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# A Comprehensive Analysis of Groundwater Quality in The Barnett Shale Region

AUTHOR NAMES:

Zacariah Louis Hildenbrand,[a,b,†,*] Doug D. Carlton Jr.,[b,c,†] Brian Fontenot,[b, ||,†] Jesse M. Meik,[b,d, †] Jayme Walton,[b,e] Josh Taylor,[a] Jonathan Thacker,[c] Stephanie Korlie,[c] C. Phillip Shelor,[c] Drew Henderson,[c] Akinde Florence Kadjo,[c] Corey Roelke,[b,f] Paul F. Hudak,[g] Taylour Burton,[h] Hanadi S. Rifai,[h] and Kevin A. Schug[b,c, *]

AUTHOR INFORMATION:

[a] Inform Environmental, LLC, Dallas TX 75206

[b] Affiliate of the Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington TX 76019

[c] Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington TX 76019

[d] Department of Biological Sciences, Tarleton State University, Stephenville TX 76401

[e] SWCA Environmental Consultants, Arlington TX 76006

[f] Department of Biology, The University of Texas at Arlington, Arlington TX 76019

[g] Department of Geography, University of North Texas, Denton, TX 76203

[h] Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204

[†] These authors contributed equally to this work

[||] Present address: Water Quality Protection Division, United States Environmental Protection Agency, Dallas TX 75202

[*] Corresponding authors. Correspondence should be addressed to: Inform Environmental, LLC, 6060 N. Central Expressway, Suite 500, Dallas, TX 75206 (ph) 915-694-7132; (email) zac@informenv.com; and/or Department of Chemistry & Biochemistry, The University of Texas at Arlington, 700 Planetarium Pl., Box 19065, Arlington TX 76019; (ph) 817-272-3541; (email) kschug@uta.edu

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.

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51 **ABSTRACT**
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53     The exploration of unconventional shale energy reserves and the extensive use of

54 hydraulic fracturing during well stimulation have raised concerns about the potential effects of

55 unconventional oil and gas extraction (UOG) on the environment. Most accounts of

56 groundwater contamination have focused primarily on the compositional analysis of dissolved

57 gases to address whether UOG activities have had deleterious effects on overlying aquifers.

58 Here, we present an analysis of 550 groundwater samples collected from private and public

59 supply water wells drawing from aquifers overlying the Barnett shale formation of Texas. We

60 detected multiple volatile organic carbon compounds throughout the region, including various

61 alcohols, the BTEX family of compounds, and several chlorinated compounds. These data do

62 not necessarily identify UOG activities as the source of contamination; however, they do

63 provide a strong impetus for further monitoring and analysis of groundwater quality in this

64 region as many of the compounds we detected are known to be associated with UOG

65 techniques.

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## 1. INTRODUCTION

80        The potential effects of unconventional oil and gas (UOG) drilling activities on

81    groundwater quality have led to much concern despite a relative lack of scientific data.

82    Recently, investigations in the Marcellus and Barnett shale formations in Pennsylvania and

83    Texas found elevated levels of dissolved methane[1, 2] and heavy metals[3] in private water wells

84    located near unconventional drilling sites. A number of extraction processes are utilized during

85    unconventional shale exploration including directional drilling, shale acidization, and hydraulic

86    fracturing, in which large quantities of water, proppants, and chemical additives are used to

87    extract sequestered hydrocarbons. Additives used during hydraulic fracturing include

88    viscosifiers, descaling agents, anti-corrosive compounds, lubricants, pH stabilizers, and other

89    solvents that could be harmful if introduced into the environment.[4] Instances of chemical

90    contamination can result from casing failures, which happen in approximately 3% of new gas

91    well operations,[4] although recent findings indicate failure rates closer to 12% within the first

92    year of operation.[5] Recent research has shown that hydraulic fracturing could potentially alter

93    contaminant pathways to aquifers via increased advective transport and/or flow through

94    existing fractures widened by UOG activities.[6, 7] Additionally, surface sources such as

95    mishandled waste fluid and produced waters or spills of UOG fluids during stimulation or

96    completion of wells may contaminate groundwater, and shallow water wells may be

97    vulnerable to such contamination. [8]

98        One of the more active regions for UOG drilling is in north-central Texas where the

99    Barnett shale formation supports approximately 20,000 UOG wells.  This region includes a

100   portion of the Dallas-Fort Worth metropolitan area and outlying areas, and groundwater is

101   potentially vulnerable to contamination from various urban and rural sources. The Trinity and

102   Woodbine aquifers overlying the Barnett shale formation have historically been described as

103   good quality with low levels of heavy metals such as arsenic, selenium, strontium, and barium

104  and naturally elevated levels of total dissolved solids (TDS).[9] However, recent research on

105  groundwater quality near Barnett shale UOG activities identified higher concentrations of

106  heavy metals compared to historical data for this region.[3] For more detailed information

107  regarding historical water quality in aquifers overlying the Barnett shale formation, we refer

108  the reader to Fontenot et al. [3] Here, we present an updated analysis of groundwater quality in

109  aquifers overlying the Barnett shale and adjacent areas of north-central Texas. The objectives

110  of this study are to assess whether or not UOG activity may have had an impact on

111  groundwater quality by screening for the presence of elevated natural constituents and

112  contaminants potentially related to UOG activity, examining correlations among groundwater

113  constituents, and to identify changes in groundwater quality since the previous study of

114  Fontenot et al.[3] A total of 550 groundwater samples were screened for the presence of

115  chemical compounds used in hydraulic fracturing, as well as for various metals and other

116  dissolved ions. We detected elevated levels of 10 different metals and the presence of 19

117  different chemical compounds, including benzene, toluene, ethyl benzene and xylene (BTEX).

