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An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett Shale Formation

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43 **ABSTRACT**

44 Natural gas has become a leading source of alternative energy with the advent of

45 techniques to economically extract gas reserves from deep shale formations. Here, we

46 present an assessment of private well water quality in aquifers overlying the Barnett

47 Shale formation of North Texas. We evaluated samples from 100 private drinking water

48 wells using analytical chemistry techniques. Analyses revealed that arsenic, selenium,

49 strontium and total dissolved solids (TDS) exceeded the Environmental Protection

50 Agency's Drinking Water Maximum Contaminant Limit (MCL) in some samples from

51 private water wells located within 3 km of active natural gas wells. Lower levels of

52 arsenic, selenium, strontium, and barium were detected at reference sites outside the

53 Barnett Shale region as well as sites within the Barnett Shale region located more than

54 3 km from active natural gas wells. Methanol and ethanol were also detected in 29% of

55 samples. Samples exceeding MCL levels were randomly distributed within areas of

56 active natural gas extraction, and the spatial patterns in our data suggest that elevated

57 constituent levels could be due to a variety of factors including mobilization of natural

58 constituents, hydrogeochemical changes from lowering of the water table, or industrial

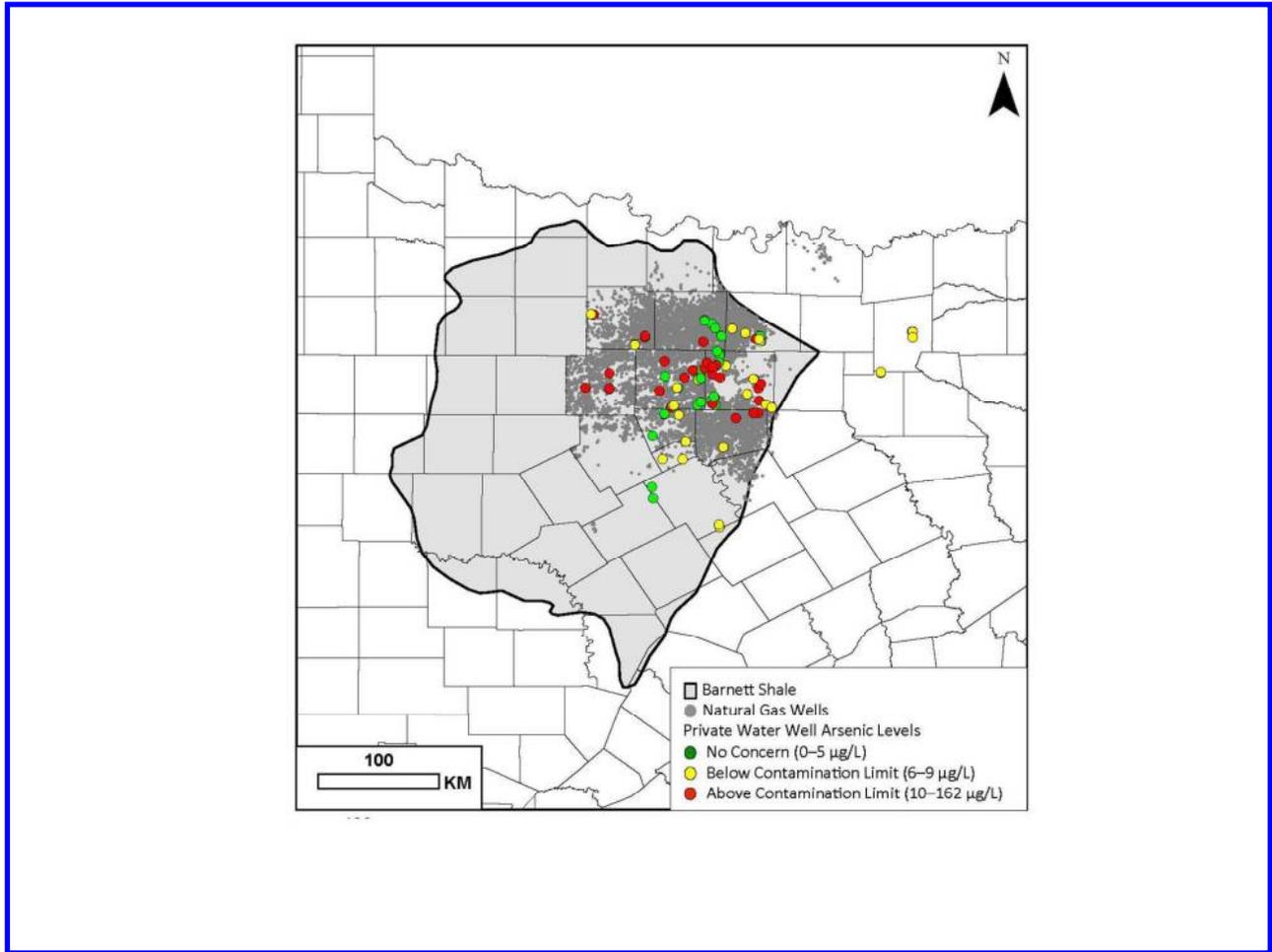59 accidents such as faulty gas well casings.

