A reconnaissance analysis of groundwater quality in the Eagle Ford shale region reveals two distinct bromide/chloride populations

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HIGHLIGHTS

- Reconnaissance groundwater analysis reveals two unique bromide/chloride populations.
- Volatile organic compounds and extreme levels of total organic carbon detected.
- Distinguishable anion and metal ion signatures found geographically clustered.
- Multiple strata influenced by various geogenic and anthropogenic processes.

GRAPHICAL ABSTRACT
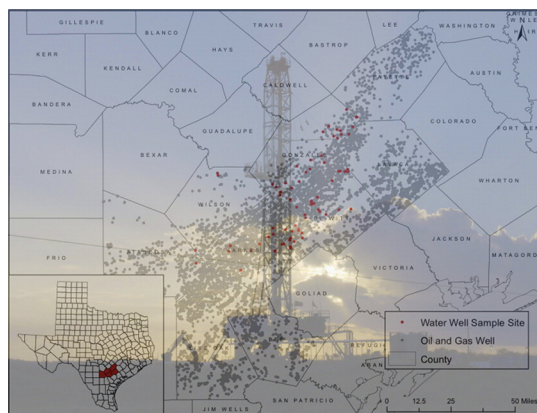
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ABSTRACT

The extraction of oil and natural gas from unconventional shale formations has prompted a series of investigations to examine the quality of the groundwater in the overlying aquifers. Here we present a reconnaissance analysis of groundwater quality in the Eagle Ford region of southern Texas. These data reveal two distinct sample populations that are differentiable by bromide/chloride ratios. Elevated levels of fluoride, nitrate, sulfate, various metal ions, and the detection of exotic volatile organic compounds highlight a high bromide group of samples, which is geographically clustered, while encompassing multiple hydrogeological strata. Samples with bromide/chloride ratios representative of connate water displayed elevated levels of total organic carbon, while

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revealing the detection of alcohols and chlorinated compounds. These findings suggest that groundwater quality in the Western Gulf Basin is, for the most part, controlled by a series of natural processes; however, there is also evidence of episodic contamination events potentially attributed to unconventional oil and gas development or other anthropogenic activities. Collectively, this characterization of natural groundwater constituents and exogenous compounds will guide targeted remediation efforts and provides insight for agricultural entities, industrial operators, and rural communities that rely on groundwater in southern Texas.

1. Introduction

The potential influence of unconventional oil and gas development (UD) on groundwater quality remains a complex and controversial topic. In the United States, where the environmental implications of UD have been the most extensively studied, investigations have revealed elevated levels of methane (Osborn et al., 2011) and stray thermogenic natural gas (Darrah et al., 2014; Jackson et al., 2013) in groundwater samples collected from aquifers located near UD activities, while others have documented the natural occurrence of dissolved gases in areas away from active drilling (Darrah et al., 2015; Molofsky et al., 2013; Siegel et al., 2015). Similarly, contamination of groundwater with inorganic constituents (metals and salts) has been attributed to surface spills (Lauer et al., 2016; Warner et al., 2013), the transport of fluids through micro-scale annular fissures in UD gas wells (Burton et al., 2016), and the physical mobilization of ions from scale/rust formations (Fontenot et al., 2013). Inorganic elements have been ascribed to biogenic sources providing evidence of hydraulic connectivity between shallow groundwaters and deeper formation brines (Darrah et al., 2015; Llewellyn, 2014; Warner et al., 2012). Recent investigations have also detected the presence of various alcohols, chlorinated species, BTEX compounds (benzene, toluene, ethylbenzene and xylenes) (Hildenbrand et al., 2015), and aldehydes (Hildenbrand et al., 2016) in groundwater overlying the Barnett and Cline shale formations in Texas. Gasoline and diesel range organic compounds (Drollette et al., 2015), phthalates (Drollette et al., 2015), and 2-butoxyethanol (Llewellyn et al., 2015) have also been detected in water wells analyzed near UD in the Marcellus Shale of Pennsylvania. Internationally, the environmental implications of UD have been evaluated in the United Kingdom and Europe (Almond et al., 2014; Gordalla et al., 2013), Canada (CCA, 2014), Australia (Lloyd-Smith and Senjen, 2011), and China (Yu et al., 2016), revealing potential risks of groundwater contamination with radionuclides, exogenous chemicals, and stray gas. Collectively, these concerns illustrate the importance of responsible shale energy extraction given the natural interplay between hydrocarbon resources and the environment.

The characterization of groundwater quality near areas of UD activity in petroliferous basins can help identify potential contamination events, differentiate between geogenic and anthropogenic contamination pathways, and guide the implementation of effective remediation strategies where needed. In shale energy plays where UD activity is expanding and contracting as a result of technological advances and fluctuations in commodity prices, the need for groundwater monitoring is critical. One of the keys to a successful reconnaissance analysis is the collection of basic water quality measurements *in situ*. For example, measurements of total dissolved solids (TDS) and conductivity can provide insight into the rate of hydrocarbon biodegradation in contaminated aquifers (Atekwana et al., 2004), whereas pH and oxidation reduction potential (ORP) can identify notable changes in groundwater composition (Hildenbrand et al., 2016) and delineate sub-surface contaminant plumes (Naudet et al., 2004), respectively. Additionally, measurements of total organic carbon (TOC) can be utilized as a cumulative assessment of volatile organic compounds (VOCs) and potential anthropogenic contamination (Spruill, 1988). The analysis of bromide/chloride ratios can be used as a metric for identifying individual sources of contamination (Behl et al., 1987; Flury and Papritz, 1993; Katz et al.,

2011), such as influence from septic tanks or sewage effluent (Vengosh and Pankratov, 1998), road salts or halites (Granato, 1996), or basin brines (Davis et al., 1998; Panno et al., 2006). En masse, these analyses, while simple to perform, provide a sentinel perspective of groundwater quality within the contexts of anthropogenic and geogenic processes.

