Methane and Benzene in Drinking-Water Wells Overlying the Eagle Ford, Fayetteville, and Haynesville Shale Hydrocarbon Production Areas

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Supporting Information

ABSTRACT: Water wells (n = 116) overlying the Eagle Ford, Fayetteville, and Haynesville Shale hydrocarbon production areas were sampled for chemical, isotopic, and groundwater-age tracers to investigate the occurrence and sources of selected hydrocarbons in groundwater. Methane isotopes and hydrocarbon gas compositions indicate most of the methane in the wells was biogenic and produced by the CO₂ reduction pathway, not from thermogenic shale gas. Two samples contained methane from the fermentation pathway that could be associated with hydrocarbon degradation based on their co-occurrence with hydrocarbons such as ethylbenzene and butane. Benzene was detected at low concentrations (<0.15 μg/L), but relatively high frequencies (2.4–13.3% of samples), in the study areas. Eight of nine samples containing benzene had groundwater ages >2500 years, indicating the benzene was from subsurface sources such as natural hydrocarbon migration or leaking hydrocarbon wells. One sample contained benzene that could be from a surface release associated with hydrocarbon production activities based on its age (10±2.4 years) and proximity to hydrocarbon wells. Groundwater travel times inferred from the age-data indicate decades or longer may be needed to fully assess the effects of potential subsurface and surface releases of hydrocarbons on the wells.

INTRODUCTION

Hydrocarbon production from unconventional oil and gas (UOG) reservoirs in the U.S. using horizontal drilling and hydraulic fracturing technologies has stimulated a substantial amount of research on the potential effects of these activities on groundwater quality. Despite these efforts, the U.S. Environmental Protection Agency concluded that data gaps limited their ability to fully assess the degree of impact in its final report on the effects of hydraulic fracturing on water resources in the U.S. The Marcellus Shale production area in the northern Appalachian Basin is the most extensively studied UOG play...
with respect to understanding the effects of UOG development on groundwater quality.6−12 Fewer peer reviewed studies have examined groundwater quality in other major U.S. shale gas and tight oil play areas such as the Bakken (Montana and North Dakota), Eagle Ford (Texas), Fayetteville (Arkansas), Haynesville (Louisiana and Texas), and Permian Basin (Texas and New Mexico).9−12

This paper examines the occurrence and sources of methane and benzene in 116 drinking-water wells overlying the Eagle Ford (EF), Fayetteville (FV), and Haynesville (HV) Shale production areas using chemical, isotopic, gas, and groundwater-age tracers (Supporting Information (SI) Figures S1−S3). Studies in other areas have suggested possible links between some methane and benzene in groundwater and UOG production activities.12−14 High methane concentrations in drinking water can present a potential explosion hazard,13 whereas high benzene concentrations can result in an increased cancer risk, among other health concerns.15 And whereas methane in groundwater is almost entirely from subsurface sources, benzene in groundwater can be derived from subsurface and surface sources.13,16

This work expands the areal coverage of previous studies that examined methane in groundwater in parts of the FV and HV play areas,9,13 provides some of the first data on co-occurrences of methane, benzene, and other VOCs in drinking-water wells in the EF−FV−HV play areas, examines possible links between biogenic methane and hydrocarbon degradation, and provides the first systematic analysis of groundwater age in the play areas, which is used to evaluate the relative importance of subsurface and surface sources of benzene. The use of consistent sampling and analytical protocols and sets of analytes provides an opportunity to compare the occurrence and sources of methane and benzene among UOG play areas representing a range of hydrogeologic conditions and hydrocarbon development histories.