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66   **TOC/ABSTRACT ART**

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1. INTRODUCTION

Recent advances in technology have facilitated a rapid and widespread expansion of natural gas production from hydrocarbon-rich deep shale formations.[1-3] The increase in drilling activity has raised concern over the potential for environmental contamination.[2, 4-6] Contamination of groundwater aquifers overlying shale formations is particularly problematic because they provide drinking water in rural areas where private wells are unregulated. A study of the Marcellus Shale formation in the northeastern United States reported increased concentrations of methane[5] in private drinking water wells near natural gas extraction sites. While this study does suggest that natural gas extraction could cause systematic groundwater contamination, most confirmed cases of contamination are the result of mechanical failures in which methane, drilling fluids, or waste products leak through faulty gas well casings,[3, 7] Despite a number of recent investigations, the impact of natural gas extraction on groundwater quality remains poorly understood. In a review of scientific literature on natural gas extraction, Vidic et al.[8] point out that there is very little information on groundwater quality prior to natural gas extraction activities.

In the past ten years, the 48,000 km^2 Barnett Shale formation in Texas has become one of the most heavily drilled shale formations in the United States with approximately 16,743 active wells as of May 2013 (http://www.rrc.state.tx.us/data/index.php). The Barnett Shale formation, located 1500 – 2400 meters below the surface of approximately 17 counties in North Texas, is composed of compressed sedimentary rocks which form a shale layer. The shale traps natural gas in interstitial pores, and modern techniques, such as hydraulic fracturing,

100   have allowed access to these gas reserves. Natural gas extraction in the Barnett Shale

101   formation should have little effect on the overlying Trinity and Woodbine aquifers as

102   they are separated from the shale formation by over a thousand meters of impermeable

103   rock. The United States Geological Survey (USGS) sampled arsenic[9] as well as

104   pesticides, nitrates, and volatile organic compounds (VOCs) in drinking water wells,

105   including wells from aquifers overlying the Barnett Shale formation.[10] Using these data

106   and other data from the Texas Water Development Board,[11] Reedy et al.[12]

107   characterized groundwater in the Trinity and Woodbine aquifers as generally good

108   quality with very few exceedances for constituents such as arsenic, selenium, strontium,

109   and barium. Slightly elevated levels of total dissolved solids (TDS) in these aquifers

110   could be attributed to evaporite and gypsum beds and potentially to legacy oil and gas

111   activities.

112   Here, we evaluate water quality in 100 private drinking water wells from the

113   Trinity and Woodbine aquifers overlying the Barnett Shale formation and the Nacatoch

114   aquifer east of the Barnett Shale formation (Figure 1). Samples were collected from

115   areas within the Barnett Shale region both with and without active natural gas

116   extraction, and from areas outside the Barnett Shale region unaffected by natural gas

117   extraction. Analytical tests were conducted to detect volatile and semi-volatile

118   compounds identified as contaminants of concern in a congressional report on hydraulic

119   fracturing fluid components,[13] and to detect arsenic, barium, selenium, and strontium.

120   These constituents are often included on lists of natural gas extraction waste

121   components.[7, 13, 14] These data were compared to a historical dataset from the same

122   aquifers prior to the expansion of natural gas extraction activities.[11] This study provides

123   information about the potential impact of natural gas extraction activities on groundwater

124   quality in aquifers overlying the Barnett Shale formation by: 1) determining if

125   constituents thought to be associated with natural gas extraction techniques are present

126   in private well water samples; 2) evaluating the relationship between water quality and

127   geographic proximity to natural gas extraction activities; and 3) discussing scenarios to

128   explain elevated constituent concentrations.

129

130   **2. MATERIALS AND METHODS**

131   **2.1 Sampling.** A total of 95 water samples were collected from private drinking

132   water wells that draw from the Trinity and Woodbine aquifers. Five reference wells

133   were sampled from the Nacatoch aquifer (Figure 1). We sampled from areas of active

134   natural gas extraction within the Barnett Shale (private wells with one or more gas wells

135   located within a 5 km radius; n = 91), non-active natural gas extraction areas within the

136   Barnett Shale (private wells with no gas wells located within a 14 km radius; n = 4), and

137   reference sites outside of the Barnett Shale (private wells with no gas wells located

138   within a 60 km radius; n = 5).

139   Private well samples were obtained from a pool of volunteers who responded to

140   a press release calling for study volunteers from 13 counties located in or near the

141   Barnett Shale region (Bosque, Denton, Hamilton, Hood, Hunt, Jack, Johnson, Kaufman,

142   Palo Pinto, Parker, Somervell, Tarrant, and Wise counties; Figure 1). Reference

143   samples from the Nacatoch aquifer were obtained by travelling door-to-door to find

144   volunteers willing to participate since well owners from this region are not impacted by

145   natural gas extraction and did not respond to our call for volunteers. Sampled water

146   wells drew from the Trinity aquifer (n = 76), the Woodbine aquifer (n = 15), the Nacatoch

147   aquifer (n = 5), and the Palo Pinto and Mineral Wells formations (n = 4) at depths

148   ranging from 9 – 427 meters with an average of 105 meters. Water wells were

149   overwhelmingly used for drinking water in rural areas without public drinking water

150   systems (n = 82). The remaining wells were used to irrigate private lawns or provide

151   drinking water for livestock (n = 18). To avoid contamination from pesticides, we did not

152   sample water wells that were used for irrigating large agricultural crops.

153   Water wells were purged for a minimum of 20 minutes, until measurements of

154   pH, dissolved oxygen (DO), and temperature stabilized, indicating fresh well water was

155   flowing. All samples were collected as close to the outdoor wellhead as possible,

156   bypassing filters or treatment systems. To ensure samples were representative of

157   shallow groundwater quality, wells that could not be purged, could only be accessed

158   through taps, or that could not be sampled before treatment or filtration were excluded.

