Research Paper:

Methane occurrences in aquifers overlying the Barnett Shale play with a focus on Parker County, Texas

Jean-Philippe Nicot[1]*, Patrick Mickler[1], Toti Larson[1,2], M. Clara Castro[3], Roxana Darvari[1], Kristine Uhlman[1+], Ruth Costley[1+]

1: Bureau of Economic Geology, The University of Texas at Austin, Austin, TX

2: Department of Geological Sciences, The University of Texas at Austin, Austin, TX

3: Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI

+: previously at

*: jp.nicot@beg.utexas.edu; 512 471-6246

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Article Impact Statement: Dissolved CH_4 in aquifers over the Barnett play is infrequent, thermogenic but natural, and related to localized shallow gas accumulations.

Abstract

Clusters of elevated methane concentrations in aquifers overlying the Barnett Shale play have been the focus of recent national attention as they relate to impacts of hydraulic fracturing. The objective of this study was to assess the spatial extent of high dissolved methane previously observed on the western edge of the play (Parker County) and to evaluate its most likely source. A total of 509 well-water samples from 12 counties (14,500 km^2) were analyzed for methane, major ions and carbon isotopes. Most samples were collected from the regional Trinity Aquifer and show only low levels of dissolved methane (85% of 457 unique locations <0.1 mg/L).

Methane, when present is primarily thermogenic ($\delta^{13}C$ 10^{th} and 90^{th} percentiles of -57.54‰ and -39.00‰ and C1/C2+C3 ratio 10^{th}, 50^{th}, and 90^{th} percentiles of 5, 15, and 42). High methane concentrations (>20 mg/L) are limited to a few spatial clusters. The Parker County cluster area includes historical vertical oil and gas wells producing from relatively shallow formations and recent horizontal wells producing from the Barnett Shale (depth of ~1500 m). Lack of correlation with distance to Barnett Shale horizontal wells, with distance to conventional wells and with well density suggests a natural origin of the dissolved methane. Known commercial very shallow gas accumulations (<200 m in places) and historical instances of water wells reaching gas pockets point to the underlying Strawn Group of Paleozoic age as the main natural source of the dissolved gas.

Introduction

The use of hydraulic fracturing (HF) stimulation for oil and gas production has considerably increased in the past 20 years; many reports and peer-reviewed papers have documented interactions between the newly perfected technology and water resources. The impact of HF on water quantity resources was well-documented early on, especially in Texas, in response to concerns from the general public and other local water stakeholders (Bené et al. 2007; Nicot et al. 2011; Nicot et al. 2012; Nicot et al. 2014; Scanlon et al. 2014a,b). On the other hand, a different type of issue emerged in response to early production from the Marcellus Shale in the northeastern United States. There, stakeholders were concerned about methane in groundwater and potential degradation of water quality. Several research papers documented the initial state of knowledge on dissolved methane distribution in groundwater (Osborn et al.,2011; Jackson, Vengosh et al.,2013; Molofsky et al.,2013. These initial studies were quickly followed by others in Pennsylvania (Heisig and Scott 2013; Baldassare et al. 2014; Darrah et al. 2014; Wilson 2014;

Siegel et al. 2015, 2016; Christian et al. 2016) and elsewhere: Colorado (Li and Carlson 2014; Sherwood et al 2016), Fayetteville in Arkansas (Warner et al. 2013), Bakken in North Dakota (McMahon et al. (2015), Texas (Nicot et al. 2015 and 2017a, b; Wen et al. 2016), and Canada (Cheung et al. 2010; Moritz et al. 2015; Humez et al. 2016). The source of the dissolved methane is sometimes clear, in particular when it is microbial (Warner et al. 2013; McMahon et al. 2015) but still the object of conflicting studies when mostly thermogenic, such as in Pennsylvania (Jackson, Vengosh et al. 2013; Molofsky et al. 2013 Darrah et al. 2014) or Texas (Darrah et al. 2014; Wen et al. 2016). If dissolved methane of microbial origin is natural in the vast majority of cases, a thermogenic dissolved gas can be naturally present in shallow groundwater or it can be anthropogenic and introduced directly or indirectly during well drilling and completion or natural gas production (Jackson, Gorody et al. 2013).