The objective of this study was to perform a reconnaissance analysis of groundwater quality in the aquifers overlying the Eagle Ford Shale within the context of natural geological processes, as well as to evaluate the impacts from UD activity and/or other anthropogenic sources of pollution. These data provide a substantive foundation for the subsequent analysis of organic and inorganic molecules in groundwater overlaying a series of highly productive strata engaged in unconventional oil and gas extraction in the Western Gulf Basin.

2. Materials and methods

2.1. Sampling

The groundwater samples analyzed in this study were collected from 77 private water wells within Atascosa, Dewitt, Gonzales, Karnes, and Wilson counties along the Stuart City shelf margin, throughout the active corridor of UD activity within Eagle Ford region (Fig. 1). Sampling sites were selected as a function of well owner participation and availability. The wells draw water from the (stratigraphically lowest to highest): Carrizo-Wilcox, Yegua-Jackson, and Gulf Coast aquifers (Fig. 1). These aquifers consist of southeastward-sloping, interbedded sedimentary formations deposited during the Tertiary and Quaternary Periods. The Carrizo-Wilcox aquifer comprises sand, clay, sandstone, silt, and lignite. Interbedded sand, silt, and clay make up the Yegua-Jackson aquifer. Similar deposits, along with gravel, are present in the Gulf Coast aquifer (TWC, 1989). These deposits are hydraulically connected, and form a leaky artesian aquifer system. The Eagle Ford Shale region also features a number of unique geological structures that can influence groundwater quality, including the San Marcos Arch (Sengelman, 2010) and the Yegua faults (Knox et al., 2007; Quick et al., 1977). Groundwater in the study area flows generally southeastward, toward the Gulf Coast (TWC, 1989). Historically, groundwater pumping along the coast has induced saltwater intrusion, but primarily near large cities along the coast rather than the study area. Because we studied multiple, regionally sloping geological strata, we observed a large range in well depth, ranging from 21.3–853.4 m. Well depth information was acquired for 42 of the 77 sampled wells from owner recollection and available documentation.

Each water sample was collected as close to the water wellhead as possible, prior to any filtration or treatment systems. The water wells were purged until temperature, dissolved oxygen (DO), conductivity, TDS, salinity, pH, and ORP measurements, as determined by a YSI Professional Plus multi-parametric probe (YSI Incorporated, Yellow Springs, Ohio, USA), stabilized to ensure that the samples were representative of groundwater from their respective aquifers following USGS protocols (USGS, 2006). At each site, multiple samples were collected in 125-mL HDPE bottles with no headspace and held for no longer than 48 h on ice before transport to The University of Texas at Arlington. Field blanks were prepared with deionized water and randomized duplicate samples were used for quality assurance. Samples collected for
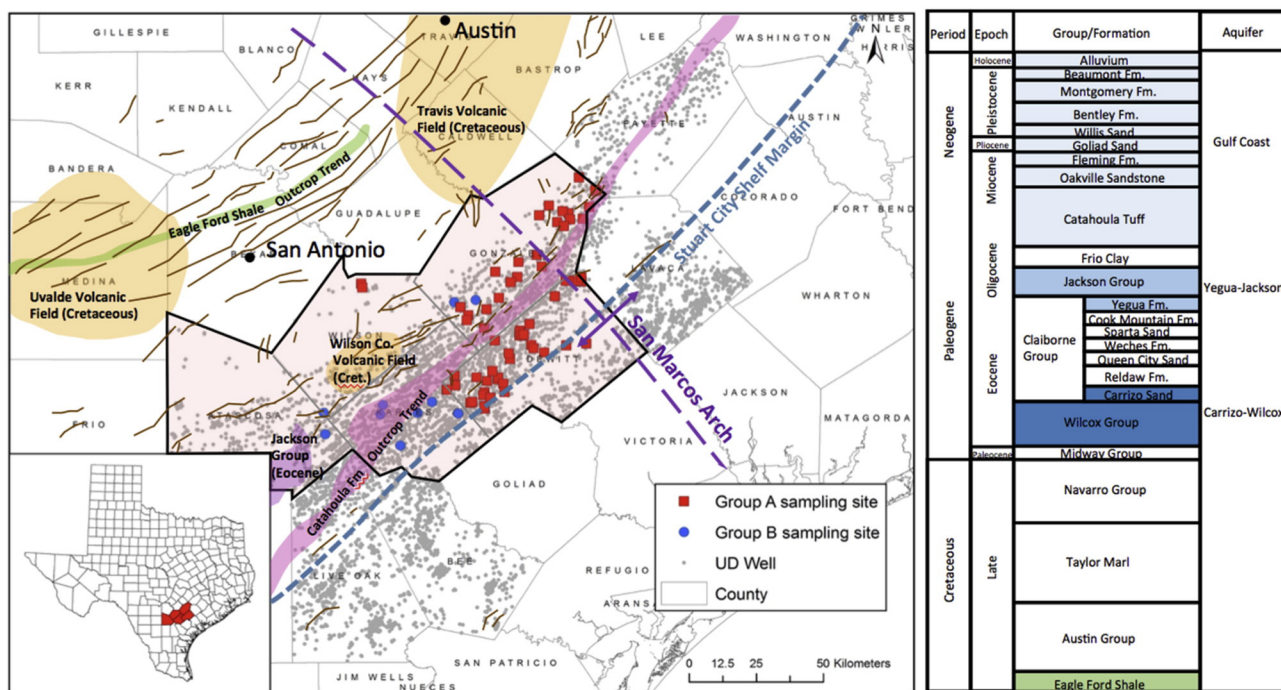
Fig. 1. Left, Group A sampling sites (red squares, n = 66) and group B sampling sites (cyan dots, n = 11) in relation to nearby unconventional oil and gas wells (grey dots). Inset illustrates the study region in relation to the state of Texas. Fault lines are illustrated in brown (Ewing and Caran, 1982; Hentz and Ruppel, 2010; UTBEG, 2016). Right, hydrogeological cross-section of the study area (Baker, 1995). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