118  These results constitute the largest analysis of groundwater quality in aquifers overlying a

119  shale formation associated with UOG activities.

120

121  **2. MATERIALS AND METHODS**

122  **2.1. Hydrogeology.**

123      Groundwater samples (n=550) were collected from water wells that draw from the

124  Trinity and Woodbine aquifers overlying the Barnett shale formation of Texas (Hereafter

125  referred to as the "Barnett shale region"; Figure 1). The Texas Water Development Board

126  classifies the Trinity and Woodbine aquifers as primary and secondary aquifers, respectively.

127  Regionally, groundwater in the study area flows southeastward, although numerous

128  groundwater production wells in the area create localized cones of depression in the water

129  table potentiometric surface.

130    Cretaceous sand formations of the Trinity Group outcrop in a north-trending band and

131    dip underground to the east, where the aquifer becomes confined. The Trinity Group consists

132    of three formations, from bottom to top: Twin Mountains, Glen Rose, and Paluxy. The Twin

133    Mountains formation includes sand, shale, clay, and a basal gravel and conglomerate.[10] Major

134    constituents of the Glen Rose formation, a confining unit, include limestone, marl, shale, and

135    anhydrite. Mainly sand and shale make up the Paluxy Formation. The Glen Rose Formation is

136    absent north of central Wise County; here, the Paluxy and Twin Mountains Formations merge

137    together to form the Antlers Formation. Precipitation and seepage from reservoirs and

138    streams recharge the unconfined Trinity outcrop zone.[11] Eastward, leakage through confining

139    beds recharges the aquifer.[12] Annual recharge to the aquifer averages approximately 2.5

140    cm.[13]

141    The Woodbine Aquifer consists of ferruginous sand and sandstone interbedded with

142    shale and clay of the Cretaceous Woodbine Formation. Discontinuous seams of lignite,

143    gypsum, and volcanic ash are also present in the Woodbine Formation.[10] Overlying the Trinity

144    Group and intervening strata, the Woodbine Formation also outcrops in the study area and

145    dips eastward. Unconfined conditions occur in the outcrop zone, and artesian conditions

146    prevail downdip.[11] Precipitation on the outcrop zone and seepage from lakes and streams

147    recharge the aquifer. Average annual recharge to the aquifer is approximately 2 cm.[13]

148    **2.2. Sample Collection.**

149    Private water well samples (n=550) were collected from wells tapping the Trinity and

150    Woodbine aquifers. Of the 550 samples, 350 came from private wells serving residential

151    purposes, while 59 samples came from agricultural water wells, and 141 samples came from

152    municipal or public water supply wells servicing communities throughout the Dallas-Fort

153    Worth Metroplex. Approximately 83% of the samples were collected from wells tapping

154    aquifers located above the Barnett shale formation, a feature populated by more than 20,000

155    UOG wells since the early 2000s. Samples were collected without prior knowledge of the

156  UOG activity in the area and all geospatial analyses were performed *ex post facto*. Samples

157  were collected throughout Montague, Wise, Parker, Hood, Tarrant, Somervell, Johnson, Hill,

158  Ellis, Dallas, Denton, Collin and Cooke counties (Figure 1). Water well depths ranged from

159  10-1200 m according to wellowners, and well depth tends to increase eastward in both

160  aquifers, following the slope of the principal water-bearing formations into the subsurface.

161  Sites were selected on the basis of well owner participation and our ability to collect

162  unfiltered/untreated water that would be representative of the underlying aquifers, as

163  described previously.[3] Measurements for basic water quality parameters such as

164  temperature, dissolved oxygen (DO), conductivity, total dissolved solids (TDS), salinity, pH

165  and oxidation-reduction potential (ORP) were performed with a YSI Professional Plus multi-

166  parametric probe, and each water well was purged until measurements for these parameters

167  had stabilized, indicating that samples were representative of fresh groundwater from the

168  underlying aquifer. Two duplicate samples from each private water well were collected in

169  photo-resistant HDPE bottles with no headspace. Samples for metals analysis were filtered

170  and preserved with nitric acid to a pH less than 2 and stored at 4 °C until laboratory

171  procedures could be performed. Samples for anion analysis were preserved with chloroform

172  and frozen to reduce microbial degradation. All laboratory measurements were made within

173  14 days, except for the metal analysis, which was measured within 6 months of collection, per

174  suggested holding times from the Environmental Protection Agency (EPA). [14] Method blanks

175  and random analytical replicates were performed for each set of samples collected across

176  multiple trips from December 2013 to August 2014 (See supporting information for exact

177  sampling dates).

178  **2.3. Analysis.**

179     Chemical analyses included gas chromatography-mass spectrometry (GC-MS),

180  headspace-gas chromatography (HS-GC), inductively coupled plasma - mass spectrometry

181  and - optical emission spectroscopy (ICP-MS and ICP-OES), and ion chromatography (IC).