The initial purpose of the study was to document and understand the distribution of dissolved methane in fresh-water aquifers overlying the Barnett Shale play in North Central Texas. As documented below, in the course of the 2-year study (Nicot et al. 2015), it became apparent that dissolved methane existed in clusters separated by wide areas with very low methane concentrations. A spatial subset of one of the well clusters, the so-called Parker County or Silverado case, had already been investigated by various groups with opposite conclusions (see supporting information SI-3 and Table S5 for timeline): US EPA (EPA 2013), Railroad Commission (RRC 2014)—the Texas state agency in charge of regulating the oil and gas industry—operators and their consultants as well as academic institutions (Darrah et al. 2014), private citizens, and work by our group (Wen et al. 2016). The consensus seems to be that methane from several water wells are indeed a natural occurrence although some authors suggest that some dissolved methane is also of anthropogenic origin (EPA 2013; Darrah et al. 2014). In the latter case, the dissolved methane can originate from the deep reservoir through deficiencies of the wellbore system or, the hypothesis usually the most favored in Parker County, it can be already be present at shallower depth and be mobilized by drilling and completion activities. We revisited the Parker County case by broadening the area of dense sampling and adding independent observations. In this paper we used the term "Parker–Hood cluster" to emphasize that the cluster includes several water wells in Hood County and covers sections of southern Parker and northern Hood counties.

The Barnett Shale is the oldest play where HF has been used systematically (Nicot et al. 2014). By the end of 2015, ~20,000 wells had been completed and stimulated in the play, including ~15,000 horizontal wells (IHS 2015). Production started in the so-called core area, which has been drilled intensively and consists of Wise, Denton, and Tarrant counties in the Fort Worth area, with mostly vertical wells producing dry gas. Production progressively expanded outwards to areas with wet gas or even condensate in parallel with the implementation of horizontal-well technology. Wet gas is defined as natural gas with dominant methane (C1) but also including an important fraction of ethane (C2) and propane (C3). Condensate is characterized by light liquid alkanes (C6-C10). North Central Texas has a long history of oil and gas production with an additional ~35,000 mostly older vertical wells drilled in the same counties (IHS 2015). As in many regions of Texas, historical oil and gas activities precludes unambiguous baseline sampling.

There was no systematic study of dissolved methane in the Barnett Shale footprint prior to this reconnaissance study except for an early RRC investigation limited to Wise County complemented by a recent EPA study (EPA 2015a, b). Because of the general lack of measurable dissolved methane in aquifers overlying the play, our efforts focused on the Parker-Hood cluster.

The cluster has been the object of considerable scrutiny, particularly in the 2010-2014 time span but has also regularly required the attention of the RRC at least since the 1980's. A historical summary is presented in SI-3.

Geologic Setting

Geological details are presented in SI-1. The Barnett Shale is a siliceous mudrock of Mississippian age (Hill et al. 2007; Loucks and Ruppel 2007; Pollastro et al. 2007; Fu et al. 2015) that can be informally described as a black shale. It lies near the base of the sediments that accumulated in the Fort Worth Basin of North Central Texas during the Paleozoic era. The thickness of the shale varies from >1000 ft (330 m) in Denton County in the core area to 200-400 ft (60-120 m) in the counties at the periphery including in Parker and Hood counties. Depth to the top of the productive Barnett Shale is also variable with a maximum of ~9000 ft (~2700 m) in the core area to ~4000 ft (~1200 m) at the periphery, the Barnett Shale crops out south of Hood County next to the Llano Uplift where Precambrian rocks are exposed (Figure S9). The Barnett Shale gets thicker and deeper toward the northeast of its domain close to the intensively drilled core area. In Parker and Hood counties, the depth to the top of the Barnett Shale varies from ~6500 ft (2000 m) to the east to ~5000 ft (1500 m) to the west. The Barnett Shale is overlain by mostly Pennsylvanian formations, particularly from the Atoka and Strawn groups, which display a considerable thickness in the core area quickly decreasing toward the west.