metal ions analysis were filtered and preserved with concentrated omnitrace grade nitric acid to a final concentration of 2% v/v. Samples collected for organic ion analysis were preserved with chromatography grade chloroform to a final concentration of 80 parts-per-million and frozen to prevent microbial degradation. Samples collected for the analysis of volatile organic and semi-volatile organic compounds, TOC and total nitrogen (TN), were untreated (Hildenbrand et al., 2015; Hildenbrand et al., 2016).

2.2. Analysis

Methodology for chemical analyses followed those from our previous studies (Fontenot et al., 2013; Hildenbrand et al., 2015) and 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) (Supplementary information methods). Specific organic chemical species were selected from a Congressional Report on hydraulic fracturing fluid ingredients (Waxman et al., 2011), frequently listed components of UD fluids in the national hydraulic fracturing chemical registry (www.fracfocus.org), and from compounds identified in previous studies (Hildenbrand et al., 2015; Thacker et al., 2015). These compounds included alcohols, aromatic compounds, aldehydes, amines, and chlorinated species. Whenever possible, we evaluated constituents in relation to their respective Primary or Secondary Maximum Contaminant Limits (MCL) as provided in the United States Environmental Protection Agency's Drinking Water Standards (USEPA, 2012).

Information about locations of UD activity in the region was obtained from www.fracfocus.org and the Texas Railroad Commission, the governing body for oil and gas drilling in the state of Texas (www.rrc.state.tx.us). Geospatial analyses were conducted using ArcGIS 10.1 (www.esri.com). The distance from sampling site to the nearest UD well was calculated using the 'Near' analysis tool to evaluate potential relationships between groundwater quality and proximity to UD activity. All statistical analyses, including Mann-Whitney U pairwise comparisons, Spearman's rank correlations, and principal components

analysis (PCA) were performed in PAST 3.08 (Hammer et al., 2001) and all graphics produced in the "ggplot2" package (Wickham, 2009), using R (www.R-project.org).

3. Results

In situ measurements of pH and TDS performed during sample collection revealed large ranges. The pH varied from 5.5–8.5 with a median value of 7.2, while TDS ranged from 227.5–4082 mg/L. 58 of 77 samples exhibited TDS values above the 500 mg/L secondary MCL of the US EPA, with a median value of 825.5 mg/L. Regionally, TDS tends to be higher in the southwestern part of the study area, decreasing toward the northeastern edge of the area. These results are generally consistent with previous reports. For example, Reedy et al. (2011) estimated that 40–80% of water wells in the Gulf Coast aquifer beneath southwestern Karnes County exceed 1000 mg/L TDS, whereas 0–20% of wells exceed that threshold in eastern Gonzales County (Reedy et al., 2011).

3.1. Detection of two distinct bromide/chloride sub-populations

Chloride was found at concentrations above 250 mg/L in 21 of the 77 samples, 15 of which were detected in wells with depths of <300 ft. Bromide also correlated strongly with TDS ($r = 0.96$, $p < 0.001$) and chloride levels ($r = 0.67$, $p < 0.001$). In the event that deep brine migrated from a uniform source and mixed with shallow groundwater, both chloride and bromide would likely be elevated (Warner et al., 2012), and the concentration of both anions would correlate positively with well depth. Such an observation would likely be constrained to geological faults or zones of intense fracturing. Naturally, chloride and sulfate concentrations tend to increase along groundwater flow paths; this process might also be reflected by a positive correlation with well depth. However, chloride and bromide concentrations were both uncorrelated with well depth ($r = -0.05$, $p = 0.67$; $r = 0.08$, $p = 0.49$, respectively) implying other controls on salt concentrations.