182     Specific organics were selected from a 2011 Congressional Report on hydraulic fracturing

183     fluid ingredients[15] as well as frequently listed components of UOG fluids in the national

184     hydraulic fracturing chemical registry (www.fracfocus.org).[16] These include metal ions,

185     alcohols, aromatic compounds, aldehydes, amines, and others (See Supporting Information

186     for a full list of screened species). Whenever possible, we evaluated constituents in the

187     context of their respective Primary or Secondary Maximum Contaminant Limits (MCL), Health

188     Advisory Levels, or other suggested levels as provided in the United States Environmental

189     Protection Agency's (EPA) Drinking Water Standards.[17]

190              Information about UOG drilling activity in the region was obtained from

191     www.fracfocus.org [16] and the Texas Railroad Commission,[18] the governing body for oil and

192     gas drilling in the state of Texas. Geospatial analyses were conducted using ArcGIS 10.1. [19]

193     Because we obtained measurements of water quality variables for nearly all sample wells, we

194     evaluated the relationship between measures of water quality and both distance to nearest

195     UOG well and depth of sample well using multiple regression and model selection based on

196     adjusted $R^2$ values. We noted spurious positive relationships between distance to nearest

197     UOG well and some water quality variables, and thus we elected to not use this predictor

198     variable further (Table 1; see Results and Discussion below). We evaluated bivariate

199     relationships for particular variables for which we had a priori reason to assume they may be

200     related, and derived a composite variable for chloride, bromide, and nitrate using a principal

201     components analysis (PCA) of these three variables based on the correlation matrix. Before

202     all analyses, we log-transformed both distance measures and $log_{10}$-transformed remaining

203     variables to normalize distributions. To evaluate geographic patterns at a coarse scale, we

204     used Pearson's chi-squared tests of independence for frequency of water well samples with

205     either detection or EPA's Drinking Water Maximum Contaminant Limit (MCL) exceedances of

206     selected compounds for each county with ≥ 40 total samples. This analysis allowed us to

207     evaluate whether particular counties in north-central Texas exhibited higher or lower than

208     expected frequencies of samples with particular compounds. All regression, correlation, and

209     principal component analyses were performed in Systat 12.02 [20] and chi-squared tests were

210     performed in the software program R.[21]

211

212    **3. RESULTS AND DISCUSSION**

213         A total of 550 groundwater samples was collected from private and public water supply

214    wells throughout the Barnett shale region. Sampled water wells ranged from 90 m away from

215    the nearest UOG well in areas of active UOG extraction to 47,220 m away from the nearest

216    UOG well in areas outside of the Barnett shale, with a median and mean distance of 807 and

217    2,315 m respectively. The large difference between median and mean values reflects the

218    influence of extreme outliers at the higher end of this range. Of the 550 samples, 339 (61.6%)

219    were collected from water wells within 1 km of the nearest UOG well, which likely reflects the

220    increased willingness of well owners to participate in this research in more heavily drilled

221    areas. Unfortunately, this opportunistic and necessarily biased sampling hindered our ability

222    to make meaningful inferences regarding levels of contamination as a function of distance

223    from nearest UOG well for several reasons: (1) the expectation of no detection of a given

224    contaminant for a given sample well assumes uniform and substantial sampling across a

225    gradient of distances from UOG wells, but the distribution of well samples as a function of

226    distance from UOG well was strongly right-skewed; (2) the radius of 1 km for the majority of

227    our groundwater samples is not an adequate distance to detect meaningful statistical patterns

228    of contaminant diffusion from the site of UOG wells; and (3) distance to nearest UOG well is

229    positively correlated with depth of groundwater well ($r = 0.36$, $p < 0.0001$) (SI Figure 1), a

230    potential confounding variable (see water quality results below). Water wells in the eastern

231    part of the study area tend to be both farther away from UOG wells (because the Barnett

232    shale formation is westward) and deeper (because the aquifers deepen eastward); thus,

233    explaining observation (3) above. We observed some weak, positive correlations between

234    UOG wells and some analytes, but interpret these results as spurious for the reasons

235    mentioned above in conjunction with the following additional considerations: (1) positive

236    relationships between analyte concentrations and distance from UOG well have no

237    reasonable causal basis, but are readily explained by the correlation with depth of sample

238    well, (2) explanatory power of the correlations using distance from UOG well was consistently

239    lower than for correlations with depth of well, suggesting that between these collinear factors,

240    it is more parsimonious to assume that relationships with distance from UOG well are

241    confounded.

242    **3.1. Water Quality**

243         Multiple regression analyses of basic water quality parameters as a function of

244    distance from nearest UOG well (distance) and depth of groundwater well sample (depth)

245    revealed that depth is a substantially better predictor of overall water quality than is distance,

246    albeit most relationships were weak (Table 1). In general, TDS concentrations tend to

247    increase eastward in the study area, as groundwater moves along the principal water-bearing

248    formations of the Trinity and Woodbine aquifers. With travel, increased residence (contact)

249    time facilitates more dissolution of aquifer constituents. For example, sodium, chloride,

250    sulfate, and various other constituents tend to increase eastward, as does water well depth.

251    All variables showed a positive relationship with depth except for dissolved oxygen, which

252    showed a negative relationship with depth. Dissolved oxygen levels tend to be higher in

253    shallower, unconfined areas of the aquifer where groundwater mixes with gases in the vadose

254    zone. Values for pH exhibited a nonlinear relationship with depth, with low values in shallow

255    wells, high values at intermediate depths, and a slight trend toward neutral pH for the deepest

256    wells. Values for pH also tend to be lower in the unconfined outcrop zones, where slightly

257    acidic rainwater recharges the aquifers. Model selection indicated that for many variables, an

258    additive or interaction model best explained the total variance in the dataset; however, the low

259    $R^2adj$ values for models including only UOG distance for each of these response variables,

260    and the collinearity between depth and UOG distance, suggest that the inclusion of distance

261    in these models is spurious. Basic water quality analyses revealed the consistent occurrence

262    of elevated TDS throughout the 13 counties sampled. Of the 550 samples, 344 exceeded the

263    Secondary MCL of 500 mg/L suggested by the EPA. TDS values ranged from 68.5 to 3328

264   mg/L with an average slightly above the MCL (630.3 mg/L). Measurements also showed pH