In Hood and Parker counties, the Strawn Group is 2500+ ft (750+ m) thick (Figure S5) and dips towards the northwest. The Strawn Group is a fluvio-deltaic system comprised of sandstone units and shales with some limestones. The Lower Strawn is shale-rich and contain sand bodies sometimes charged with hydrocarbons. Its top subcrops in the Parker–Hood cluster area (SI-1). A major unconformity lies between the Strawn Group and the Trinity Group and other formations of Cretaceous age. The Cretaceous rocks have been partially eroded and do not exist west of Parker and Hood counties. The thickness of the Cretaceous units increases from ~0 in these counties to ~2000 ft (600 m) in the core area to the east. The Cretaceous sequence contains three sand-dominated strata with carbonate-dominated intervals in between. These are, from the base to the top (Kelley et al. 2014): (1) the Twin-Mountain Formation (Fm.) (also known as the Travis Peak Fm.), which is the only sand present in the Parker–Hood cluster area where the overlying Glen Rose carbonates crop out and forms bluffs; (2) the Paluxy Fm. present just to the west of the Parker-Hood cluster (Twin Mountain, Glen Rose and Paluxy formations (Fms.) form the Trinity Group); and (3) the Woodbine Fm., cropping out in the core area. All Cretaceous Fms dip toward the east. Although several known major faults impact at least some of the Paleozoic section (Ewing, 1991), none has been documented impacting Cretaceous strata in Parker and Hood counties (SI-1).

The Barnett Shale is mostly a gas play; that is, most of the formation has been exposed long enough to conditions favorable to gas generation (gas window). However to the North, in Montague County where substantial amounts of condensate are produced, the formation is still in the oil window (Montgomery et al. 2005; Pollastro et al. 2007). To the west, including in Parker and Hood counties, the Barnett Shale is not as mature as in the core area and produces wet gas. The Barnett Shale is the main source rock of hydrocarbon accumulations in the Fort Worth Basin; other younger Paleozoic source rocks may have contributed in a minor way to commercial accumulations in the Atoka and Strawn groups. Some hydrocarbon accumulations are present at very shallow depths in Parker and Hood counties (Herkommer and Denke 1982). There are no known hydrocarbon accumulations in the Cretaceous formations of the Fort Worth Basin.

Fresh-water Trinity and Woodbine Aquifers are hosted by formations of Cretaceous age. Only the Trinity Aquifer is present in Parker and Hood counties. The Trinity Aquifer is hosted by the sand-rich Twin Mountains and Paluxy Fms., as well as by other permeable intervening units. However, only the Twin Mountains Fm., in addition to very minor Brazos River alluvium, holds water in the Parker–Hood cluster area (Figure S10). On the western edge of the productive Barnett, only small disconnected aquifers hosted by sand lenses of Paleozoic age are present (Nicot et al. 2013). It is understood that a hydraulic connection exists between Strawn sand lenses and the basal Trinity sands across the unconformity when a sand-on-sand contact is present; however the average vertical flow direction and its spatial and temporal variability are unknown. Well drillers often drill through and screen Strawn sandy intervals when they are in vertical continuity with Trinity sands. The general flow direction in the Trinity Aquifer is along the regional topographic slope to the east.

The surface topography of the Fort Worth Basin is that of a gently rolling plateau but one that is dissected by numerous rivers and streams including the Trinity and Brazos Rivers. Average precipitation ranges from 32 to 38 inches (800-970 mm) per year increasing toward the east. The area is densely populated with the major urban centers of Fort Worth, Dallas and neighboring cities next to the core area. The rest of the study area includes many smaller cities, towns, subdivisions, and ranches.

Methodology

Methodology is similar to that used in Nicot et al. (2017a, b). It is described in SI-2 and summarized below. The study included most of the footprint of the productive Barnett Shale with a total of 457 unique locations sampled over 14,500 km^2 (5600 mi^2) in 12 counties (Figure 1). The counties included are, from north to south: Montague (64 samples), Cooke (11), Wise

(39), Denton (54), Parker (124), Tarrant (45), Dallas (1), Hood (48), Johnson (44), Ellis (1), Somervell (21), and Hill (5).