■ MATERIALS AND METHODS

In 2015 and 2016, samples of groundwater were collected from 30 domestic wells in each play area (Supporting Information (SI) Table S1). Twenty-six public-supply wells were also sampled in EF and HV. One sample of produced water was collected from a gas well in the Haynesville Shale in Rusk County, Texas in 2010, and five samples of produced water were collected from oil and condensate wells in the Eagle Ford Shale in Gonzales and Lavaca Counties, Texas in 2015. Water wells were screened in aquifers composed of semiconsolidated sands and clays to interbedded shale, sandstone, and limestone that were generally hundreds to thousands of meters above the UOG-bearing shales (SI Section 1, Figures S1−S4). Water wells were selected at random from populations of existing wells located ≤1 and >1 km from UOG wells to examine methane and benzene in groundwater in relation to hydrocarbon-well proximity (SI Section 2). Distances to UOG wells ranged from 0.11 to 25 km, maximum densities of hydrocarbon wells of any kind within 1 km of the water wells ranged from 0 to 62 wells, and drill years of the nearest hydrocarbon well of any kind ranged from 1929 to 2014 (SI Figure S5, Table S2). The 2015 IHS Global data set for oil and gas wells and State databases were used to determine the number and distance of hydrocarbon wells from sampled water wells.17 UOG wells refer to hydrocarbon wells completed in the Eagle Ford, Fayetteville, or Haynesville Shales, and hydrocarbon wells of any kind refer to UOG wells plus hydrocarbon wells completed in other formations in the study areas.

Water-well samples were analyzed for major ions, nutrients, and trace elements; methane, methane H and C isotopic compositions, and C1−C5 gas composition; H and O isotopic composition of water; noble gas concentrations and isotopic compositions; tritium, sulfur hexafluoride (SF6), carbon-14 in dissolved inorganic carbon (DIC), and δ13C-DIC; and volatile organic compounds (VOCs) (SI Tables S3−S5). Water from hydrocarbon wells was analyzed for a subset of these constituents (SI Table S6). Details on the methods of sample collection and analysis are in SI Section 2. Details on assessing VOC detections in groundwater are in SI Section 3.

Tritium, SF6, carbon-14, and tritogenic helium-3 concentrations were modeled using the software TraceLPM18 to determine fractions of post-1950s groundwater in the samples and mean ages of the pre- and post-1950s fractions. Pre- and post-1950s groundwater are defined as water recharged before or after the early 1950s start of above ground nuclear weapons testing, respectively. Details on the analysis of groundwater ages are in SI Section 4.

Mann−Whitney tests on ranked data were used to test for significant differences in methane concentrations between water wells ≤1 and >1 km from hydrocarbon wells (SI Table...
Spearman correlation analysis was used to examine relations between concentrations of methane and location, density, and age of hydrocarbon wells (SI Table S8). A significance level of 0.05 was used for each test.

RESULTS AND DISCUSSION

Major-Ion Chemistry of Groundwater. Total dissolved solids (TDS) concentrations in groundwater ranged from 99–7750 mg/L in EF (median = 493 mg/L), 34–509 mg/L in FV (median = 159 mg/L), and 76–1401 mg/L in HV (median = 511 mg/L) (SI Table S3). The lowest TDS waters were characterized as calcium–sodium-chloride (pH < 5) to calcium-bicarbonate and mixed cation-bicarbonate (pH > 6) types (SI Figure S6). The highest TDS waters were mostly characterized as sodium-bicarbonate to sodium-chloride and sodium-sulfate types. These TDS and major-ion characteristics are similar to previously published data for the areas and have been attributed to varying amounts of calcite, silicate, gypsum, and halite dissolution; ion exchange; iron and sulfate reduction; and possible mixing with small amounts of saline groundwater.9,12,20 Cross plots of major-ion concentrations from this study are generally consistent with those processes (Figure 1 and SI Figure S7).

Mixing with even small amounts of brine from shales could contribute substantial amounts of salt and gas to groundwater.6,21 Data for water isotopes, chloride concentrations, and Br/Cl mass ratios in groundwater and shale water indicate the groundwater contained little (<1%), if any, water from the Eagle Ford, Fayetteville, or Haynesville Shales (Figures 1 and S8).9,22–24 Groundwater samples had water isotopic compositions that plotted on or near global or local meteoric water lines (SI Figure S8), whereas shale water was isotopically enriched compared to groundwater from the same study area. Several EF samples with relatively high methane and chloride concentrations had Br/Cl ratios that appeared to be more consistent with dilute groundwater mixing with small amounts of a saline endmember having a Br/Cl ratio resembling that of seawater than with Eagle Ford Shale water (Figure 1A). Saline formation waters with Br/Cl ratios similar to seawater have been reported elsewhere in the Texas coastal plain,24,25 but seawater is used as an analog here because the source of the saline water is unknown. EF3 was unusual among the mixed samples because of its high TDS concentration (SI Figure S6), large fraction of saline water (>10%) (Figure 1), and methane isotopic composition (discussed below).