265   values ranging from 5.3 to 9.4 with a mean value of 8.1. Collectively, 254 samples were

266   outside of the range of 6.5-8.5 suggested by the EPA MCL, with 15 samples having pH

267   measurements below 6.5 and 239 samples having pH measurements above 8.5. Elevated

268   TDS and pH measurements are not unusual for the Trinity and Woodbine aquifers, as similar

269   results have been reported previously.[3, 22]

270   **3.2. Anions in Groundwater**

271        Subsequent analyses using ion chromatography (IC) were performed to assess the

272   prevalence of selected water quality anions in the Trinity and Woodbine aquifers. Nitrate and

273   fluoride were measured to characterize the relative effect of agricultural surface activities on

274   the underlying groundwater. Nitrate was detected in 223 of the 550 samples, and 2 samples

275   were found to be elevated above the 44.3 mg/L MCL, with a maximum value of 55.7 mg/L. As

276   a whole, nitrate values were higher (median = 0.95 mg/L) than those previously reported in

277   the Trinity and Woodbine aquifers, each with median values of 0.4 mg/L.[22] High levels of

278   nitrate in shallow groundwater often stem from agricultural processes, such as the use of

279   fertilizer and organic manures, as well as septic systems and decaying vegetation. Nitrate

280   values tend to be higher in the outcrop zones of the aquifers, where they are more vulnerable

281   to contaminants originating from the land surface. Generally, the outcrop zone of the Trinity

282   aquifer is more rural than that of the Woodbine aquifer, and agricultural activity in the Trinity

283   outcrop zone may account for higher median nitrate values observed in that aquifer. Fluoride

284   was found to be elevated above its 4 mg/L MCL in 2 wells with a median value of 0.3 mg/L,

285   less than previous measurements collected in the 2000s (0.7 and 1.3 mg/L for the Trinity and

286   the Woodbine aquifers, respectively).[22] Elevated fluoride levels may originate from phosphate

287   fertilizers and mineral constituents in the aquifers, especially in the Woodbine aquifer.[23, 24] For

288   example, fluoride is known to occur at relatively high levels in parts of the Woodbine aquifer,[24]

289   a plausible source being volcanic ash deposits.

290      An overall prevalence of nitrate and the lack of covariation between nitrate and fluoride

291   $(r = -0.05)$ suggest that they may be coming from different sources, such as agricultural

292   sources for nitrate and natural sources for fluoride. Sulfate levels (median value of 52.8 mg/L)

293   were below those discovered in previous measurements; 79 and 114 mg/L for the Trinity and

294   Woodbine aquifers in samples collected in the 2000s.[22] Chloride levels were also found to be

295   consistent with historical measurements with a median value of 25.4 mg/L compared to 35

296   and 36.3 mg/L discovered in samples previously collected from the Trinity and Woodbine

297   aquifers, respectively.[22] However, chloride was found to be elevated above the 250 mg/L MCL

298   threshold in 21 wells with a maximum value of 3373.8 mg/L, a value over 3 times greater than

299   previously observed.[22]

300      Formation water in general contains elevated concentrations of chloride, bromide,

301   sodium, and sulfate.[25] Of these ions, bromide has recently been used when attempting to

302   identify formation water intrusion with the aquifer because of its naturally low abundance and

303   conservative behavior in groundwater. High levels of chloride and bromide can be an

304   indication of anthropogenic contamination, one possibility being UOG activity,[26] a result of

305   groundwater mixing with produced water from the shale formation.[25] Bromide was detected in

306   170 water wells ranging from 0.03 to 6.4 mg/L (Supporting Information Descriptive Statistics

307   Table). Previous groundwater monitoring efforts within a few of the counties sampled in this

308   study showed bromide concentrations up to approximately 3.5 mg/L, with an outlier of 8.4

309   mg/L; however, bromide was not detected in the majority of samples.[26, 27]

310      Overall, bromide showed a moderately high positive correlation with chloride when

311   both compounds occurred together ($r = 0.32$, $p < 0.0001$), with a particularly strong log-linear

312   trend along a ratio within the ~100–150 range (Figure 2). Additionally, a composite variable

313   derived from a PCA of chloride, bromide, and nitrate (all three compounds were strongly

314   positively correlated with the first principal component axis, which had an eigenvalue of 1.351

315   and explained 45.1% of the total variance in this combination of variables) was negatively

316    correlated with depth of groundwater well ($r$ = -0.34, $p$ = 0.002), suggesting a surface source

317    may contribute to observed concentrations of these contaminants (SI Figure 2). It should be

318    noted that denitrification and reducing conditions at higher depths could also lead to this

319    correlation.

320         Calculating the chloride/bromide mass ratio of groundwater samples can be useful for

321    sourcing contamination or mixing of sources.[28] Previous investigators used chloride/bromide

322    ratios to identify potential sources of groundwater contamination.[29] Based upon several

323    published studies, chloride/bromide ratios generally range from 50-150 in atmospheric

324    precipitation, 300-600 in domestic sewage, 1000-10,000 in dissolved evaporites, and 100-200

325    in unimpaired, shallow groundwater.[30] In oilfield brine (formation water), chloride/bromide

326    ratios vary widely, but typically fall between 100 and 300. This ratio can also be achieved by

327    mixing unimpaired groundwater with groundwater impaired by evaporites. Mixing of

328    groundwater from multiple sources leads to intermediate ratios of these conservative ions. Of

329    the 550 samples, 170 (30.9%) had detectable amounts of bromide. The median

330    chloride/bromide ratio of all samples with detectable bromide was 239, with a minimum of 3

331    and a maximum of 1465. Of the 170 wells with bromide, 97 wells (57.1%) had a

332    chloride/bromide ratio between 100 and 300. Of the 550 well samples, 17.6% had a

333    chloride/bromide ratio between 100 and 300. A localized area in southern Parker County

334    showed the highest chloride/bromide ratios, ranging from 725 to 1465. These relatively high

335    ratios may reflect dissolution of evaporites present in the aquifers or confining formations. A

336    less likely, though plausible explanation is saline surface water (e.g. waters impacted by road

337    salt[31]) mixing with relatively shallow groundwater in or near the Trinity aquifer's outcrop zone.