Data acquisition

The reconnaissance study approach consisted of contacting well owners with the help of the local Groundwater Conservation Districts (GCD) and obtaining permission to sample their water well with the goal of having a good spatial distribution across the play. The reconnaissance sampling (452 unique locations, 469 samples) was conducted by Inform Environmental, LLC between December 2013 and August 2014. Duplicate, triplicate and additional samples (40 samples, 5 new unique locations) were collected in the Parker–Hood cluster area by Bureau of Economic Geology (BEG) personnel between September 2014 and February 2015, done in parallel to noble gas sampling using copper tubes (Wen et al. 2016) and nitrogen isotope sampling (Nicot et al. 2015). Dissolved gas concentrations and isotopic composition quality control was ensured by using the Isotech Isoflask® technology on seven duplicate samples. Water samples were collected in 30-ml polyethylene bottles for major ion analysis after field parameters stabilized. Samples for δ^{13}C of dissolved inorganic carbon (DIC) were collected in a 20-ml vial with no head space and were not acidified. Samples were collected for analyses of major ions, isotopes, and dissolved gases through any available valve that was as close to the wellhead as possible and always before any storage tank. We used a flow-through sampling approach to collect samples for dissolved gas analysis in a 70-ml serum vial (SI-2). Serum vials were first capped and then filled using two flow-through syringes (fill and vent). Samples were stored upside down in an ice-cooled container, shipped to the laboratory and acidified to pH<2 upon reception of the samples. The method is appropriate for sampling dissolved methane below saturation at atmospheric pressure but, like all surface sampling, gives less accurate results if the in situ concentration at depth is above saturation at the surface because dissolved gas outgassing and bubble formation limit the likelihood of having a fully representative sample.

Unlike all the other wells whose wellbore was obstructed by their pump system, we were able to sample free-flowing gas (i.e., not headspace) out of two water wells (#BS555 and #BS556 in Hood County) that had been abandoned because of gas lock of the water pump but still left open, which is not uncommon (Baldassare et al 2014). We used an inflatable bladder as packer to isolate a short section of the wellbore above the water level. The natural-gas pressure buildup purged the air from the restricted section and allowed easy sampling using the Isotech Isobag® technology. We succeeded in sampling the water in only one of these wells (#BS555) using a Bennett compressed air-operated submersible piston pump. The same well was previously entered with a video camera to observe the origin of the effervescing gas, and we were able to visualize gas bubbles passing through the screen strongly suggesting two-phase flow and free gas in the formation. One of the wells of the Public Water Supply Lake Country Acres well field was abandoned for the same reason as these two wells (Table S5). We also sampled nine gas wells, including one producing from a Strawn reservoir and eight from the Barnett Shale in Parker and Hood counties (Table S4), using the Isotech Isotube® technology.

Chemical analyses

Dissolved gas concentration analyses were performed at the University of Texas (SI-3). Concentrations were calculated using measured headspace gas concentrations and Henry's law relationships (Kampbell and Vandegrift 1998). Detection limits (upper bound) of 0.001 mg/L for methane (C1), 0.002 mg/L for ethane (C2), and 0.003 mg/L for propane (C3) were achieved. Replicate analyses of dissolved gas samples, which combines errors associated with sample preparation and analysis were less than 4% (± 0.05 mg/L for a sample with a 1.0 mg/L dissolved methane and ± 0.5mg/L for a sample with 8.0 mg/L dissolved methane). Samples with sufficiently high dissolved methane concentrations (>~0.3 mg/L) were analyzed for stable carbon isotope compositions. Replicate analyses of dissolved methane samples resulted in a standard deviation of ± 0.35‰ for $\delta^{13}C$. DIC ′ ^{13}C values and concentrations were measured on an Isotope Ratio Mass Spectrometer directly coupled to the GC (GC-IRMS). Major cations and anions of water samples were analyzed on two Ion Chromatography systems. Samples were diluted with de-ionized water to ensure no component exceeded 100 mg/L. Analyses of gas samples (a total of 11) were performed by Isotech.