An analysis of bromide/chloride ratios revealed two distinct sub-populations: one that appears to fall on a mixing line exhibiting bromide/chloride ratios around 0.0034 (n = 66, hereafter Group A),

which is close to seawater composition (Davis et al., 1998; Hem, 1992) and connate formation water (Kreitler and Richter, 1986), yet consistent with historical measurements (Chowdhury et al., 2006); and one with surprisingly higher levels of bromide (>0.5 mg/L) exhibiting bromide/chloride ratios ranging between 0.022 and 0.101 (n = 11, hereafter Group B) (Fig. 2). The median well depth within Group B was greater than that of Group A, albeit not statistically significant (106.7 vs. 61.0 m, $p = 0.076$). This is representative of the fact that 34 of the 66 Group A wells had a depth of 61.0 m or less, while none of the Group B wells had a depth <73.2 m. However, it is also important to note that 11 of the 66 wells within Group A were collected from wells drawing groundwater at depths >304.8 m, whereas only one well had a depth >304.8 m in Group B. The wide range in well depths within Group A is likely a reflection of varying uses from residential (shallow wells generally <61.0 m) to agricultural and industrial service wells (deeper wells generally >304.8 m). Additionally, there was a geographical separation between the collection sites of the Group A and Group B samples. The majority of samples within Group B were geographically clustered within Karnes County (8/11), while the samples within Group A were collected throughout Dewitt (n = 38), Gonzales (n = 23), Wilson (n = 2), and Karnes (n = 2) counties (Fig. 1). The overall frequency of Group A samples within 1 km of a UD well was not significantly different from the frequency of Group B samples within 1 km of a UD well (Fisher's Exact Test, $p = 0.4415$). We performed a series of Mann-Whitney U tests to compare median values of water quality measurements and concentrations of anions and metals between these subpopulations (Table 1).

The basic water chemistry was found to be statistically similar between the two bromide/chloride sub-populations, as observed by median pH and ORP values (Table 1). However, nitrate, fluoride and sulfate levels were all found to be notably higher in Group B when compared with Group A (Table 1). Median nitrate was found to be 20-fold higher in Group B (5.6 vs. 0.26 mg/L) and also correlated negatively with increasing well depth ($r = -0.60$, $p < 0.001$), which has been observed previously in the Catahoula Formation, of the Gulf Coast aquifer (Hudak, 2003). In addition to UD activities, the Eagle Ford Shale region also facilitates a variety of agricultural practices including, but not limited to, cattle, poultry, and grass production. It is quite possible that these processes contribute nitrate to shallow groundwater from the surface; as overall, 26 of the 42 nitrate detections were observed from water wells with a depth <61.0 m (6 of the 42 nitrate detections also came from wells of unknown depth).

Median fluoride was also found to be elevated within Group B (0.69 vs. 0.38 mg/L, Table 1, $p = 0.068$), despite three observations of fluoride persisting above the 4 mg/L MCL threshold detected exclusively within the Group A population. Unlike nitrate, fluoride concentrations correlated positively with well depth; however, this observation also was only marginally significant ($r = 0.23$, $p = 0.059$). The lack of covariation between nitrate and fluoride within Group A ($r = 0.16$, $p = 0.156$) suggests that the sources of these constituents may be attributed to different processes, such as agricultural activities for nitrate and natural sources like volcanic ash from the Catahoula Formation for fluoride (Hildenbrand et al., 2015). Interestingly, fluoride concentrations were found to be weakly correlated with bromide ($r = 0.343$, $p = 0.005$) and chloride concentrations ($r = 0.315$, $p = 0.010$) within Group A, but not within Group B (bromide $r = -0.264$, $p = 0.433$; chloride $r = -0.436$, $p = 0.180$). These findings suggest that the loading of fluoride in Group A may be attributable to the leakage of brines and possible rock-water interactions (Uddameri et al., 2014), whereas the loading of fluoride in Group B may be attributed to other processes. One possible anthropogenic source of fluoride would be from the mixing of groundwater with rogue hydrofluoric acid that is used in the Eagle Ford shale during the well stimulation process. However, if rogue hydrofluoric acid from UD operations were contributing to the elevated levels of fluoride, one would expect to observe a drop in pH that would be represented by an inverse correlation between fluoride concentrations and pH. This relationship was not observed in the dataset as a whole ($r = 0.06$, $p = 0.611$). In fact fluoride concentrations correlated positively with pH values within the Group B samples ($r = 0.60$, $p = 0.051$), further indicating that fluoride levels detected in the Group B samples were likely not attributed to contamination from shale-drilling-related acidization. The lack of covariation between fluoride and a majority of all of the other analytes in Group B, except for inorganic carbon ($r = 0.673$, $p = 0.023$), suggests that the fluoride detected in the Group B samples may be attributed to other naturally occurring hydrogeochemical processes that have not been previously documented in the southern Texas region.

Sulfate was detected at a median concentration of 41.9 mg/L with 9 samples exceeding the recommended MCL value of 250 mg/L. Unlike nitrate, sulfate was not found to be present in statistically higher concentrations at shallower depths ($r = -0.05$, $p = 0.686$); however, 8 of the 9 MCL exceedances were detected in wells with depths <117.3 m (1 MCL exceedance was detected in a well of unknown depth). Median sulfate within Group B was 3.5-fold higher than Group A (128.1 mg/L vs. 36.5 mg/L, $p = 0.002$). High sulfate has been observed with the hydrostratigraphic units of the Gulf Coast aquifer (Chowdhury et al., 2006); however, limited historical water quality data are available to make this assessment of the Jackson, Yegua, and Carrizo aquifers.