338    Only eight samples had a chloride/bromide ratio less than 10.  In previous studies, such

339    extremely low ratios have been attributed to mixing of groundwater with runoff impacted by

340    brominated gasoline additives.[32, 33] Five of the eight samples with chloride/bromide ratios

341    below 10 are located adjacent to a state highway or interstate.

342    **3.3. Metals Analysis**

343        ICP-MS and ICP-OES analyses were used to evaluate the concentrations of 15

344    different metal ions that are good indicators of groundwater condition. Of the 550 collected

345    samples, 10 were found to have arsenic levels above the 10 µg/L MCL threshold, with a

346    maximum value of 114 µg/L. Similarly, strontium was found to be elevated above the 4.0 mg/L

347    MCL threshold in 9 wells with a maximum detection of 8.9 mg/L. Selenium was detected more

348    frequently than in previous investigations [3] (detected in 507 of the 550 samples), but in much

349    lower concentrations than the MCL. A prior analysis of 100 private wells in the Barnett shale

350    by Fontenot et al. revealed higher levels of arsenic, barium, selenium, and strontium than

351    seen in this study.[3] Fontenot et al. suggested that these naturally occurring groundwater

352    constituents could concentrate in iron-oxide rust/scale formations that can build up in water

353    wells, which could then be liberated by mechanical perturbances of private water wells such

354    as those generated by nearby UOG activities.[3] While this remains a plausible explanation for

355    the elevated concentrations of heavy metals observed by Fontenot et al.,[3] decreased drilling

356    activity and a likely decrease in mechanical disturbances in 2014 compared to 2011 (1,902

357    permits issued in 2013-14 versus 4,136 in 2010-2011), may explain the decreased levels of

358    dissolved metals compared to previous measurements. [34]

359        These ions can also originate from natural sources such as the mineral constituents of

360    the aquifers. Changes in oxygen-reduction potential can also change valence states, which

361    may liberate or bind some of these species. As such, some fluctuation is expected to occur

362    naturally, as well as be induced by changes in water levels and redox conditions caused by

363    pumping. Compared to the previous measurements collected by Fontenot et al.[3], ORP values

364    suggested a more oxidative environment with a median value of 80.7mV compared to a

365    previous median value of 28.6. Coupled with an increase in pH from 7.69 to 8.30, the current

366    conditions are less favorable for dissolved metals compared to the conditions observed in

367    2011. Additionally, the samples in Fontenot et al.[3] were not acidified and filtered as they were

368   sampling for total metals not dissolved metals as in the current study. However, it should be

369   noted that this difference in sampling protocol likely cannot account for the large variations in

370   metals concentrations between the two studies as total metals analysis usually leads to a

371   more conservative concentration estimate than dissolved metals analysis.

372          Beryllium, iron, and molybdenum were also elevated in 75, 87, and 187 of the

373   groundwater samples, respectively, with a higher than expected frequency of MCL

374   exceedances in Montague County based on chi-squared tests (Table 2). Beryllium

375   exceedances (0.004 mg/L MCL) were also detected at a higher than expected frequency in

376   Parker and Tarrant counties; whereas iron exceedances (0.3 mg/L MCL) levels were also

377   higher than expected in Cooke and Johnson counties, and molybdenum exceedances (0.04

378   mg/L MCL) were more frequent in Parker and Wise counties (Table 2). The significance of

379   these three ions remains to be determined, as there is no historical precedent for reference.

380   Other metal ions found in excess of their respective MCL values include barium (1 sample),

381   chromium (1 sample), copper (1 sample), nickel (16 samples), and zinc (1 sample).

**3.4. Gas Chromatography Analyses**

383          GC-MS and HS-GC analyses revealed the most striking results of this study. Of the 39

384   volatile and semi-volatile compounds that were screened, 13 compounds were detected at

385   least once. In particular, methanol and/or ethanol were detected in 35 and 240 wells

386   respectively with average concentrations of 0.5 and 3.2 mg/L and maximum concentrations of

387   44.6 and 394.2 mg/L, respectively. Methanol and ethanol both are used extensively in

388   unconventional drilling as anti-corrosive agents and gelling agents (www.fracfocus.org);[16]

389   however, these two alcohols can also be produced *in situ*. Methanol can be produced through

390   the digestion of methane by methanotrophic bacteria,[35] whereas ethanol can be produced

391   organically by thermophilic bacteria,[36] albeit typically in much smaller concentrations than was

392   observed here. Both methanol and ethanol were found in 19 wells from Denton, Parker, and

393   Montague counties, in localized areas similar to the areas exhibiting high bromide. These two

394    alcohols have been detected previously in this region, but at that time, no conclusions could

395    be made about their origin.[3] Propargyl alcohol and isopropyl alcohol were also detected in

396    155 and 8 water wells, respectively, with maximum concentrations of 26.4 and 9.4 mg/L,

397    respectively. Moreover, when present together, ethanol levels were correlated with propargyl