Sample depth and aquifer

We sampled mostly domestic wells in the western half of the producing Barnett footprint then we turned to municipal and irrigation wells to the east, as the Trinity Aquifer deepens following its dip and the area becomes more urbanized with many less domestic wells to sample (Figure S12). Well depth varies from 30 ft (9 m) to 2409 ft (734 m) with an average of 453 ft (138 m) and a large standard deviation of 408 ft (124 m). The position of the unconformity in Parker and Hood counties between Cretaceous and Paleozoic formations, in particular relative to the water wells screened interval, was determined by examining driller logs from 800+ water wells (TWDB 2015b) guided by oil and gas well logs used in a previous study (Kelley et al. 2014).

Detailed information about well characteristics is not always available for domestic wells. The state databases (TWDB 2015a, b) provides depth and screened interval for ~90% of the sampled wells. We cross-checked information from the state database with information provided by the regional groundwater models (Harden et al. 2004; Bene et al. 2007; Kelley et al. 2014) to assign the correct aquifer to each sample. A few wells (52 out of 457) were missing depth information;

in these cases, we used well-owner information coupled with well-water temperature to confirm sampled depth.

Results

Dissolved methane concentrations (457 unique locations) are generally low with 387 samples (84.7%) having concentrations <0.1 mg/L, 30 samples (6.6%) ranging from 0.1 to 1 mg/L, and 29 samples (6.3%) between 1 and 10 mg/L including three clearly microbial samples in Montague, Parker and Hood counties; the remaining 26 samples are all in Parker and Hood counties. A total of 11 (2.4%) samples have concentrations >10 mg/L, all in Parker and Hood counties. A dissolved methane concentration of 10 mg/L is generally accepted as the action level at which a water well should be vented (NGWA 2010). Note that the amount of methane for samples >20 mg/L is only semi-quantitative because of the sampling methodology at ~atmospheric pressure (Molofsky et al. 2016). Several authors (Wardrop 2013; Christian et al. 2016; Loomer et al. 2016) have documented seasonal and other temporal variations of dissolved methane but the variations rarely show large swings from high methane to none. Resampling of several wells two or three times, particularly in the Parker County area, showed good agreement between sampling events with no dramatic change, that is, individual wells may display some variations but the variations will not impact the interpretation of results, which rely on aggregate not on results of a specific well.

The cluster area is estimated at ~10×13 km^2 (Figure 2) and includes wells and patches with little methane. Sampling was executed outwards from the perceived center of the cluster (Silverado neighborhood area, 2×3 km^2 area) until all samples taken showed no dissolved methane. Methane concentration does not seem to be a function of depth (Figure S16) but rather of the vertical distance to the geological unconformity (Figures 4 and S17). The Parker–Hood cluster was determined to extend to the city of Granbury to the south and also west of the Brazos River, and is significantly larger than the area investigated by the RRC and EPA. Another apparently smaller cluster can be defined on the Hood–Somervell county line but its true extent is unknown because of the limited sampling (Hood–Somervell cluster). Northeastern Palo Pinto County may contain another cluster (RRC 2015) but it was not investigated in this study.

Methane carbon isotopes were measured at 58 unique locations, i.e., most of the samples with dissolved methane >0.1 mg/L (Table S2). All are in Parker (n=40) and Hood (n=16) counties except one each in Somervell and Montague counties and are relatively heavy (mean -48.31‰; median -48.59‰; 10th and 90th percentiles -57.54 and -39.00‰; minimum at -83.18‰ in Montague County; maximum at -26.22‰ in Parker County).

Ethane was detected in ~85 of the 457 unique location samples (detection limit of 0.002 mg/L), mostly in Parker, Hood and Somervell counties and related to the Parker–Hood and Hood–Somervell clusters (Table S2). The highest ethane concentration (6.2 mg/L) corresponds to the highest measured methane concentration (31.0 mg/L; #BS199). Like methane, ethane concentration does not seem to be a function of depth but rather a function of the distance to the unconformity (Figure S18). Samples in southern Wise County with methane between 0.1 and 1 mg/L also show some ethane. Ethane was detected in several samples across the play with dissolved methane concentrations <0.1 mg/l. Propane was detected in ~50 samples (detection limit of 0.003 mg/L) and follows the pattern outlined for ethane: highest in sample #BS199 (2.2 mg/L), and present in Parker and Hood counties as well as in southern Wise County.