3.2. Elevated levels of metal ions

Of the 14 ions that were quantified (arsenic, barium, beryllium, chromium, cobalt, iron, molybdenum, nickel, selenium, strontium, titanium, vanadium, zinc and zirconium), arsenic was found to have the highest frequency of elevated detections, exhibiting a median concentration of 0.80 μg/L and exceeding the 10 μg/L MCL value in 10 samples. 5 of these exceedances were detected within Group B (5/11), which had a higher median arsenic concentration than Group A (4.28 μg/L vs. 0.67 μg/L, $p = 0.051$; Table 1). Elevated levels of arsenic have been previously characterized in the south-central Texas region, particularly in the Gulf Coast aquifer (Glenn and Lester, 2010; Hudak, 2003). Gates et al. attributed elevated arsenic concentrations to the volcanic ashes in the Catahoula Formation followed by sorption onto iron oxides and desorption by silica (Gates et al., 2009). Similarly, Scanlon et al. postulated that elevated levels of arsenic in the Gulf Coast region from a geogenic origin, related primarily to volcaniclastic deposits and reworked grains that form aquifer materials, rather than from systematic contamination associated with cotton production (Scanlon et al., 2005). Our data does not support this hypothesis, as we did not observe a co-existence of arsenic and fluoride in either Groups A ($r = -0.099$, $p = 0.433$) or B ($r = -0.554$, $p = 0.08$), as would be indicative of arsenic leaching
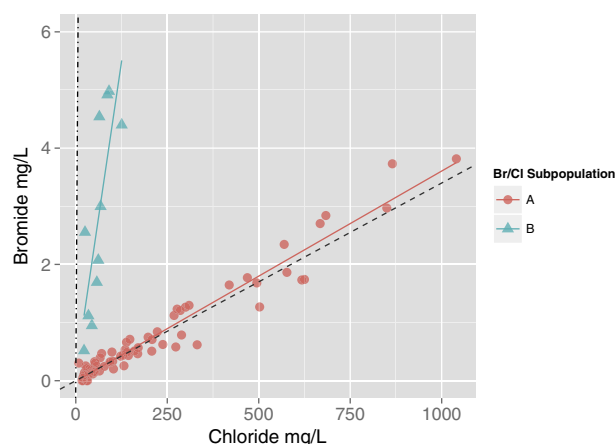
Fig. 2. Relationship between concentrations of bromide and chloride (mg/L) across all samples, depicting our delineation of two distinct concentration ratio gradients. Dot-dash line corresponds to a 1:1 Br/Cl ratio, dashed line corresponds to Br/Cl ratio of seawater (0.0034).

Table 1
Summary statistics for comparisons of water quality, anions, and metals between Group A (n = 66) and Group B (n = 11). *p*-Values are for two-sample Mann-Whitney *U* tests.

	Group A			Group B			
	Median	Mean	SD	Median	Mean	SD	*p*-Value
Temperature (°C)	25.00	27.10	5.90	25.40	25.00	2.00	0.9480
Dissolved oxygen	2.52	2.90	1.80	3.46	3.29	1.80	0.4800
SC (mS/cm)	1.12	1.46	0.99	2.91	3.19	1.49	0.0001
TDS (mg/L)	728.00	942.20	633.80	1891.00	2075.20	966.40	0.0002
Salinity (g/L)	0.56	0.73	0.52	1.50	1.64	0.82	0.0001
pH	7.18	7.24	0.42	7.45	7.55	0.48	0.0540
ORP (mV)	45.55	37.82	162.40	30.10	-5.21	109.50	0.3520
Total organic carbon (mg/L)	0.50	12.34	33.34	0.59	3.10	7.07	0.5170
Total carbon (mg/L)	78.82	91.24	52.84	67.81	75.24	34.34	0.2590
Inorganic carbon (mg/L)	78.50	90.87	52.26	67.49	75.00	35.60	0.2240
Total nitrogen (mg/L)	1.19	2.35	3.03	1.52	2.02	1.22	0.1690
Bromide (mg/L)	0.48	0.80	0.89	2.55	2.79	1.68	0.0001
Chloride (mg/L)	136.74	224.67	238.56	61.48	61.80	30.82	0.0150
Fluoride (mg/L)	0.38	0.70	1.08	0.69	0.91	0.77	0.0680
Nitrate (mg/L)	0.26	8.93	13.77	5.59	7.32	8.61	0.4860
Sulfate (mg/L)	36.48	126.10	303.97	128.09	187.76	216.55	0.0020
Arsenic (µg/L)	0.67	2.67	6.12	4.28	17.83	21.43	0.0510
Barium (µg/L)	97.15	119.59	89.08	78.95	78.90	48.96	0.2200
Beryllium (µg/L)	0.01	0.04	0.16	0.01	0.01	0.01	0.8480
Cobalt (µg/L)	0.09	0.14	0.20	0.13	0.16	0.12	0.1010
Chromium (µg/L)	0.00	0.10	0.48	0.23	2.12	5.67	0.0040
Iron (µg/L)	38.95	314.70	874.50	39.43	308.03	359.83	0.1480
Molybdenum (µg/L)	0.87	1.61	2.19	1.93	3.64	4.02	0.0310
Nickel (µg/L)	0.16	0.35	0.65	0.16	1.20	3.44	0.6470
Selenium (µg/L)	0.48	2.16	3.02	5.71	5.53	4.49	0.0130
Strontium (µg/L)	622.75	906.66	983.10	1832.00	3005.30	4292.10	0.0008
Titanium (µg/L)	1.58	2.28	2.23	2.49	3.12	2.17	0.0140
Vanadium (µg/L)	0.62	4.30	7.40	8.87	12.11	11.48	0.0130
Zinc (µg/L)	4.07	134.00	845.40	4.09	23.17	46.30	1.0000
Zirconium (µg/L)	0.00	0.03	0.14	0.00	0.03	0.09	0.2560