398    alcohol levels ($r = 0.53$, $p < 0.0001$), but not with methanol levels ($r = -0.13$, $p = 0.517$). The

399    source of these alcohols remains to be determined; however, methanol, ethanol, and

400    propargyl alcohol were all detected at a greater percentage within the Barnett shale (89, 92,

401    and 90%, respectively) than the percentage of total samples collected within the producing

402    region (83.1%). In particular, ethanol was detected at a higher frequency than expected in

403    Montague, Parker, Tarrant, and Wise counties based on chi-squared analysis; whereas

404    propargyl alcohol was found at a higher incidence in samples from Johnson, Parker, Tarrant

405    and Wise counties (Table 2). These counties comprise the most productive sub-region of the

406    Barnett shale; 18,559 UOG well stimulation events were recorded here since the year 2000,

407    and collectively, these species constitute a specific sub-set of compounds commonly used in

408    unconventional well stimulation per the 2011 Congressional Report on hydraulic fracturing.[15]

409    Of the four alcohol species that were detected throughout the study, only methanol showed a

410    negative correlation with well depth ($r = -0.39$, $p = 0.034$), suggesting the source of the

411    methanol originated from the surface, as could result from the mishandling of waste solutions

412    and/or fluid spills. The correlations between well depth and ethanol and propargyl alcohol

413    were not significant ($p > 0.05$), and there were insufficient detections of isopropyl alcohol to

414    perform a correlative analysis with well depth.

415         Dichloromethane (DCM) was detected in 122 samples, with 121 of these detections

416    exceeding the suggested MCL of 0.005 mg/L, and 93% of the detections coming from

417    samples collected within the Barnett shale region. DCM had a mean concentration of 0.08

418    mg/L across the dataset, with a maximum concentration of 2.9 mg/L. The source of this

419    industrial solvent remains to be determined; however, DCM has been detected in a previous

420  study of groundwater quality in the Permian Basin, a region in western Texas that has recently

421  seen increased UOG activity (Hildenbrand et al., in review). DCM has also been implicated in

422  air quality contamination events associated with unconventional drilling in Colorado[37] and

423  UOG flowback water.[38] There is no known natural occurrence of DCM except through the

424  microbial degradation of chlorinated solvents with higher degrees of chlorination like

425  chloroform.[39] This explanation is plausible and could apply to the data set given that

426  chloroform was also detected in 330 of the collected samples, and in 41 of the 122 samples

427  where DCM was detected. Consistent with this explanation, a scatterplot of DCM levels as a

428  function of chloroform levels (when both compounds were present in a sample) revealed two

429  discrete clusters of samples with distinct, inverse ratios of these compounds (Figure 3). For

430  one cluster of samples, the ratio of DCM/chloroform was ~62:1, whereas in the other, the

431  dominant compound was chloroform with a DCM/chloroform ratio of ~1:32. These striking

432  clusters may be the signatures of two widespread and temporally distinct types of

433  contamination events. The cluster with the higher DCM/chloroform ratio may represent an

434  older contamination event, in which microbial degradation of chloroform had progressed

435  farther than in the more recent event, which accordingly exhibits less degradation of

436  chloroform to DCM. Regardless, the consistent, but distinct, ratios of these compounds for

437  samples constituting those clusters is striking. Alternatively, DCM may also have been

438  introduced from an exogenous source. DCM is a commonly used degreasing agent,[40] and

439  raw use of large volumes of concentrated DCM at the well pad could present a possible

440  pathway for contaminating nearby surface water and shallow groundwater. A breach of

441  flowback waste pits, whether from overflow or faulty linings, can also introduce DCM and

442  many other species into the surface environment.[41] A spill of the solvent solution would

443  account for DCM being present without other chlorinated species. Additionally,

444  trichloroethylene (TCE) was detected in 14 samples at very low levels ranging from 0 to 0.04

445  mg/L, and was detected exclusively from samples collected within the Barnett shale region.

446    Collectively, a possible co-migration of dichloromethane, chloroform, and trichloroethylene is

447    consistent with the previous detection of these chlorinated compounds in flowback water from

448    unconventional drilling operations.[42]

449        At least one of the BTEX (benzene, toluene, ethylbenzene and xylene) class of

450    compounds was detected in 381 of 550 collected samples, and 10 wells had detectable

451    amounts of all four BTEX compounds. These compounds collectively can be found in

452    hydrocarbon fuels, whether raw, processed, or waste, and some individually as industrial

453    solvents or as intermediates in the chemical industry. Benzene was detected in 34 wells, 91%

454    of which were detected from samples collected within the Barnett shale region. Benzene

455    concentrations exceeded the MCL guideline of 0.005 mg/L in all 34 of the detections and

456    reached a maximum concentration of 0.09 mg/L. Toluene, ethylbenzene, and three xylene

457    isomers were also found to be prevalent throughout the Trinity and Woodbine aquifers, being

458    detected in 240, 22, and 240 wells respectively, although at trace concentrations well below

459    their individual MCL values. Interestingly, 83% of samples within Montague County (55 of 66)

460    contained a BTEX compound. This area houses underground injection wells for drilling waste

461    disposal across north-central Texas and Oklahoma, thus it is exposed to the largest volume of

462    produced waters in the region through either trucked or injected water, which must be

463    disposed of with great care.[41] Furthermore, this area is also vulnerable to contamination

464    because it occupies the unconfined outcrop zone of the Trinity aquifer. Of the four BTEX

465    compounds, toluene was the only constituent to have a significant relationship with respect to

466    well depth ($r = -0.20$, $p = 0.003$). This observation is consistent with that of methanol and well

467    depth, suggesting that the source of these two constituents originated from the surface.