159   Water quality data collected on site included DO, pH, specific conductance,

160   conductivity, temperature, salinity, TDS, turbidity, and oxidation-reduction potential

161   (ORP). Four duplicate water samples were collected in 40 mL glass vials without

162   headspace and held at 4°C during transport to The University of Texas at Arlington for

163   chemical analyses. Because the objective of this study was to assess potential

164   exposure risks of drinking water from wells in this region, we chose not to use filtration

165   and acidification techniques. This allowed us to obtain samples representing the quality

166   of water our participants would consume, as well as increased versatility in the number

167   of constituents that could be probed by analytical techniques. We acknowledge that

168   foregoing filtration and acidification can introduce a negative bias into metals analysis;

169   however, this would result in a conservative underestimation of concentrations.[15]

170   Furthermore, the MCL values for drinking water are based on unfiltered samples that

171   have not been acidified.[15]

172   **2.2 Analysis.** Chemical analyses were conducted using gas chromatography-

173   mass spectrometry (GC-MS), headspace-gas chromatography (HS-GC), and inductively

174   coupled plasma-mass spectrometry (ICP-MS). See Supporting Information (SI) Table

175   S1 for a list of compounds screened. Arsenic, selenium, strontium, barium, methanol,

176   ethanol, TDS, and volatile organic compounds (VOCs) such as benzene, toluene,

177   ethylbenzene, and xylenes (collectively referred to as BTEX) were the primary targets of

178   chemical analyses. Historical data for the concentrations of target compounds (except

179   alcohols) in private water well samples from this region were obtained to evaluate their

180   occurrence before the expansion of natural gas extraction activities.[11] This historical

181   dataset is comprised of 330 private drinking water wells from the Trinity, Woodbine, and

182   Nacatoch aquifers sampled over a ten year period (1989 – 1999) before natural gas

183   activities began. Wells were located in the same counties that we sampled in this study

184   (SI Figure S1). All wells were used for water withdrawal and ranged in depth from 14 –

185   1090 meters with an average depth of 207 meters. For more detailed description of

186   methods and analyses, see SI Methods.

187

188   **3. RESULTS AND DISCUSSION**

189   **3.1. Water Quality.** The dataset detailing well depth, distance to the nearest

190   natural gas well, concentration of constituents, and the suite of general water quality

191   parameters of each private well sample is provided in the online Supporting Information.

192   We found no evidence of BTEX compounds using both LC-UV-MS and GCMS. Levels

193   of TDS in active extraction areas averaged 585 mg/L and ranged from 200 – 1900

194   mg/L, while TDS in nonactive/reference areas averaged 500 mg/L and ranged from 400

195   – 600 mg/L. Exceedances for the Environmental Protection Agency's (EPA) TDS

196   Drinking Water Maximum Contaminant Limit (MCL) of 500 mg/L were detected in 50 of

197   91 samples from active extraction areas and 7 of 9 samples from the non-

198   active/reference areas (Table 1). The maximum TDS values detected in the active

199   extraction area were over three times higher than the maximum value from the non-

200   active/reference areas. These aquifers naturally show somewhat elevated levels of

201   TDS so these concentrations are not unusual for the area,[12] and the mean TDS

202   concentration in active extraction areas is similar to levels seen in historical data for this

203   region (585 mg/L versus 670 mg/L).

204

205   **3.2. Levels of Heavy Metals in Private Well Water.** Arsenic, selenium,

206   strontium, and barium are known to occur naturally at low levels in aquifers overlying

207   the Barnett Shale formation.[12, 16] Chemical analysis using ICP-MS (see SI Methods)

208   detected arsenic in 90 of 91 samples from active extraction areas and 9 of 9 samples

209   from non-active/reference areas. Concentrations were significantly higher in active

210   extraction areas compared to reference samples and historical samples (Table 1).

211   Arsenic concentrations in active extraction areas ranged from 2.2 – 161.2 µg/L, with an

212   average of 12.6 µg/L. The maximum concentration of arsenic detected in a sample

213   from an active extraction area was almost 18 times higher than both the maximum

214   concentration among the non-active/reference area samples and historical levels from

215   this region. Notably, 29 of 90 water wells in active extraction areas exceeded EPA's

216   arsenic MCL for drinking water of 10 μg/L.[17]

217   Arsenic in this region is derived from Oligocene-Miocene volcanic ash, and is

218   adsorbed onto metal oxides and clays.[18] Common forms of arsenic in groundwater are

219   As (V) and As (III), also known as arsenate and arsenite respectively.[19] Arsenite, a

220   reduced form of arsenate, is more mobile and toxic than arsenate.[18, 20, 21] Sorption of

221   arsenate is strongest at near-neutral pH, with adsorption rapidly weakening above pH

222   ~8.5;[22] the pH values in our groundwater samples averaged 7.9 with values as high as

223   9.3. Although we cannot identify the biogeochemical processes that lead to higher pH

224   values and subsequent arsenite mobilization, small perturbations such as lowering of

225   the water table either through groundwater withdrawals or drought conditions could

226   explain these results.[18]

227   Elevated arsenic concentrations can also occur in agricultural areas where

228   pesticide application leads to arsenic introduction,[12] or in areas with cultivated cotton as

229   arsenic was used as a defoliant.[23] Reedy et al.[24] showed that applied arsenic is limited

230   to shallow surface soils due to strong interactions between arsenic and iron oxides and

231   clays in soil. Given the low mobility of applied arsenic and the fact that none of our

232   samples were collected from private wells in or adjacent to crop fields, we find

233   agricultural arsenic introduction is unlikely to be the source of elevated arsenic

234   concentrations. Moreover, if agriculture were the cause of elevated arsenic levels, then

235   concentrations in the historical data would likely have been high as well and we found

236   no evidence of this.