from fluoride-rich volcaniclastic deposits. Instead we found pH and ORP to be much stronger predictors of arsenic concentrations. Chowdhury et al. discovered higher arsenic concentrations in slightly-reducing to slightly-oxidizing (-100 to $+100$ mV) conditions in the Gulf Coast region, potentially due to the preferential dissolution of iron sulfides and iron oxides in this redox environment (Chowdhury et al., 2006). The majority of Group A (~60%) and Group B (~80%) samples that had arsenic MCL exceedances exhibited ORP measurements within this favorable redox range, respectively. These data suggest that redox chemistry is a contributing factor to elevated arsenic levels (Group A $r = 0.50$, $p \leq 0.001$; Group B $r = 0.74$, $p = 0.001$), as well as concentrations of selenium (Group A $r = 0.70$, $p \leq 0.001$; Group B $r = 0.75$, $p = 0.008$) and vanadium (Group A $r = 0.80$, $p \leq 0.001$; Group B $r = 0.66$, $p = 0.026$). Subsurface chemical and microbial reactions can also mobilize arsenic from the solid to liquid phase, or desorb arsenic from aquifer solids (Glenn and Lester, 2010; Korte and Fernando, 1991; Nickson et al., 1998).

Strontium levels were also elevated above the 4 mg/L MCL value in two samples, and the median concentration was notably higher within Group B (1832 µg/L vs. 623 µg/L, $p \leq 0.001$). Selenium also followed this trend with a ten-fold higher median value within Group B compared with Group A (5.57 µg/L vs. 0.48 µg/L, $p = 0.013$). Like arsenic, strontium and selenium concentrations did not correlate positively with fluoride concentrations in Group B (strontium $r = -0.81$, $p = 0.003$; selenium $r = -0.57$, $p = 0.07$), further suggesting that the elevated levels of these metal ions is likely not attributed to rock-water interactions with volcanic ash deposits that are characteristic of the Catahoula Formation. Collectively, the signature of high levels of arsenic, selenium, and strontium has been observed in private water wells near UD activity before (Fontenot et al., 2014; Fontenot et al., 2013). Fontenot et al. (2013) suggested that under favorable oxidation conditions, the mechanical force produced during the UD well stimulation process could facilitate the mobilization of metal ions into groundwater from naturally occurring rust and scale formations found in private water wells (Fontenot et al., 2013).

3.3. Total organic carbon and VOCs

Historical data collected between 2002 and 2009 by the Texas Water Development Board illustrates TOC levels as high as 2.0 mg/L in the Eagle Ford region (Palacios, 2012). Of our recent samples, 24 of 77 had a TOC concentration above 2.0 mg/L and the complete dataset ranged from 0.02–138.9 mg/L with a median value of 0.55 mg/L. TOC correlated with well depth ($r = 0.51$, $p < 0.001$) and all 7 TOC measurements above 20 mg/L were acquired exclusively from Carrizo-Wilcox water wells with depths >390.1 m. In particular, three water wells had TOC values above 130 mg/L, which might be reflective of the fact that these wells were once shallow conventional oil wells converted into water wells to service the nearby unconventional oil and gas activity. No VOCs were detected in any of these three samples; however, the high TOC values could be attributed to dissolved gases as the water from each of these wells was effervescent and consequently exhibited a phase separation at the surface indicative of a large amount of dissolved gases being present. The dissolved hydrocarbons methane, ethane, propane, butane, pentane, and hexane were not quantified as part of this study; however, subsequent compositional and possible isotopic characterization appears to be warranted.

Median TOC levels were similar between the two bromide/chloride sub-populations (0.59 mg/L vs. 0.50 mg/L); yet, the detected chemical species were highly variable. TOC levels weakly correlated with bromide ($r = 0.38$, $p < 0.002$) and chloride ($r = 0.30$, $p < 0.014$) concentrations in Group A, an observation which can be indicative of groundwater quality being influenced by rogue industrial fluids and/or brine solutions. In fact within Group A, chloroform and propargyl alcohol were both detected in three samples. These two compounds have also been detected in the Barnett Shale region (Hildenbrand et al., 2015). In

particular, propargyl alcohol is characterized as part of a specific subset of compounds commonly used in unconventional well stimulation as per a Congressional Report on hydraulic fracturing (Waxman et al., 2011). Both were observed exclusively at well depths <126.5 m and exclusively within Dewitt County, the second most productive county in the Eagle Ford Shale region behind Karnes County. There were insufficient detections of chloroform and propargyl alcohol to perform correlative analyses with well depth; however, drilling-related VOCs detected in shallow groundwater have been attributed to surface spills in the Marcellus (Drollette et al., 2015) and Bakken Shale (Lauer et al., 2016) regions, respectively. Interestingly, other lower-order chlorinated compounds were not detected in this study. Chloroform can be degraded to dichloromethane and ultimately to formate as a result of microbial metabolism (Cappelletti et al., 2012), as has been observed in a time-series analysis of groundwater quality in the Cline Shale region (Hildenbrand et al., 2016). These data indicate that these chloroform and propargyl contamination events may have occurred relatively recently or that a higher order chlorinated solvent was used, and had since degraded to chloroform.

