

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

Brian E Fontenot, Laura R Hunt, Zacariah Louis Hildenbrand, Doug D Carlton, Hyppolite Oka, Jayme L Walton, Dan Hopkins, Alexandra Osorio, Bryan Bjorndal, Qinhong Hu, and Kevin Albert Schug

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7 **AUTHOR NAMES:**

8 Brian E. Fontenot,^{a,#†} Laura R. Hunt,^{a,#†} Zacariah L. Hildenbrand,^{a,#} Doug D. Carlton
9 Jr.,^{a,#} Hyppolite Oka,^a Jayme L. Walton,^a Dan Hopkins,^b Alexandra Osorio,^c Bryan
10 Bjorndal,^c Qinhong H. Hu,^a and Kevin A. Schug^{a,*}

11
12
13 **AUTHOR INFORMATION:**

14 ^a Department of Biology, Department of Chemistry and Biochemistry, and Department of Earth and
15 Environmental Sciences, The University of Texas at Arlington, Arlington, TX 76019

16 ^b Geotech Environmental Equipment Inc., Carrollton, TX 75006

17 ^c Assure Controls Inc., Vista, CA 92081

18 [#]These authors contributed equally to this work

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

21 ^{*} To whom correspondence should be addressed: Department of Chemistry & Biochemistry, The
22 University of Texas at Arlington, 700 Planetarium Pl., Box 19065, Arlington, TX 76019; (ph) 817-272-
23 3541; (email) kschug@uta.edu

24
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33
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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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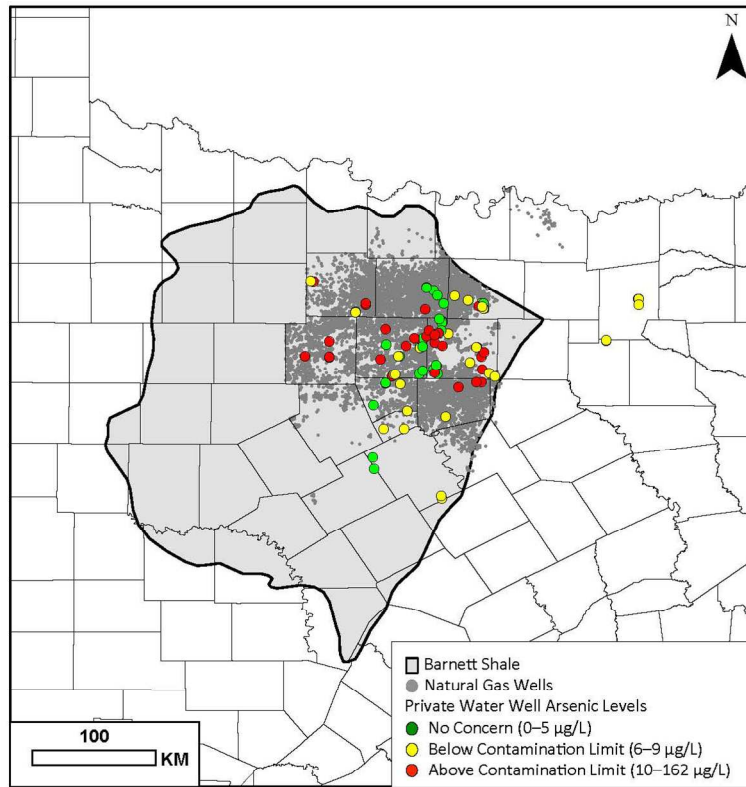
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77 1. INTRODUCTION