FV17 had the highest chloride, sodium, and boron concentrations among FV samples. Although the Cl+/Br− data indicate FV17 could have contained a small (<1%) fraction of Fayetteville Shale water (Figure 1B), the sodium and boron seem less likely to have been derived from shale water. The sodium and boron concentrations were highly correlated (rho = 0.90, p < 0.001) (SI Figure S7L), and a previous study concluded on the basis of boron isotopic data that the sodium–boron relation in groundwater was related to boron mobilization from clays in the aquifer by ion-exchange processes rather than substantial mixing with boron-rich shale water.9 This apparent lack of shale-water input is consistent with methane isotopic data for FV17 (discussed below).

Several HV samples with higher chloride concentrations also appeared to contain chloride from a source other than shale water based on their low Br/Cl ratios (although we only have one sample to characterize Br/Cl in Haynesville Shale water) (Figure 1C). Halite dissolution might be a relatively important source of chloride in HV groundwater. Several of the highest TDS samples were sodium-chloride type waters that plot along sodium-chloride concentration trend lines with molar ratios
Concentrations of Methane in Groundwater. Methane was detected at concentrations ≥0.001 mg/L in 81% (EF), 89% (FV), and 100% (HV) of the groundwater samples (SI Table S4; Figures S1–S3). Concentrations exceeded 10 mg/L, a proposed action level for methane in groundwater,14 in 7% (EF), 7% (FV), and 12% (HV) of the samples. The exceedance rate for FV was about 3 times higher than the rate (2%) previously reported for a smaller part of the play area in Faulkner and Van Buren Counties.9 For HV, the exceedance rate was lower than the rate (17%) reported for the Texas part of the play area;12 however, that study focused its sampling on a methane hotspot near the Mount Enterprise fault zone where we also detected methane >10 mg/L (well HV16) in this study (SI Figure S3). The highest methane concentrations mostly occurred in higher TDS sodium-bicarbonate waters (SI Figure S6), consistent with findings from several other studies.3,9,10,12,20 Some sodium-chloride waters in EF and HV also contained high methane concentrations. Methane concentrations were not significantly correlated with well depth (SI Table S8), but in HV, there was a noticeable clustering of high concentrations in the 40–100 m depth interval, similar to previous findings in that area (SI Figure S9).12

Methane concentrations were not spatially correlated with hydrocarbon well locations in any of the study areas. There were no statistically significant differences in methane concentrations between water wells located ≤1 km and >1 km from UOG wells or from hydrocarbon wells of any kind (SI Table S7); nor were there significant correlations between methane concentrations and distance to either UOG or hydrocarbon wells of any kind (SI Table S8). There were also no significant correlations between methane concentrations and number of hydrocarbon wells within 1 km of the water wells, or between methane concentrations and drilling year of the nearest hydrocarbon well.

Sources of Methane in Groundwater. Most samples that contained enough methane to measure its isotopic composition had values of δ13C–CH4 < −60‰, δ2H–CH4 between −250 and −150‰, and C1/C2+C3 molar ratios >1000 (Figure 2); and 87% (FV) to 95% (HV) of the samples that had detectable methane concentrations did not have detectable concentrations of C1–C5 hydrocarbons (SI Tables S4 and S5). These geochemical characteristics are typical of biogenic gas produced primarily by the CO2 reduction pathway.8–10 The predominance of biogenic gas in FV and HV is generally consistent with previous studies in smaller parts of those areas.9,12

Methane isotopic and hydrocarbon-gas compositional data from this and previous studies indicate shale gas in the study areas was thermogenic and compositionally different from most of the groundwater methane (Figure 2).27–30 The data indicate the UOG plays were not important sources of methane in the sampled wells. This conclusion is supported by the Br/Cl data and lack of correlation between groundwater–methane concentrations and hydrocarbon well locations, densities, and drilling years.