468        No research has been reported on organics leaching from underground injection wells,

469    but salt contamination has been identified in association with injection wells and plugged oil

470    and gas wells in southeast Texas.[43] Compared to equivalent studies, the abundance of BTEX

471    compounds in the Barnett shale region is consistent with the characterization of produced

472  water. Previous findings have detected various BTEX compounds in fracturing influents

473  (mixed fluids before injection) across 22 drilling sites of the Marcellus and Barnett shales. The

474  concentration and occurrence of these BTEX compounds increased in samples collected after

475  multiple days of flowback because of the influent's extended contact with the shale

476  formation.[42] Cyclohexane was also detected in 221 of the 550 collected samples with a

477  maximum concentration of 1.3 mg/L. Interestingly, 75% of the cyclohexane detections were

478  observed in samples collected within the Barnett shale, below the percentage of water

479  samples collected within the shale region (83%). However, based on chi-squared analysis

480  cyclohexane was detected at higher than expected frequencies in Cooke, Denton, Johnson

481  and Hood counties, all of which are highly productive areas with respect to UOG extraction,

482  with the exception of Cooke County (645 UOG stimulation events since the year 2000; Table

483  2).

484      Collectively, these data constitute one of the largest studies of groundwater quality in a

485  shale formation associated with UOG activities. The detection of numerous volatile organic

486  compounds in aquifers above the Barnett shale does not necessarily implicate unconventional

487  UOG extraction as the source of contamination; however, it does provide an impetus for

488  further monitoring and analysis of groundwater quality in this region.

489  **ASSOCIATED CONTENT**

490  **Supporting Information**

491  Additional materials and methods, figures, tables, and the complete water quality data set

492  referenced in the text. This information is available free of charge via the Internet at

493  http://pubs.acs.org.

494  **AUTHOR INFORMATION**

495  **Corresponding Authors**

496  *Phone: 817-272-3541. E-mail: kschug@uta.edu

497  *Phone: 915-694-7132. E-mail: zac@informenv.com

498  **Present Address**

499　<sup>∥</sup> Present address: Water Quality Protection Division, United States Environmental Protection

500　Agency, Dallas TX 75202

**Author Contributions**

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

512

**Notes**

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514　**Disclaimer.** This work is not a product of the United States Government or the United States
515　Environmental Protection Agency, and the authors did not do this work in any governmental
516　capacity.  The views expressed are those of the authors only and do not necessarily represent
517　those of the United States or the United States Environmental Protection Agency.
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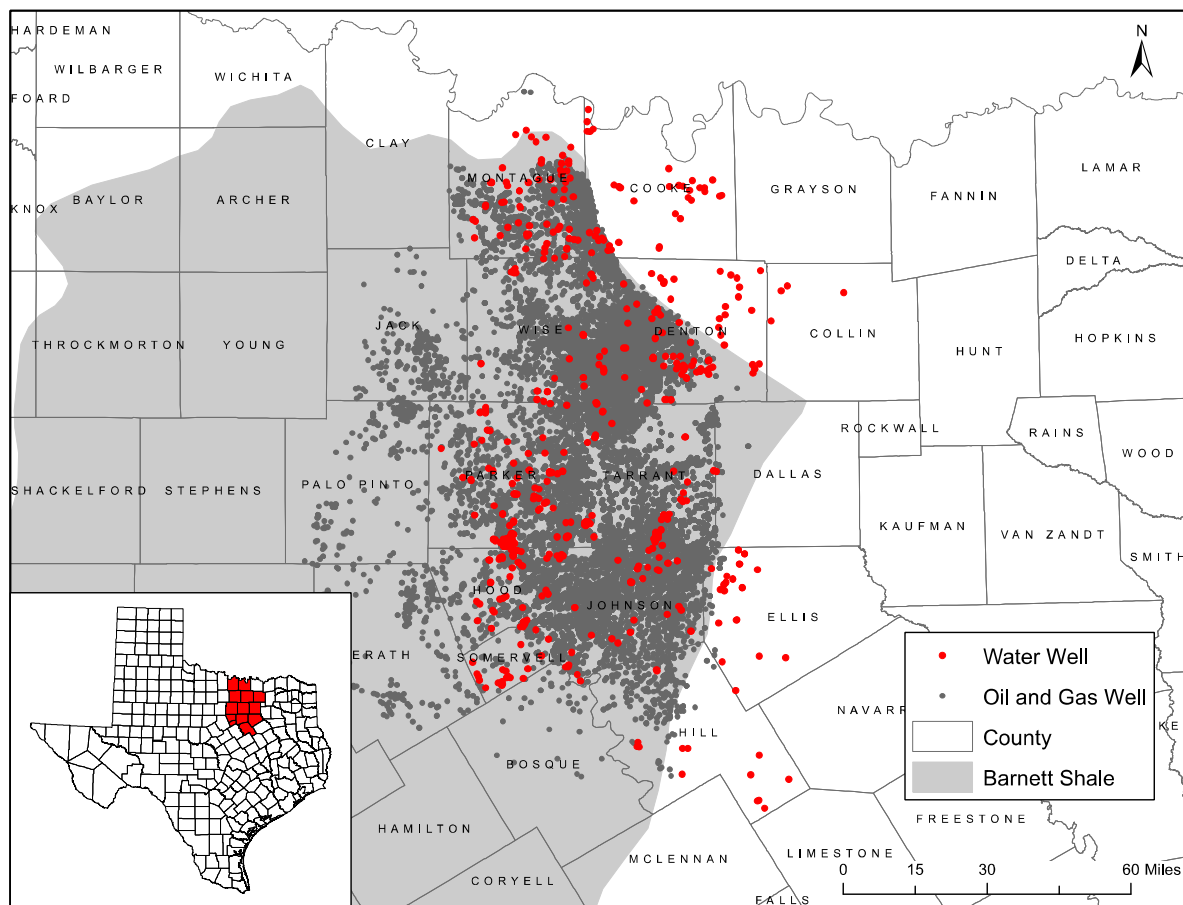631    southeast Texas, USA. *Environ Int* **2001,** *26*, (7-8), 497-503.
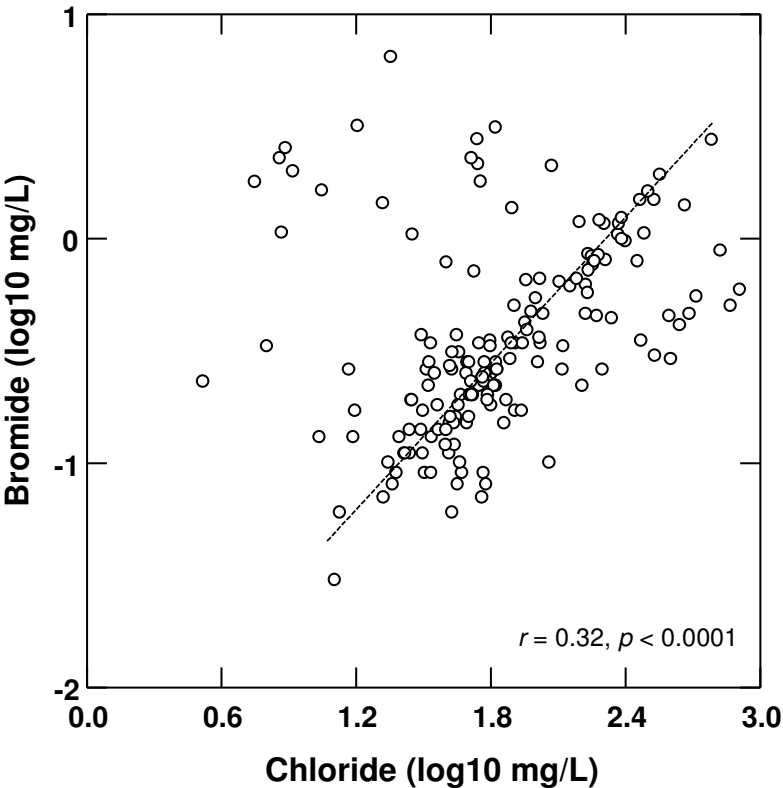
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639    **FIGURES AND TABLES**