237   Selenium was less prevalent in the water samples, detected in 10 samples

238   exclusively from active extraction areas. Selenium concentrations averaged 33 µg/L

239   and ranged from 10 – 109 µg/L, a stark contrast to the historical levels which averaged

240   4 µg/L and ranged from 0 – 50 µg/L. Two samples exceeded the selenium MCL of 50

241   µg/L,[17] and concentrations in active extraction areas were significantly higher than

242   historical levels although our sample size is too small to make definitive conclusions

243   (Table 1).

244   Strontium was detected in 90 of 91 samples from active extraction areas as well

245   as 9 of 9 samples from the non-active/reference areas. Strontium concentrations in

246   active extraction areas ranged from 66 – 18,195 µg/L, and were significantly higher than

247   historical levels (Table 1). There is no established MCL for the stable strontium species

248   analyzed in this study; however, an Agency for Toxic Substances and Disease Registry

249   toxicological profile reports that the EPA currently recommends no more than 4,000

250   µg/L in drinking water.[28] Seventeen samples from the active extraction area and one

251   sample from the non-active/reference areas exceeded this recommended limit.

252   Barium was also found in 90 of 91 samples from active extraction areas and 9 of

253   9 samples from non-active/reference areas. None of the barium samples exceeded the

254   MCL value of 2,000 µg/L;[17] however, the maximum value was much higher in the active

255   extraction area compared to the non-active/reference areas (174 µg/L and 60 µg/L,

256   respectively). Additionally, the concentrations of arsenic and selenium as well as the

257   concentrations of strontium and barium were positively correlated with one another (SI

258   Table S2).

259   These constituent concentrations could be due to mechanisms other than

260   contamination of aquifers with fluids used in natural gas extraction. For example,

261   lowering of the water table can lead to changes in pH that cause desorption of arsenic

262   and selenium from iron oxide complexes or mobilization of arsenic through pyrite

263   oxidation.[22] The regional water table has slowly risen in recent years as the population

264   has shifted from groundwater to surface water for drinking water (See SI Table S3).[29]

265   Recent drought conditions have also not had a severe impact on the water table as

266   levels in the Trinity and Woodbine aquifers are influenced more by the amount of

267   groundwater withdrawal than the lack of recharge from decreased rainfall.[30] While the

268   regional water table has not decreased dramatically in the last ten years, rural areas

269   with high water withdrawal rates and/or withdrawal of large amounts of groundwater for

270   use in hydraulic fracturing could lead to localized lowering of the water table. Bene et

271   al.[30] project that industrial use of groundwater for hydraulic fracturing will rise from 3% of

272   total groundwater use in 2005 to 7% in 2025, which suggests that current and future

273   industrial water use could cause localized water table reductions. Additionally, pyrite is

274   not found at high levels in these aquifers[31] so it is an unlikely source of arsenic.

275   Another potential mechanism is detailed in a report[7] suggesting that mechanical

276   disturbances, such as pressure waves from drilling activity, could loosen iron oxide

277   particles from the casings of private water wells, leading to increased turbidity of well

278   water. Arsenic and selenium could be mobilized into groundwater if iron oxide

279   complexes are agitated. Strontium and barium form sulfate or carbonate scales on the

280   interior casings of poorly maintained water wells and mechanical disturbance could also

281   lead to mobilization of these constituents. While arsenic, selenium, strontium, and

282   barium are present at low levels in many private water wells,[9, 24, 25] the levels seen in

283   this study warrant further investigation, as arsenic in groundwater is a health concern.[26,

284   27]

285   **3.3. Constituents and Distance to Nearest Gas Well.** Arsenic, selenium,

286   strontium, barium, and TDS reached their highest concentrations in areas of active

287   extraction in close proximity to natural gas wells (Figure 2 and SI Figure S2). Samples

288   that exceeded the MCL for TDS, arsenic, and selenium were located an average of 1.1

289   km from the nearest natural gas well. Similarly, the highest values for both strontium

290   and barium were over twice as high in areas less than 2 km from the nearest natural

291   gas well compared to more distant gas wells. The geographic patterns in our data

292   suggest that lowering of the water table during a drought period cannot fully explain

293   these elevated constituent levels. Concentrations that exceed the MCL occur only in

294   close proximity to natural gas wells (Figure 2) suggesting that mechanical disturbances

295   or localized groundwater withdrawals near natural gas wells could play a role in

296   elevated constituent concentrations. If regional drought or widespread public water

297   withdrawals were the cause of elevated constituent levels, then the geographic localities

298   of MCL exceedances would be more evenly distributed throughout the study area,

299   rather than in close proximity to natural gas wells. Additionally, regional lowering of the

300   water table should have resulted in similar constituent concentrations in these aquifers

301   during historical periods when groundwater withdrawal rates were even higher than

302   present levels.