78 Recent advances in technology have facilitated a rapid and widespread expansion of
79 natural gas production from hydrocarbon-rich deep shale formations.¹⁻³ The increase in
80 drilling activity has raised concern over the potential for environmental contamination.²
81 ⁴⁻⁶ Contamination of groundwater aquifers overlying shale formations is particularly
82 problematic because they provide drinking water in rural areas where private wells are
83 unregulated. A study of the Marcellus Shale formation in the northeastern United States
84 reported increased concentrations of methane⁵ in private drinking water wells near
85 natural gas extraction sites. While this study does suggest that natural gas extraction
86 could cause systematic groundwater contamination, most confirmed cases of
87 contamination are the result of mechanical failures in which methane, drilling fluids, or
88 waste products leak through faulty gas well casings,^{3, 7} Despite a number of recent
89 investigations, the impact of natural gas extraction on groundwater quality remains
90 poorly understood. In a review of scientific literature on natural gas extraction, Vidic et
91 al.⁸ point out that there is very little information on groundwater quality prior to natural
92 gas extraction activities.

93 In the past ten years, the 48,000 km² Barnett Shale formation in Texas has
94 become one of the most heavily drilled shale formations in the United States with
95 approximately 16,743 active wells as of May 2013
96 (<http://www.rrc.state.tx.us/data/index.php>). The Barnett Shale formation, located 1500 –
97 2400 meters below the surface of approximately 17 counties in North Texas, is
98 composed of compressed sedimentary rocks which form a shale layer. The shale traps
99 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 arsenic⁹ 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 $\mu\text{g}/\text{L}$.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 aquifers³¹ so it is an unlikely source of arsenic.

275 Another potential mechanism is detailed in a report⁷ 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 Texas³²
310 and the Paluxy aquifer,³³ which is part of the larger Trinity aquifer. Glenn and Lester³²
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.

428 **AUTHOR INFORMATION**

429 **Corresponding Author**

430 * Kevin Schug; University of Texas at Arlington, 700 Planetarium Pl., Arlington, TX
431 76019; Phone: 817-272-3541; email: kschug@uta.edu

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443 would like to thank the participating well owners for their invaluable contribution to this
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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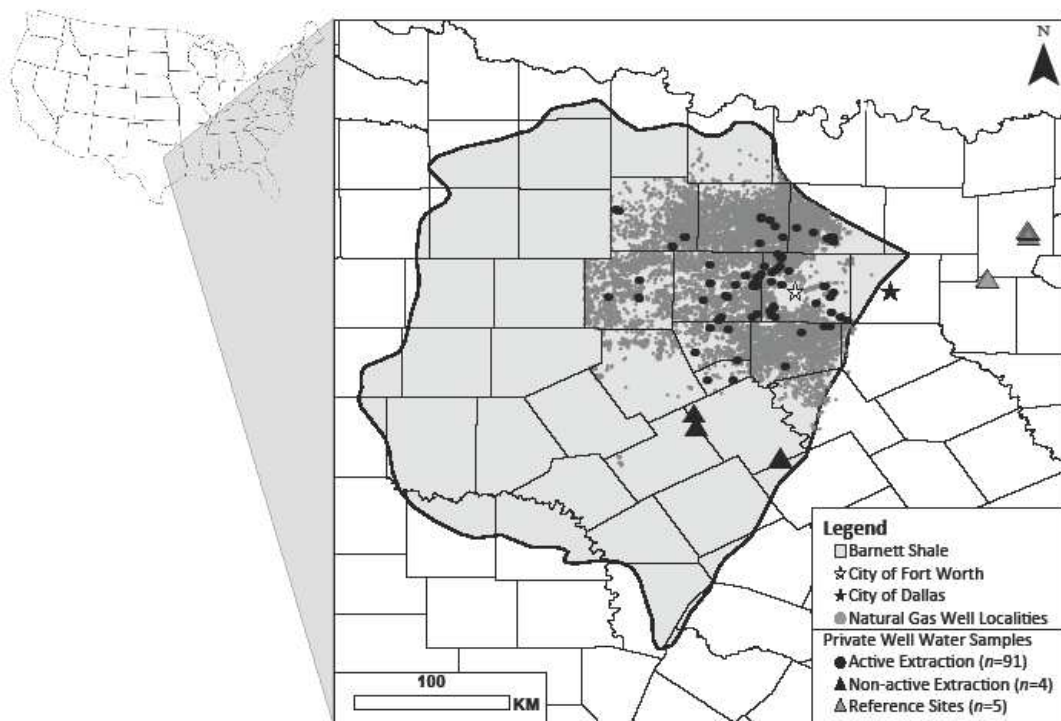
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- 600