FV17 was the only FV sample with C1/C2+C3 < 1000, and Cl–Br/Cl data indicate it could have contained a small (<1%) fraction of Fayetteville Shale water (Figure 1B). However, FV17 did not contain detectable concentrations of C3–C5 hydrocarbons and its methane isotopic data indicate a predominantly biogenic gas (CO2 reduction) component in the sample (Figure 2B and E). δ34S–CH4 and C1/C2+C3 values for HV16, HV25, and HV29, and HVP98 plot between the biogenic and thermogenic fields in Figure 2F, suggesting a mixed source for methane in those samples and/or alterations due to methane oxidation. Methane oxidation processes clearly affected the δ34S–CH4 and δ2H–CH4 values of HVP98 (Figure 2C). However, HV16, HV25, and HV29 had δ2H values for methane and water close to what could be expected for biogenic methane produced by the CO2 reduction pathway (Figure 3),31 consistent with the formation pathway in almost all the other water samples that contained biogenic methane. The three HV wells were completed in the Wilcox Group and had methane isotopic compositions similar to coalbed methane in the Wilcox (Figure 2C). Wilcox coalbed methane collected east of the study area in north-central Louisiana was considered primarily biogenic in origin and produced by the CO2 reduction pathway.52

Lignite in relatively close vertical proximity to water wells could increase the likelihood of coalbed methane mixing with groundwater. Lignite sample PA-2 and well HV16 were located in southern Panola County, Texas and had similar methane isotopic compositions and C1/C2+C3 ratios, although PA-2 contained detectable C3–C4 hydrocarbons and HV16 did not (Figures 2C, 2F).36 PA-2 was collected from a depth of 112 m,66 and HV16 from 64 m (SI Table S1). Previous studies suggested the Mount Enterprise fault in Panola County could be a migration pathway for coalbed methane to enter overlying aquifers.12 Thirty-four to 44% of the domestic wells in Caddo and Bossier Parishes, Louisiana, where HV25 and HV29 were located, had at least one lignite layer described in their boring logs.28 HV25 and HV29 also did not contain C1–C5 hydrocarbons. Groundwater interaction with lignite could account for the Br/Cl enrichment in HV16, given that lignite samples from the Wilcox Group (n = 44) had Br/Cl ratios ranging from 0.006 to 0.076 (median 0.027),67 well above the Br/Cl ratio in HV16. Boron enrichment in several higher methane HV samples, including HV16 and HV25, relative to lower methane samples, could be further evidence for groundwater interaction with lignite (SI Figure S7M). Co-occurrence of high boron and biogenic methane concentrations
in groundwater were also reported in the lignite-rich Fort Union Formation in the northern Great Plains.\textsuperscript{10} \textsuperscript{13}C enrichment of Wilcox coalbed methane in north-central Louisiana relative to typical biogenic gas (Figure 2C) has been attributed to substrate depletion during methanogenesis.\textsuperscript{37} $\delta^{13}$C–CH$_4$ and $\delta^{18}$O–DIC data for HV16, HV25, and HV29 appear consistent with that process (SI Figures S10A, S10B). HV25 was the only high-methane sample that appeared to be substantially stripped of light noble gases (SI Figure S10C), suggesting direct contact with a local gas accumulation.\textsuperscript{39} Given that methane in HV25 was compositionally different from Haynesville Shale gas (Figures 2C, 2F) and other lines of evidence presented here, it seems unlikely that the inferred local gas accumulation was from the Haynesville Shale.