303

304   **3.4. Constituents and Private Water Well Depth.** Arsenic, strontium and

305   barium all showed significant negative correlations with the depth of private water wells

306   (SI Table S2). This could be due to contact with surface sources as the highest

307   concentrations of arsenic and other compounds occur at the shallowest depths of

308   private water wells (Figure 3). Previous studies also found negative correlations with

309   depth in studies of arsenic and other compounds in the Gulf Coast aquifer of Texas[32]

310   and the Paluxy aquifer,[33] which is part of the larger Trinity aquifer. Glenn and Lester[32]

311   attributed their elevated constituent concentrations to a geologic origin and we cannot

312   rule out that scenario with these data. It is also possible that improper handling of

313   waste materials and faulty gas well casings could result in the introduction of these

314   compounds into shallow groundwater.[34] Healy et al.[35] demonstrated that fluid-matrix

315   interactions in unlined wastewater tanks cause mobilization of naturally occurring salts

316   and other constituents into groundwater, and Vidic et al.[8] indicate that faulty casing

317   seals in natural gas wells can cause groundwater contamination, although these casing

318   failures occur infrequently (1 – 3% incidence rate in Marcellus Shale operations).

319

320   **3.5. Heavy Metals and Total Dissolved Solids.** Selenium was not correlated

321   with TDS (likely due to small sample size), while strontium and barium showed

322   significant negative correlations with TDS (SI Table S2). Arsenic showed a significant

323   positive correlation with TDS (SI Figure S3 and SI Table S2), suggesting that it may be

324   concurrently mobilized into groundwater with TDS during the natural gas extraction

325   process. Again, mechanical disturbances (high pressure fluid injection, mechanical

326   vibration, etc.) associated with natural gas extraction activities could be the cause of

327   elevated levels of TDS and arsenic. Scanlon et al.[23] also found a positive correlation

328   between arsenic and TDS levels from the High Plains aquifer in a semiarid region of

329   western Texas. They attributed this correlation to a counterion effect from an influx of

330   saline water from the underlying Dockum aquifer that triggered a shift from calcium-rich

331   to sodium-rich water, mobilizing arsenic from chemical complexes. Because arsenic

332   levels in this region have historically been low (< 10 µg/L) and TDS levels have not

333   changed appreciably compared to historical levels, it seems unlikely that this scenario

334   could explain the correlation between arsenic and TDS seen in this study.[12]

335   Additionally, the clay and non-karstic carbonate layers separating the Woodbine and

336   Trinity aquifers would not seem to allow a large influx of deep saline water to trigger a

337   similar change in hydrogeochemistry.

338

339   **3.6. Comparison to Historical Data.** Concentrations of arsenic, strontium, and

340   selenium were significantly higher in samples from active extraction areas compared to

341   historical data (Table 1). Non-active/reference area samples also showed a significant

342   increase in arsenic compared to historical data (Table 1). Both active extraction and

343   non-active/reference areas showed a significant decrease in barium concentrations

344   from historical levels (Table 1). Historical TDS concentrations were not significantly

345   different from non-active/reference area concentrations but were significantly higher

346   than active extraction area samples (Table 1). On average, wells from the historical

347   dataset were 102 meters deeper than our wells and this could explain the difference in

348   some constituents. While we cannot draw definitive conclusions due to the fact that the

349   historical data was collected under different sampling conditions, these data do provide

350   a baseline for comparison to pre-industrial conditions which is generally lacking in

351   studies of this nature.[8]

352

353   **3.7. Methanol and Ethanol in Private Well Water.** Supporting Information

354   Table S1 lists 29 compounds selected for GC-MS analysis based on their inclusion in

355   hydraulic fracturing fluid mixtures.[13] Only methanol and ethanol, often included as anti-

356   corrosive agents in natural gas extraction, were detected in this study. Methanol and

357   ethanol concentrations were quantified using HS-GC with flame ionization detection

358   (See SI Methods). Twenty-nine private water wells contained detectable amounts of

359   methanol ranging from 1 – 329 mg/L with the highest concentrations from active

360   extraction areas (Table 1).   All six samples from Wise County contained methanol

361   concentrations ranging from 7 – 54 mg/L, with an average concentration of 28 mg/L.

362   These water wells are located between 215 – 610 meters from the nearest natural gas

363   wells, and could represent concurrent contamination of multiple private wells although

364   we cannot identify the contamination source using these data. Ethanol was detected in

365   12 samples, ranging in concentration from 1 – 11 mg/L. Four out of nine samples from

366   non-active/reference areas contained both methanol and ethanol, suggesting that these

367   chemicals are already present in groundwater in these areas and could have been

368   introduced through something other than natural gas extraction. Methanol is known to

369   occur naturally in groundwater as a byproduct of microbial metabolism,[5, 36] but it could

370   also be introduced through contact with industrial wastewater. Similarly, ethanol can

371   occur naturally or be introduced to groundwater through contact with industrial fuels.[37]

372   Naturally occurring ethanol is ephemeral and restricted to deep, anoxic environments

373   different from shallow groundwater.[38] Methanol and ethanol concentrations were not

374   correlated with distance to the nearest gas well.

375   The historical data did not include methanol and ethanol so we cannot examine

376   the historical occurrence of these constituents. The samples containing alcohol were

377   collected and analyzed during multiple sampling and analysis events over the entire

378   study, ruling out laboratory contamination as the source. The occurrence of alcohols in

379   our samples is relatively low, but it does warrant further research, as these compounds

380   should have a very short lifespan in the environment and likely require an active source

381   to sustain high concentrations.