640

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

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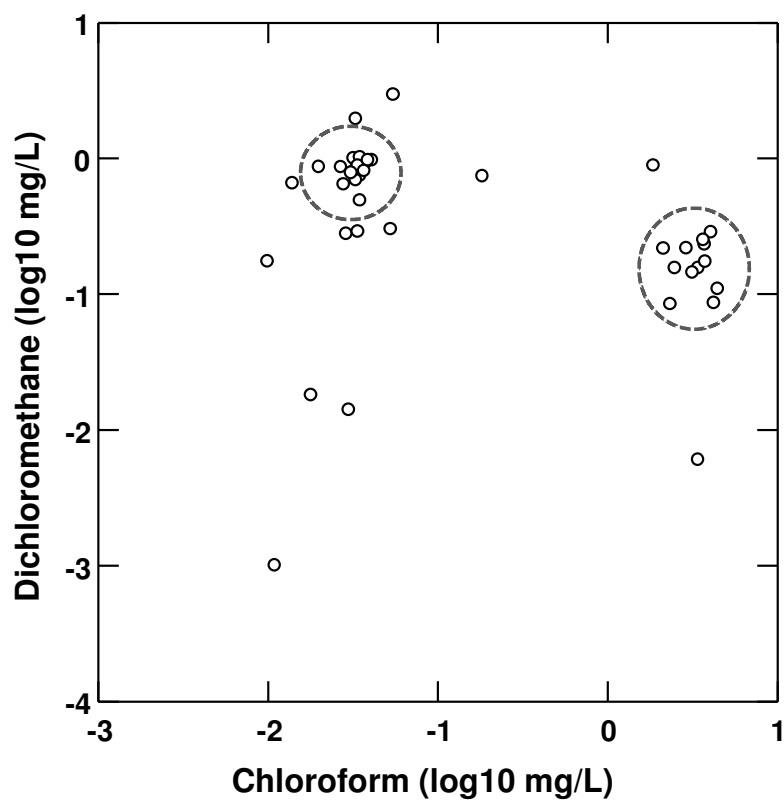
**Figure 3.** Dichloromethane concentrations in relation to chloroform concentrations in the samples where the two constituents were both detected (*n*=41).

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

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685    [#] Relationship is nonlinear; low pH at shallow depths, high pH at intermediate depths, and
686    slight trend toward neutral pH at deepest depths ($R^2adj$ is based on linear approximation).
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707 **Table 2.** Pearson's chi-squared tests of independence for frequency of either detection[1] or
708 MCL exeedances[2] of select compounds for counties with ≥40 total samples. For significant
709 tests, + and - symbols indicate whether observed detection and/or exceedance frequencies
710 occurred more or less frequently than would be expected under the null hypothesis of
711 dependence of observations. Compounds were selected based on whether expected
712 frequencies were > 5 for most cells, as recommended for contingency table analysis.
713

| | $X^2$ | $p$ | 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 | - | - | - | - | + | + | - | + |

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Photo credit:  Doug D. Carlton, Jr.