Wetness, and the reciprocal property, dryness, is measured by the molar ratio of methane over ethane and propane (C1/C2+C3). A wet gas contains a significant amount of C2+ gases and has a low C1/C2+C3 ratio. A crossplot of carbon isotopic composition and C1/C2+C3 ratio (so-called

Bernard plot) is a powerful tool for differentiating microbial vs. thermogenic methane: a thermogenic source tends to be heavy and wet whereas a microbial source is light and dry (Figure 3). Dissolved gas in the Barnett Shale tends to have a low C1/C2+C3 ratio suggesting a thermogenic origin without much alteration (Table S2). The median of the ratio is 15 and 10th and 90th percentiles are 5 and 42, respectively. There seems to be some uncommon mixing with microbial gas as evidenced by the few data points on the lower left quadrant of the Bernard plot (Figure 3). We were also able to gather data from previous sampling campaigns by other groups in the Parker County area to better delineate the area with high methane concentration. The additional data (Figures S1 and S2) bring no new element that would modify the interpretation presented here.

The water samples were withdrawn mostly from the Trinity Aquifer and, occasionally, from the hydraulically connected underlying Paleozoic Strawn strata in Parker and Hood counties (25 samples), from the outcropping Paleozoic in Montague and Wise counties (33 samples) and, covering 8 counties in the eastern half of the Barnett Shale footprint, from the Woodbine Aquifer (26 samples). The groundwater is generally fresh with mean total dissolved solids (TDS) in the 700–800 mg/L range and a 300–500 mg/L standard deviation (Table S1). The water type is generally Na-bicarbonate with or without sulfate. Sulfate and dissolved methane concentrations are weakly negatively correlated (Figures S19a and S20) suggesting limited anaerobic methane degradation. On the other hand, nitrate is depleted when methane is present (Figure S22).

DIC values range from ~250 to ~500 mg/L (Table S1). $\delta^{13}C$ analyses of DIC were performed on 29 samples with detected methane in Parker and Hood counties. Values range from - 11.45‰ (#BS347) to -0.11‰ (#BS200) (median -6.98‰, average - 7.36 ‰). Samples with the highest $\delta^{13}C$ value of DIC also exhibit the highest DIC concentration. The opposite trend would be expected in case of significant methane or organic material oxidation suggesting that methane oxidation is minor. The trend is more likely because of dissolution of marine carbonate ($\delta^{13}C$~0) from the Glen Rose Fm.

In the Marcellus Shale area, some authors have postulated that methane concentration is, at least in part, a function of proximity to gas wells (Osborn et al. 2011; Jackson, Vengosh et al. 2013) or a function of topography (Molofsky et al. 2013). The Parker-Hood cluster lies in an area with small topographic relief limited to limestone bluffs and distance to nearest gas well does not seem to control dissolved methane distribution in the Barnett Shale (Figure 5, SI-4, and Table S9 for statistical results). Given the paucity of methane hits in the Barnett Shale footprint it is expected that a region-wide plot of dissolved methane vs. distance to the closest Barnett well will not be very informative (Figure S13a). Plots displaying methane vs. distance to Barnett and non-Barnett wells in Parker, Hood, and Somervell counties (Figures 5a, b and S13b) show that the highest methane concentration are not closest to gas wells—either Barnett or non-Barnett wells—and that methane concentrations do not increase monotonically as the sampling point approaches a gas well. Furthermore, if, instead of being plotted against distance to the nearest gas well, dissolved methane concentration is plotted against more integrated parameters such as gas well density and cumulative lateral length density of gas wells, one would expect to find areas with higher well density to present more cases of dissolved methane in groundwater. This is not observed as visually confirmed by mapping trace of well laterals with sampled water wells (Figure 5c, d). Plotting ethane concentrations and C1/C2+C3 ratios (Figure S15) confirms the lack of correlation with well density and cumulative lateral length density.