382   Our results show elevated concentrations of constituents in the Barnett Shale

383   region; however, we are unable to determine the ultimate source of these elevated

384   concentrations directly. Previous studies in the Marcellus Shale used geochemical and

385   isotopic tracers to provide a direct link to the source of industrial or geological

386   contamination (e.g. non-thermogenic methane and deep brine mixing with shallow

387   groundwater[5, 6]). Analyses to identify the origin of elevated constituent concentrations

388   are beyond the scope of this study, which was intended simply to examine water quality

389   in areas of natural gas extraction. In lieu of these analyses, we chose to evaluate the

390   geographic occurrence and absolute concentration changes for these constituents over

391   time by comparing this study's data against previous characterizations of groundwater

392   in this region from the scientific literature and a large historical dataset from the same

393   region. This comparison shows a significant increase in the mean concentration,

394   maximum detected concentration, and MCL exceedances for As, Se, and Sr in our

395   study area when compared to historical data and previous characterizations of these

396   aquifers (Table 1).[12, 31]

397   While our data indicate elevated levels of potentially harmful compounds in

398   private water wells located near natural gas wells, it is important to recognize that there

399   were also a number of private water wells in close proximity to natural gas wells that

400   showed no elevated constituents. This indicates that natural gas extraction activities do

401   not result in systematic contamination of groundwater. We suggest that episodic

402   contamination of private water wells could be due to a variety of natural and

403   anthropogenic factors such as the mobilization of naturally occurring constituents into

404   private wells through mechanical disturbances caused by intense drilling activity,

405   reduction of the water table from drought or groundwater withdrawals, and faulty drilling

406   equipment and well casings. The geographic locations of elevated constituent levels in

407   our study are consistent with the notion that mechanical disturbance of private water

408   wells and industrial accidents (e.g. equipment failure, faulty well casings, fluid spills,

409   etc.) are more frequent in areas where natural gas extraction is active.

410   To draw definitive conclusions about the origin of elevated constituent levels in

411   these water wells would require a focused study of groundwater before, during, and

412   after natural gas extraction activities. This was logistically impossible as industrial

413   activities have been ongoing for over ten years in this area. Given this limitation, our

414   discussion of the source of elevated constituents is speculative, but we have provided

415   plausible scenarios to explain our data in an effort to increase scientific understanding

416   of this topic and spur future research. At a minimum, these data suggest that private

417   wells located near natural gas wells may be at higher risk for elevated levels of

418   constituents than those located further from natural gas wells. We advocate regular

419   water monitoring utilizing targeted analytical chemistry along with toxicity assays to

420   understand the complex interactions among groundwater constituents and biological

421   organisms.[39] Future research will focus on monitoring private wells in the Permian

422   Basin Shale of Texas before, during, and after natural gas extraction activities,

423   understanding the role of mechanical disturbances in mobilizing naturally occurring

424   constituents into groundwater, and evaluating the effects of industrial accidents and

425   waste disposal practices. Water quality in the Barnett Shale region is likely to become

426   an even more contentious issue as public concerns and prolonged drought conditions

427   place pressure on water reserves in the region.

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444   research.

445   **ASSOCIATED CONTENT**

446   **Supporting Information Available**

447   Additional materials and methods, figures, tables, and the complete water quality

448   dataset referenced in the text. This information is available free of charge via the