601 FIGURES AND TABLE



U 13

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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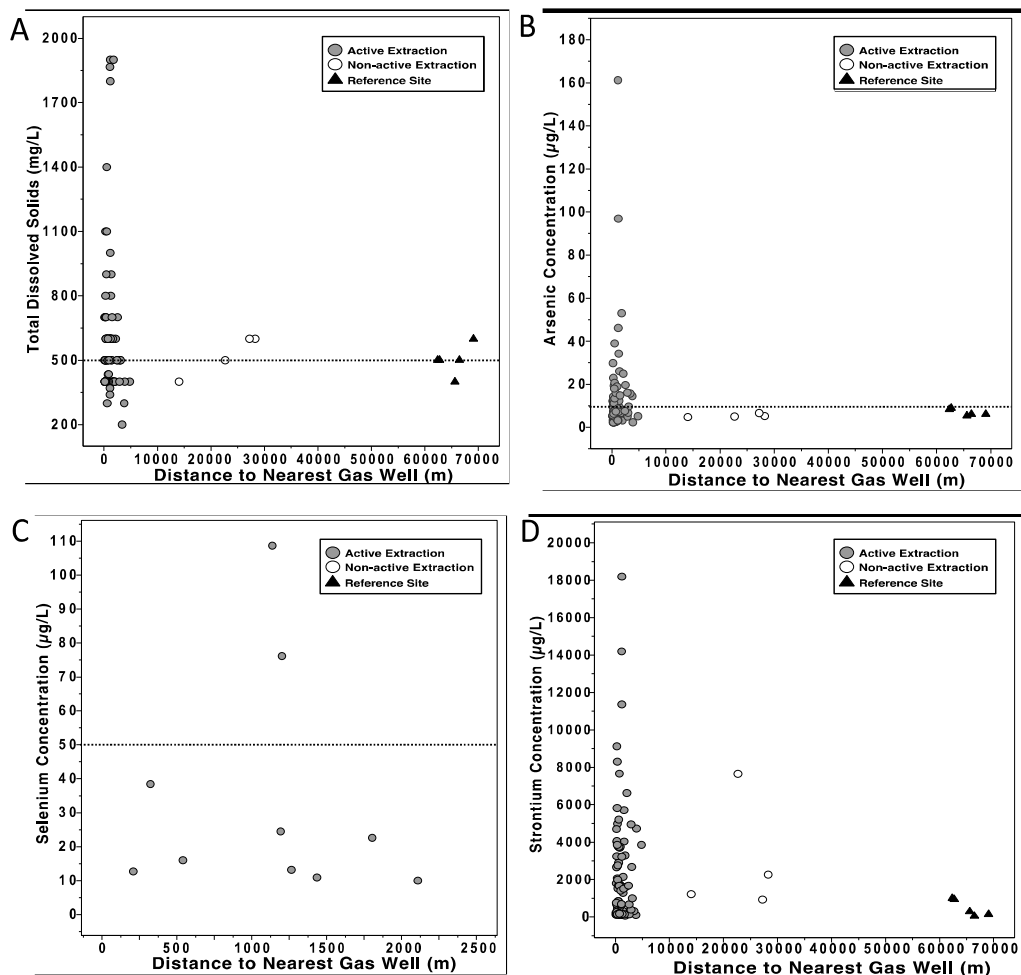
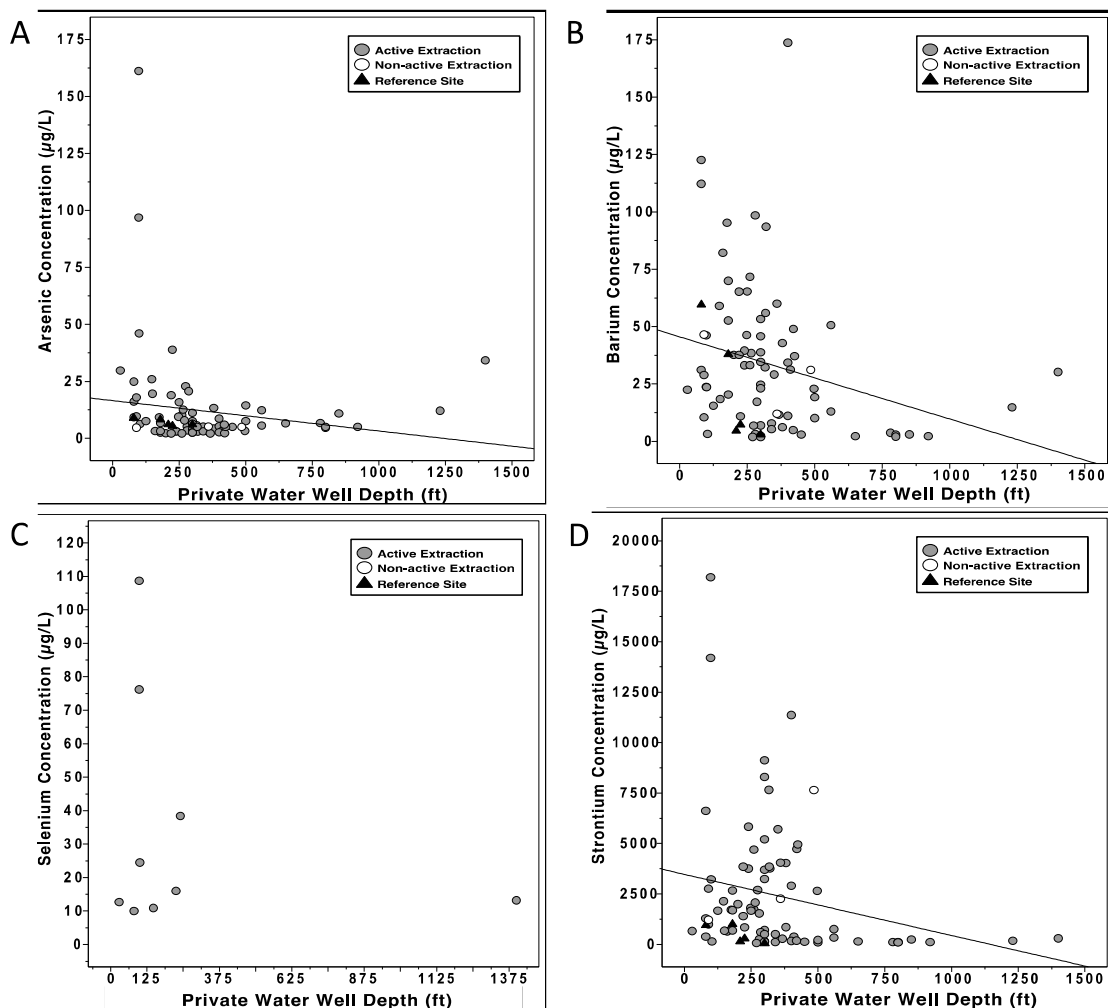


Figure 2. (A) Total dissolved solids, (B) arsenic concentration, (C) selenium concentration, and (D) strontium concentration versus distance to the nearest natural gas well in Barnett Shale private water well samples. The dashed lines in A–C represent the Environmental Protection Agency’s Drinking Water Maximum Contaminant Limit (MCL) for each constituent. Note that the horizontal axis for C is a different scale.



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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; $p < 0.05$).
 706

	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