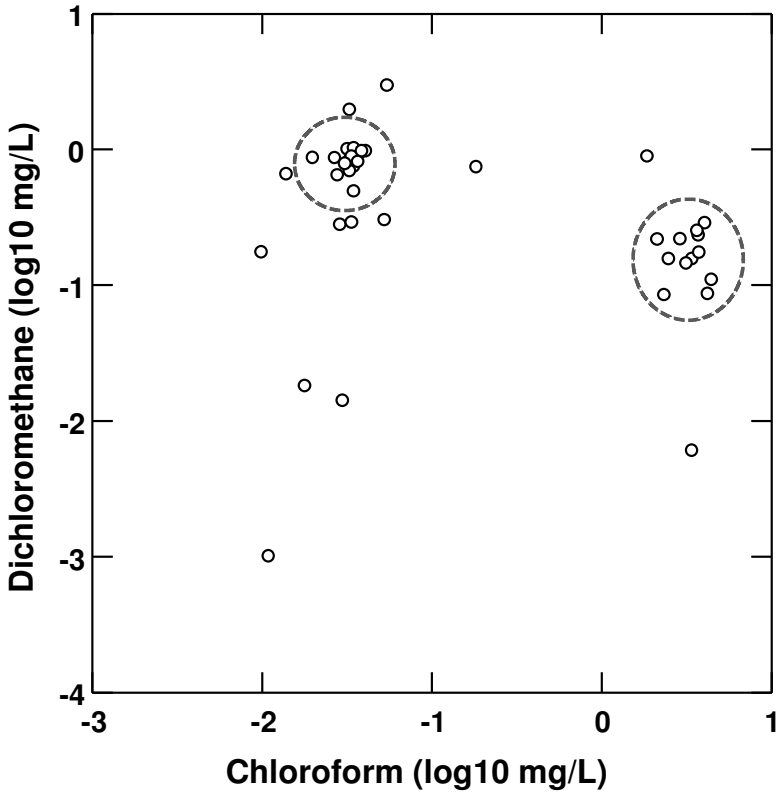

Figure 3. Dichloromethane concentrations in relation to chloroform concentrations in the samples where the two constituents were both detected (*n*=41).

Table 1. Measures of general water quality variables as a function of distance from nearest gas well (log meter) and depth of sample well (log meter), using multiple regression and model selection (see text for details). Asterisks indicate that the 95% confidence interval for the slope parameter does not include zero.

Variable	**Best Model**	**Slope**	***P*-value**	***R^2adj***
Log_{10}-Temperature	Dist + Depth + Dist*Depth	+0.04* (interaction)	< 0.0001	0.463
Log_{10}-DO	Depth	-0.13*	< 0.0001	0.220
Log_{10}-Conductivity	Dist + depth	Dist = +0.03* Depth = +0.05*	< 0.0001	0.125
Log_{10}-TDS	Dist + depth	Dist = +0.05* Depth = +0.03*	< 0.0001	0.127
Log_{10}-Salinity	Dist + Depth	Dist = +0.02* Depth = +0.05*	Dist = 0.001 Depth = < 0.0001	0.096
Log_{10}-pH[#]	Depth	+0.03*	< 0.0001	0.307
ORP	Depth	+20.07*	< 0.0001	0.024

[#] Relationship is nonlinear; low pH at shallow depths, high pH at intermediate depths, and slight trend toward neutral pH at deepest depths (R^2*adj* is based on linear approximation).

Table 2. Pearson's chi-squared tests of independence for frequency of either detection[1] or MCL exeedances[2] of select compounds for counties with ≥40 total samples. For significant tests, + and - symbols indicate whether observed detection and/or exceedance frequencies occurred more or less frequently than would be expected under the null hypothesis of dependence of observations. Compounds were selected based on whether expected frequencies were > 5 for most cells, as recommended for contingency table analysis.

	X^2	*p*	Cooke *n* = 40	Denton *n* = 82	Hood *n* = 52	Johnson *n* = 43	Montague *n* = 66	Parker *n* = 116	Tarrant *n* = 47	Wise *n* = 41
Methanol[1]	2.75	0.908								
Ethanol[1]	80.1	< 0.0001	-	-	-	-	+	+	+	+
Propargyl Alcohol[1]	43.4	< 0.0001	-	-	-	+	-	+	+	+
DCM[2]	93.3	< 0.0001	-	-	+	+	-	+	-	-
Chloroform[1]	62.9	< 0.0001	-	-	-	-	+	+	+	+
Benzene[2]	12.6	0.084								
Cyclohexane[1]	55.5	< 0.0001	+	+	+	+	-	-	-	+
Bromide[1]	16.7	0.019	-	-	-	-	+	+	-	+
Beryllium[2]	57.4	< 0.0001	-	-	-	-	+	+	+	-
Iron[2]	37.6	< 0.0001	+	-	-	+	+	-	-	-
Molybdenum[2]	118.0	< 0.0001	-	-	-	-	+	+	-	+

Photo credit: Doug D. Carlton, Jr.