449   Internet at http://pubs.acs.org.

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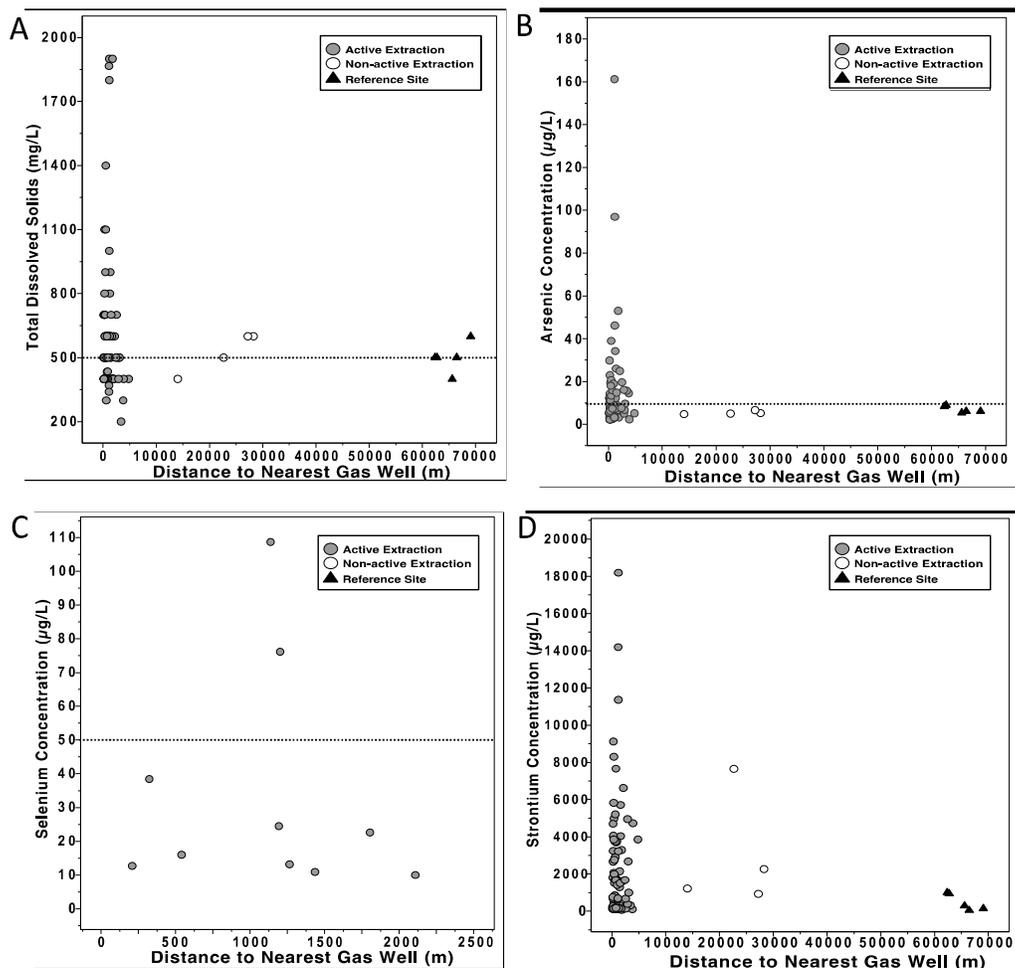599   *54* (12), 1857-67.
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601 **FIGURES AND TABLE**
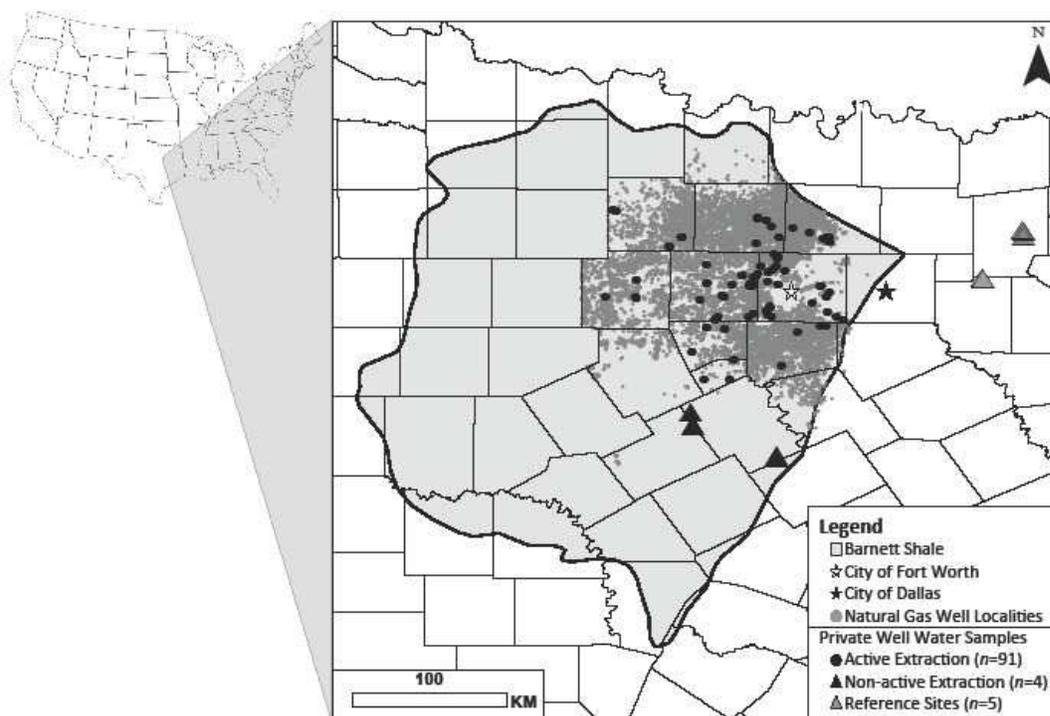
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614 **Figure 1.** Location of private water well samples and natural gas wells in the Barnett

615 Shale Formation of Texas. Private water wells are classified as coming from areas of

616 active natural gas extraction if there are one or more natural gas wells located within a 5

617 km radius from the water well.

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661   **Figure 2.** (A) Total dissolved solids, (B) arsenic concentration, (C) selenium

662   concentration, and (D) strontium concentration versus distance to the nearest natural

663   gas well in Barnett Shale private water well samples. The dashed lines in A–C

664   represent the Environmental Protection Agency's Drinking Water Maximum

665   Contaminant Limit (MCL) for each constituent. Note that the horizontal axis for C is a

666   different scale.