EFP72 was the only sample with a C$_3$–C$_4$ hydrocarbon detection (0.0004 mol % propane) that also had a methane concentration $>$1 mg/L (6.7 mg/L), $\delta^{13}$C–CH$_4$ $> -50^{\circ}\text{C} (-43.7^{\circ}\text{C})$, and C$_4$/\{C$_2$+C$_3$\} $< 1000$ (551), indicating it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $\sim 150^{\circ}\text{C}$) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area ($1.38^{\circ}$C/100 m).\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS composition and Br/Cl ratio of EFP72 indicate it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $60.8^{\circ}$C) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area (2.7–3.6 $^{\circ}$C/100 m)\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS composition and Br/Cl ratio of EFP72 indicate it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $60.8^{\circ}$C) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area (2.7–3.6 $^{\circ}$C/100 m)\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS composition and Br/Cl ratio of EFP72 indicate it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $60.8^{\circ}$C) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area (2.7–3.6 $^{\circ}$C/100 m)\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS composition and Br/Cl ratio of EFP72 indicate it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $60.8^{\circ}$C) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area (2.7–3.6 $^{\circ}$C/100 m)\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS composition and Br/Cl ratio of EFP72 indicate it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $60.8^{\circ}$C) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area (2.7–3.6 $^{\circ}$C/100 m)\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS composition and Br/Cl ratio of EFP72 indicate it contained thermogenic gas. EFP72 was also unusual in that it was the deepest (1299 m) and hottest (water temperature of $60.8^{\circ}$C) water well sampled. The depth and temperature of that well are consistent with geothermal gradients previously reported for that area (2.7–3.6 $^{\circ}$C/100 m)\textsuperscript{40} (SI Figure S11A), suggesting this was not an anomalous temperature associated with leakage of deeper, hotter fluids. The water isotopic composition and Br/Cl ratio of EFP72 indicate it contained little (<1%) if any, Eagle Ford Shale water, and its TDS
relatively young and less chemically evolved (Figure S6). The bicarbonate type water, consistent with the groundwater being from an UOG well. FV-12 was a low-TDS, mixed-cation-remaining eight samples only contained pre-1950s water with benzene that could be from a surface release. 15 ages of post-1950s recharge suggest groundwater travel times contaminated groundwater overlying the wells moves deeper could become more vulnerable with time as potentially the wells were sampled (blue bands in Figure 4). The wells indicate benzene in those samples was from subsurface sources such as natural hydrocarbon migration or leaking hydrocarbon wells. Those samples were sodium-bicarbonate type waters with benzene in those samples was from subsurface sources such as natural hydrocarbon migration or leaking hydrocarbon wells. HV29 also contained trace amounts of hydrocarbon detections. Hydrocarbon abbreviations: B, benzene; E, ethylbenzene; T, toluene; X, xylenes; MTBE, methyl tert-butyl ether; C2, propane; C4, butanes; C5, pentanes. Samples with benzene detections highlighted in red. 14% (HV) of the samples (SI Figure S12), indicating they contained at least some groundwater recharged after the early 1950s (post-1950s) (SI Section 4).13,44 The large percentage of FV samples containing post-1950s recharge likely reflects the shallow water-well depths there (SI Table S1), and higher recharge rates driven by the relatively low mean annual air temperature and high mean annual precipitation in FV.16,45 Conversely, 86% (HV), 80% (EF), and 13% (FV) of the samples were tritium dead (<0.1 to 0.2 TU) and appeared to only contain pre-1950s recharge. For the pre-1950s samples in EF and HV, median carbon-14 and helium-4 concentrations were 10 and 5 pmc, respectively, and 4.4 × 10−7 and 1.6 × 10−8 cmSTP/gH2O (∼10−100 times air saturation levels), respectively, suggesting many of those samples had ages older than several thousand years.6,10,39

The presence of post-1950s recharge in some samples does not necessarily mean the water was recharged after the onset of UOG development, so the lumped-parameter modeling software TracerLPM18 was used to estimate fractions of post-1950s water in the samples and the mean ages of the pre- and post-1950s fractions (SI Table S9) (SI Section 4). Despite the large percentage of FV samples that contained post-1950s recharge, only three of them had mean ages that overlapped the period of UOG development (Figure 4). The data indicate groundwater in the depth zones of the drinking-water wells was not particularly vulnerable to surface releases of contamination potentially associated with UOG activities, at least not in the ~7−11 year time frame of UOG development relative to when the wells were sampled (blue bands in Figure 4). The wells could become more vulnerable with time as potentially contaminated groundwater overlying the wells moves deeper into the aquifers. This is particularly relevant in FV where mean ages of post-1950s recharge suggest groundwater travel times from recharge areas to many of the wells were on the order of 15−40 years.