Within the 11 samples in Group B, only one sample exhibited discernible VOCs. 2-butanone, tetrahydrofuran, and cyclohexanone were detected in high concentrations in one sample (1.88, 4.439, and 0.615 mg/L, respectively). To our knowledge, this is the first time that these constituents have been detected in shallow groundwater (250 ft well) near UD operations (0.267 km to nearest UD well) or in the Gulf Coast aquifer. A series of three unknown organic constituents were also detected in multiple samples within Group B. Unknown compounds A–C were detected in a total of 1, 3, and 4 wells, respectively. Of these eight wells with unknown compounds, 6 occurred within the 11 samples from Group B and 2 within the 66 samples from Group A. The origins of these large exotic molecules in groundwater (and others like them) remain unknown, and potential associations with UD are difficult to assess due to the need for industry wide protection of proprietary or trade secret formulas.

3.4. Principal components analysis of TDS and select anions

Because simple analysis of median values can be misleading with highly unbalanced sample sizes, we elected to more fully characterize the two bromide/chloride subpopulations using principal components analysis (PCA) of the correlation matrix of TDS and various inter-correlated anions (bromide, chloride, fluoride, nitrate, and sulfate). PCA uses orthogonal transformation to reduce dimensionality of sets of possibly correlated variables into composite variables that are linearly uncorrelated; therefore, PCA is often effective for exploring gradients of variation in multivariate datasets. We interpreted the first four principal component axes, as these collectively accounted for approximately 93.7% of the total variance (Table 2; Fig. 3). The first PC axis explained 47.7% of the total variance and was structured mostly by moderate positive correlation between bromide, chloride, TDS, and sulfate, whereas nitrate and fluoride weighted minimally on this axis. Variation along PC2 (19.1% of variance) was structured primarily by a moderate inverse

relationship between fluoride (which weighted strongly along the negative axis of PC2) and both nitrate and sulfate. PC3 accounted for 16.8% of the total variance and was structured mostly by an inverse relationship between samples with high nitrate, which weighted strongly in the positive direction, and low sulfate, which weighted moderately in the negative direction. Finally PC4 accounted for 10.1% of the total variance; both bromide and TDS had strong negative factor loadings, while the remaining variables had low to strong positive factor loadings (Table 2).

Although Group B showed high median values on PC1, indicating relatively high overall concentrations for bromide, chloride, sulfate, and TDS, only PC4 served to differentiate this subpopulation from Group A (Fig. 3). Collectively, all samples from Group B were situated within the major gradients of variation present within Group A for the first three principal component axes (Fig. 3), indicating that for the most part, Group B samples were not extreme, and varied independently, for concentrations of fluoride, nitrate, and sulfate. However, TDS values were strongly correlated with Group B and not with other variables or principal component axes, indicating that high TDS values are driven by the Group B subpopulation. In other words, some latent variable(s) contributing to TDS, which might be higher concentrations of metals and/or constituents not analyzed for this study, are also strongly associated with Group B and not with Group A. We noted significantly higher concentrations of various metals in Group B than in Group A, including chromium, molybdenum, selenium, strontium, titanium, and vanadium (Table 1). Moreover, four samples from Group B (sample IDs 166, 167, 168, and 175) were extreme in their bromide concentrations, and consistently clustered together in the PCA. These four samples, and all of the Group B samples in general, originate from the southwestern periphery of the study area and may represent extreme concentrations of organic and inorganic constituents along a natural gradient. The geospatial separation from the Group A sample may indicate greater evapotranspiration toward the western part of Eagle Ford Shale region. High temperatures coupled with porous surficial materials in this region could facilitate faster evaporation of groundwater, thus resulting in the evaporative enrichments of various ions (Chaudhuri and Ale, 2014).

4. Discussion

The analysis of bromide/chloride ratios has been utilized in a number of groundwater studies conducted previously (Katz et al., 2011), where generally a wide range of values is observed (Davis et al., 1998; Hildenbrand et al., 2015). However, the identification of two sole bromide/chloride sub-populations presented here, is unique. Of particular interest is the range of bromide/chloride values observed in Group B, which is consistent with contamination from brominated gasoline (Behl et al., 1987; Flury and Papritz, 1993) or the influence from pesticides like methyl bromide (Flury and Papritz, 1993; Wagman et al., 1981; Whittemore and Davis, 1995). Bromide/chloride ratios above 0.02 have previously been observed across the continental interior of the United States (Davis et al., 2004); however, to our knowledge these data mark the first reporting of elevated bromide/chloride ratios in Western Gulf Basin.

One potential source of bromide in groundwater is the biodegradation of organic material, which can enhance bromide, iodine, and ammonium concentrations while having little effect on chloride concentrations (Martin, 1999; Martin et al., 1993). However, in exploring this hypothesis the similarity in median TOC values between the two bromide/chloride sub-populations suggest that the degradation of organic material is not a major contributor to the disproportionally high levels of bromide observed in Group B, unless the flux of this metabolism has already exhausted the organic substrate at these sites. Alternatively, the diagenesis of organic material in fine-ground sediments could account for relatively elevated levels of bromide, as has been observed previously (Davis et al., 1998). It is also possible

Table 2
Factor loadings, eigenvalues, and percentage of variation explained for the first four principal components based on the correlation matrix of bromide, chloride, fluoride, nitrate, sulfate, and TDS.