Discussion

In the following discussion, we show that the overall body of evidence, i.e., sampling results aided by earlier observations, strongly suggests a natural origin for the dissolved methane in the Parker–Hood cluster. Such conclusions are also supported by other observations by our group described elsewhere such as the heavy noble gas analysis (Wen et al. 2016) and the nitrogen isotope analysis (Nicot et al. 2015). Trying to prove a negative in this context, that is, that no oil or gas well ever leaked natural gas, is impossible; however, if a leak occurred, it was small enough not to noticeably alter the natural system. In other words, there is no need to invoke gas leakage to explain field observations. Structural and stratigraphic features explain the presence of thermogenic methane in shallow groundwater. We based this conclusion on the following points developed sequentially in this section:

- Close-by, documented very shallow gas accumulations in the Parker–Hood cluster area are the most likely sources of dissolved methane although there are other potential sources.
- Numerous historical and more recent observations of high dissolved methane concentrations in aquifers are all spatially located at the western edge of the Trinity Group where the Paleozoic formations are at or close to the ground surface.
- There is no strong correlation between dissolved methane concentration and distance to the nearest gas well (Figure 5). The correlation is even weaker when considering well density and lateral length density vs. distance to the nearest gas well. This is certainly true at the level of the entire Barnett Shale play but also in the Parker–Hood cluster area.
- Work by Wen et al. (2016) show that most well water with dissolved methane has not been exposed to a gas phase (that is, to a potential leakage event).

It is worth noting that some earlier observations made prior to this study apparently do not fit the natural methane model.

- An apparent increase in dissolved methane through time in several wells in the Silverado neighborhood, a spatial subset of the Parker–Hood cluster (RRC 2014).
- Methane in water wells with arguably no methane at the time of drilling (that is, not described in driller logs) (EPA 2013).
- The suggestion that the natural gas comes directly from the Barnett Shale through pathways combining hydraulic fractures and naturally occurring faults (RRC 2011; Myers 2012).

The following are potential sources of methane in the Barnett Shale footprint: (1) the Barnett Shale itself, which is the main source rock in the Fort Worth Basin; (2) reservoirs charged by hydrocarbons from the Barnett Shale, the reservoirs are mostly present at the edge of the basin; and (3) lignite and bituminous coal also present in the basin. Option (3) can be disregarded. There are no known abundant coal seams near the Parker–Hood cluster but such seams have been described in Palo County and further north (Mapel 1967; Evans 1974). Minor coal seams have been noted on water well driller logs in the Parker–Hood cluster. However, the thermogenic character of the dissolved gas is too marked. It is generally accepted that lignite- and bituminous coal-generating conditions are not favorable for producing thermogenic gas (Rice 1993).

Shallow gas accumulations have been documented in the Strawn Group in the Parker–Hood cluster area (Herkommer and Denke 1982; Ehlmann and Ehlmann 1985; IHS 2015). The small Center Mills field at a depth of 400 ft (120 m) produced gas in 1984-86 and is located less than a mile from the Silverado neighborhood (IHS 2015). Several studies have established that the dissolved gas present in water wells originated from shallow Strawn accumulations by examining nitrogen concentrations (Kornacki and McCaffrey 2014), noble gas compositions (Wen et al. 2016), nitrogen isotopes (Nicot et al. 2015), and a combination of parameters (Darrah et al. 2014). In particular, the noble gas content shows a long geological interaction with the Strawn sediments (Wen et al. in review). The dissolved gas does not originate directly from the Barnett Shale, but rather from the Strawn accumulations charged from the Barnett Shale.

There is substantial anecdotal information on methane seeps that are all located on the western edge of the Trinity Group (SI-5). The spatial correlation suggests that the presence of dissolved methane is related at least in part to local geology and natural processes, not industry practices. If that were not the case, one would expect dissolved methane to be more randomly distributed. The lack of hydrocarbon reservoirs at the vertical of the core area in Tarrant, Denton and Johnson counties suggests that most of the geological secondary gas migration from the Barnett Shale into the reservoirs occurred mostly horizontally along the regional dip direction.

The highest gas well densities are in Denton, Wise and Johnson counties. Because well density is comparatively low in Parker and Hood counties, it is not surprising that at the entire play level the relationship with gas well density is weak but it is also weak when considering only Parker and Hood county wells (Table S9).