Of the nine samples with benzene detections, only FV12 contained benzene that could be from a surface release associated with UOG production activities based on its groundwater age (Figure 4). FV12 contained about 80% post-1950s water, had a mean age for that fraction (10 ± 2.4 years) that overlapped UOG development, and was 0.36 km from an UOG well. FV-12 was a low-TDS, mixed-cation-bicarbonate type water, consistent with the groundwater being relatively young and less chemically evolved (Figure S6). The remaining eight samples only contained pre-1950s water with mean ages ranging from 2,600 to >30,000 years, indicating the benzene in those samples was from subsurface sources such as natural hydrocarbon migration or leaking hydrocarbon wells. The occurrence of benzene in old groundwater is consistent with previous work near California oil fields.16 The results differ from findings in the Marcellus play where a predominantly surface source for diesel-range organic compounds and other hydrocarbons in groundwater was observed,13 which could reflect differences in recharge conditions and histories of hydrocarbon production between the areas. Previous studies have shown that old groundwater ages can be indicators of slow groundwater velocities.10,47−49 A study in the EF area reported groundwater velocities on the order of 1−3 m/year in parts of an aquifer containing groundwater >5000 years old,47 suggesting any benzene releases into old groundwater from leaking UOG wells might have only traveled short distances in the eight years since UOG production commenced. The closest UOG well to an EF water well with a benzene detection was 1.26 km away (SI Table S2), suggesting the benzene detections probably were not from UOG wells. An UOG source can also be ruled out for the highest benzene concentration detected in pre-1950s groundwater (HV29). Benzene was detected in HV29 by the USGS in 2004 (SI Table S5), about 4 years before to the start of UOG production in the HV play area but well after the drilling year (1955) of the nearest hydrocarbon well (0.13 km away) (SI Table S2). HV29 also had 62 hydrocarbon wells within 1 km, 92% of which predated UOG activity. This information indicates benzene in HV29 was not from UOG production activities, but an association with older hydrocarbon production activities is possible given the proximity and age of those hydrocarbon wells. HV29 also contained trace amounts of chloroform and bromodichloromethane that could be associated with well chlorination, a recommended well-maintenance practice in parts of Louisiana.50

Implications. UOG operations did not contribute substantial amounts of methane or benzene to the sampled drinking-water wells. However, groundwater travel times inferred from the age-data indicate decades or longer may be needed to fully assess the effects of potential subsurface and surface releases of hydrocarbons on the wells.49 In EF and HV, where there was a long history of non-UOG hydrocarbon production (Figure S5), the few water wells with detections of

Figure 4. Mean age of the pre-1950s (lower half of y-axes) and post-1950s (upper half of y-axes) fractions of water as a function of the fraction of post-1950s water in groundwater samples from the (A) Eagle Ford, (B) Fayetteville, and (C) Haynesville study areas. Blue bands indicate the period of UOG development relative to the sample year in each study area. Error bars represent 1-sigma errors. Orange symbols indicate samples with hydrocarbon detections. Hydrocarbon abbreviations: B, benzene; E, ethylbenzene; T, toluene; X, xylenes; MTBE, methyl tert-butyl ether; C2, propane; C4, butanes; C5, pentanes. Samples with benzene detections highlighted in red.
benzene or C$_3$–C$_6$ generally appeared to be closer to non-UOG hydrocarbon wells than to more recently drilled UOG wells (Figure 5), suggesting a connection between hydrocarbon detections and older wells (e.g., HV29). We cannot, however, rule out a possible natural subsurface source for some hydrocarbon detections (e.g., EFP72).\(^{16}\)

Our results may not be representative of the entire study areas. Only 130 hydrocarbon wells of any kind, out of a combined population in the study areas of >100 000 wells (SI Figure S5),\(^{17}\) were within 1 km of the sampled water wells. Sampling near more hydrocarbon wells could be warranted. Generally, samples were not collected at the water table where the aquifers are most vulnerable to surface releases of contamination. We also did not collect samples from multiple depths at any one location. It could be helpful to understand vertical variability in groundwater chemistry in close proximity to hydrocarbon wells.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00746.

Further information on study design, sample collection and analysis, assessing VOC detections, and groundwater data and associated figures and tables. The data are also available for download from https://doi.org/10.5066/F77D2SC4 (PDF)

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**Notes**

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