Variable	PC1	PC2	PC3	PC4
Bromide	0.523	−0.013	0.183	−0.492
Chloride	0.444	0.149	0.113	0.728
Fluoride	0.158	−0.812	0.275	0.282
Nitrate	−0.104	0.404	0.866	0.028
Sulfate	0.431	0.381	−0.346	0.184
TDS	0.555	−0.097	0.091	−0.337
Eigenvalue	2.86	1.147	1.011	0.606
% variance explained	47.7	19.1	16.8	10.1
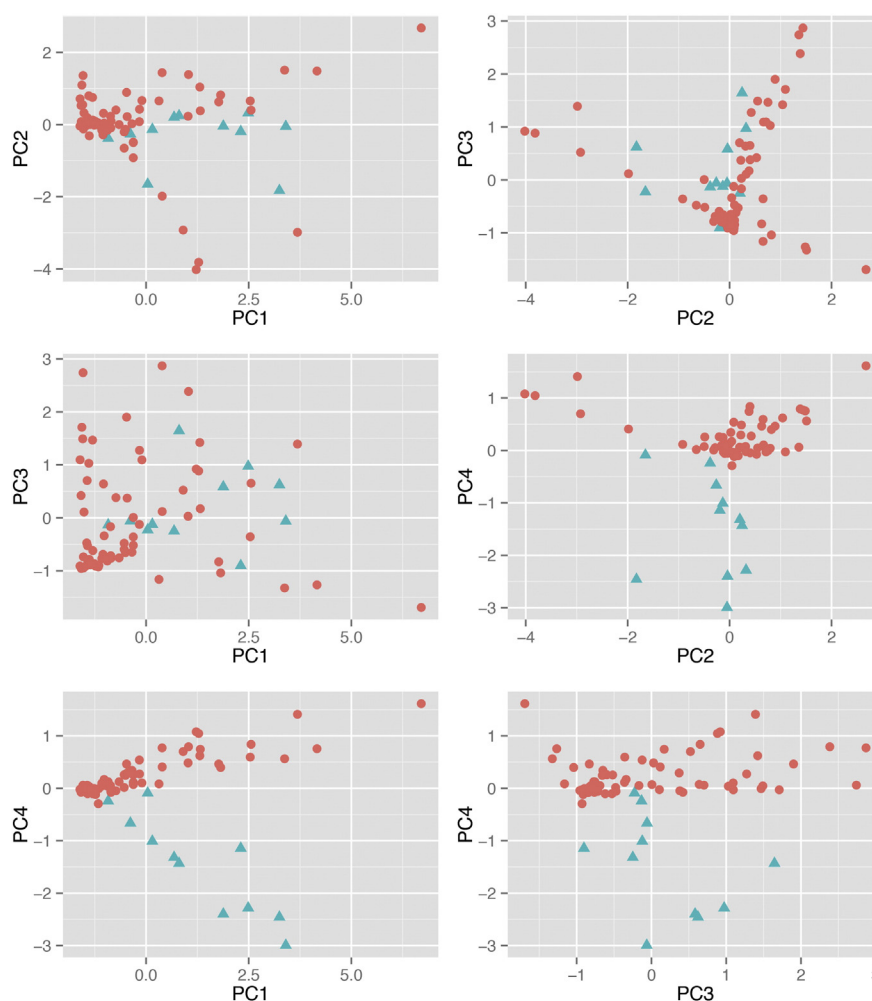
Fig. 3. Scatterplots of factor scores from principal components analysis (PCA) based on the correlation matrix of bromide, chloride, fluoride, nitrate, sulfate, and TDS. Samples from bromide/chloride Group B (triangles) segregate from all other samples (bromide/chloride Group A; circles) along the fourth axis.

that water-rock interactions with volcanic ash deposits contained within the region may have contributed to anomalous patterns of bromide/chloride due to the accumulation of bromide (Hudak, 2003). This is a plausible explanation given that volcanic ash may have also contributed to the elevated levels of fluoride and arsenic that were observed in this study. However, the lack of correlation between fluoride and bromide, and fluoride and heavy metals ions, suggests that these elements in the Group B samples are likely sourced from other processes.

The geographical clustering of Group B samples in areas with a similar frequency of UD activity as compared with Group A samples (Fig. 1), coupled with low levels of chloride that are not consistent with oil field brine contamination, suggest that the elevated bromide/chloride ratios defining the Group B samples are unlikely to be attributed to contamination from UD activities. Nonetheless, the sporadic detection of multiple volatile organic compounds and the observation of dissolved gas effervescence in both groups A and B, provide evidence that groundwater quality is potentially being affected by neighboring UD activity, or other anthropogenic activities, in an episodic fashion. The findings presented here provide an impetus for agricultural entities, industrial operators, and rural communities to examine their groundwater quality more closely, given their reliance on viable groundwater in southern Texas.

Collectively, these data illustrate the value of monitoring organic and inorganic groundwater constituents within the context of geogenic and anthropogenic processes; an approach that can be implemented in various international shale energy basins where there is overlying groundwater. These data also suggest that a subsequent larger scale and more extensive investigation of groundwater quality in the Eagle Ford region is warranted. In particular, the quantification of noble gas analytes and dissolved compound-specific hydrocarbon isotopes will help differentiate between naturally occurring and anthropogenic contamination pathways (Darrah et al., 2014). Additionally, the analysis of chloride/iodine and chloride/ammonium ratios (Vengosh and Pankratov, 1998) may provide additional insight into the mechanism(s) contributing to the highly variable levels of bromide in the Western Gulf Basin.

Author contributions

[†]These authors contributed equally to this work. Additionally, ZLH, DDC, and KAS designed research; ZLH, DDC, JTT, DH, JT, SK, performed research; JMM, BEF, ZLH, DDC, CJW, PH, and JLW analyzed data; and ZLH, JMM, BEF, DDC, PH, and KAS wrote the paper.

Notes

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.09.070.

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