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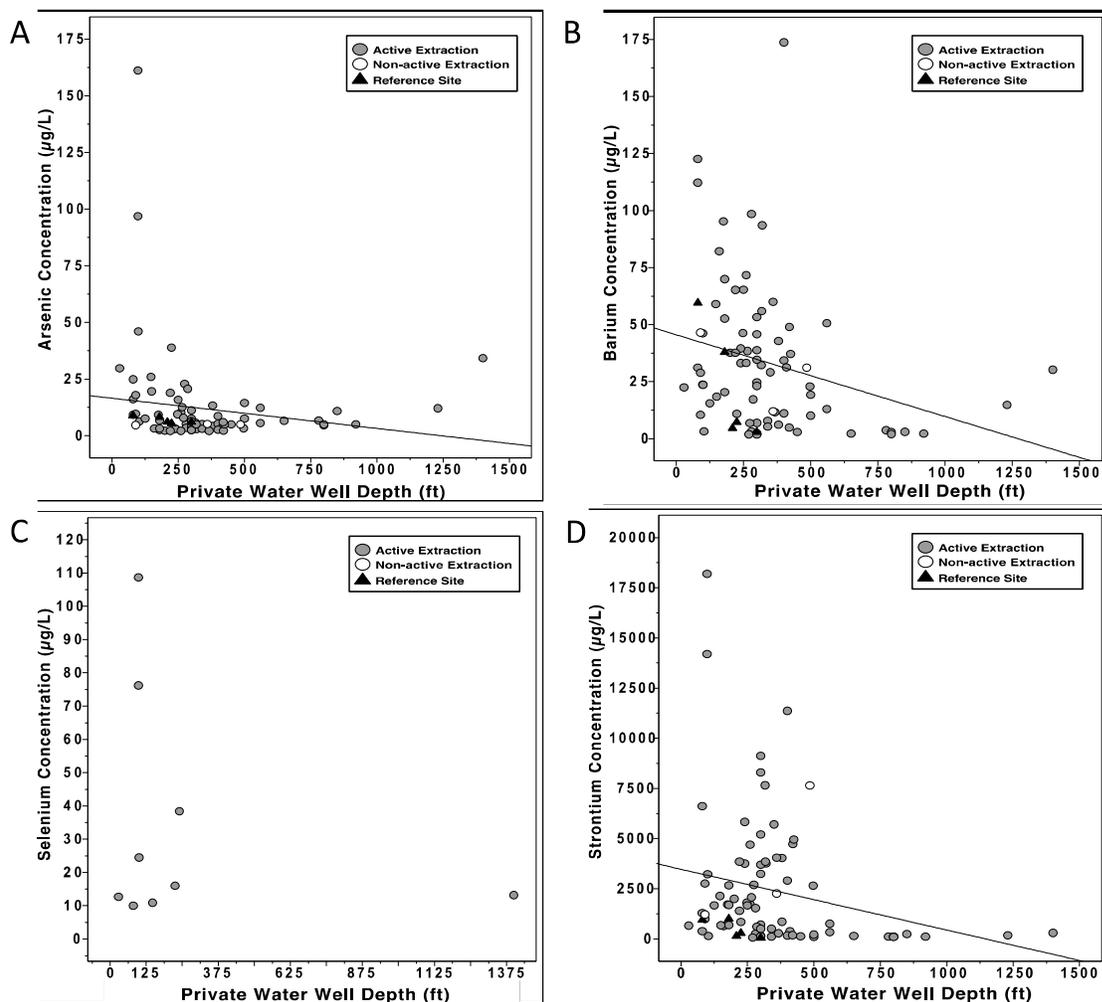
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697 **Figure 3.** Barnett Shale private water well depth versus (A) arsenic concentration
698 (Spearman correlation coefficient = -0.28; p < 0.05; r^2 = 0.023), (B) barium
699 concentration (Spearman correlation coefficient = -0.359; p < 0.05; r^2 = 0.075), (C)
700 selenium concentration (Spearman correlation coefficient = 0.142; p = 0.715; r^2 =
701 0.057), and (D) strontium concentration (Spearman correlation coefficient = -0.35; p <
702 0.05; r^2 = 0.05). Note that trend line is not shown for C due to small sample size.

703   **Table 1.** Concentrations of constituents in Barnett Shale private water well samples. All values are measured in µg/L

704   except Total Dissolved Solids (TDS), methanol, and ethanol in mg/L. Values denoted by asterisks represent statistically

705   significant differences from historical data values (Mann-Whitney U pair wise analysis; $p < 0.05$).

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	Historical Data (1989-99)				Active Extraction Area Wells (N = 91)				Non-active and Reference Area Wells (N = 9)			
	N	Range	Mean ± Std Error	% ≥ MCL	N	Range	Mean ± Std Error	% ≥ MCL	N	Range	Mean ± Std Error	% ≥ MCL
TDS	344	129–3302	670.3 ± 21.5	61	91	200–1900	585.1 ± 35.1*	54.9	9	400–600	500 ± 31.6	77.8
Arsenic	241	1–10	2.8 ± 0.1	0	90	2.2–161.2	12.6 ± 2.2*	32.2	9	4.7–9.0	6.9 ± 0.7*	0
Selenium	329	0.1–50	3.9 ± 0.2	0.3	10	10–108.7	33.3 ± 10.5*	20	–	–	–	–
Strontium	99	20–16700	1028.9 ± 213.7	N/A[†]	90	66.2–18195	2319.8 ± 330.1*	N/A[†]	9	52.4–7646.2	1610 ± 787.1	N/A[†]
Barium	357	0.1–382	57.2 ± 2.9	0	90	1.8–173.7	32.3 ± 3.3*	0	9	2.9–60	22.4 ± 11.3*	0
Methanol	–	–	–	N/A	24	1.3–329	33.6 ± 13.3	N/A	5	1.2–62.9	27.4 ± 13.7	N/A
Ethanol	–	–	–	N/A	8	1–10.6	4.5 ± 1.2	N/A	4	2.3–11.3	6.8 ± 2.4	N/A

Historical data for the counties sampled in this study were obtained online at www.TWDB.state.TX.us/groundwater/
Maximum Contaminant Limits (MCL) obtained from the Environmental Protection Agency's (EPA) National Primary Drinking Water Regulations, 2009
TDS MCL = 500 mg/L, Arsenic MCL = 10 µg/L, Selenium MCL = 50 µg/L, Barium MCL = 2000 µg/L, N/A indicates no MCL has been established
[†] EPA recommends stable strontium values in drinking water do not exceed 4,000 µg/L