Noble gas and nitrogen studies by our group (Wen et al. 2016; Nicot et al. 2015) have strongly suggested that the dissolved gas has not contacted a gas phase in most instances except when known shallow gas accumulations are nearby. Wen et al. (2016) looking at fractionation of heavy noble gas isotopes concluded that most water samples were never exposed to a gas phase. Nitrogen isotopes analysis (Nicot et al. 2015) suggests that only those water samples with documented gas flow in the subsurface show a gas flux high enough to shift the atmospheric signature of nitrogen isotopes in the direction of that of the deep-sourced nitrogen (#BS555;

#BS553 and #BS551; Lake Country Acres PWS), and #BS355. These samples show depletion in heavy noble gases and atmospheric nitrogen demonstrating that all the other samples cannot have a gas phase leakage as source.

Critical observation of data suggests that the low dissolved gas values, lower than earlier sampling (maximum of dissolved methane of 2.8 mg/L and ethane of 0.36 mg/L) observed between December 2010 and January 2011 were due to sampling limitations (see Table S6) negating a perceived increase in methane concentration in the months and years that followed (RRC 2014). Sampled wells show no change in order of magnitude in the dissolved methane content. However, at least one water well has been described as having contained no methane when drilled but now show high dissolved methane (#199). Some authors (Kreitler 2014) have proposed as an explanation that large water withdrawals would have progressively depressurized the aquifer leading to methane outgassing. Unfortunately, no heavy noble gas was sampled from this well to determine whether the water with dissolved gas had been exposed to a gas phase.

As documented above using multiple lines of evidence, the shallow dissolved gas is very likely sourced from the Strawn Group not the Barnett Shale and therefore likely did not use potential fast pathways between the Barnett Shale and the shallow subsurface.

There is also evidence of biodegradation. Kornacki and McCaffrey (2014) suggested that the light alkanes were biodegraded as documented by the shift towards heavier carbon isotopes of ethane and propane consistent with known behavior of microorganisms which favor ethane over methane and isotopically light molecules. Our observations are consistent with this hypothesis (Figure 6). Both dissolved methane $\delta^{13}C$ and δD and $\delta^{13}C$ of dissolved ethane and propane are distinct from their potential source in the Strawn and Barnett reservoirs. They show a clear biodegradation pattern with an increase in heavy carbon and hydrogen isotopes (e.g., Whiticar

1999) from initial Strawn values of - 47‰ and - 180‰ (C1 $\delta^{13}C$ and δD), - 34.5‰ (C2 $\delta^{13}C$), and - 31‰ (C3 $\delta^{13}C$) (Table S4). However, although bio-oxidation is likely, our current observations do not point out to abundant methane oxidation and do not clearly elucidate the predominant oxidation mechanisms.

Conclusions

Groundwater sampling (457 water well unique locations) in the footprint of the Barnett Shale confirmed the high dissolved methane values previously observed in the Parker County area (a subset of our Parker–Hood cluster) but also revealed that aquifers overlying the Barnett Shale generally have low to very low levels of dissolved methane except in localized areas. It is possible that there are other areas with elevated dissolved methane that we did not sample (northeast Palo Pinto County is such a case) but they are unlikely to be as large as the Parker–Hood cluster. When present, dissolved methane is clearly thermogenic with $\delta^{13}C$ ranging from -57.54‰ to -39.00‰ and C1/C2+C3 ratios ranging from 5 to 42 (10^{th} and 90^{th} percentiles, respectively). Companion analyses (Wen et al. 2016; Wen et al. in review) strongly point to Strawn shallow gas accumulations as the source of the dissolved gas that is supported by the circumstantial evidence presented in the paper: co-located high dissolved methane and shallow gas accumulations, numerous historical observations of dissolved methane at the western edge of the Trinity Group outcrops, weak to no correlation between dissolved methane and distance to gas wells, and possibly well-established methane biodegradation. It follows that the presence of high dissolved methane is almost certainly natural. A more extensive sampling campaign for heavy noble gas and nitrogen isotopes would be a significant step forward for removing any remaining ambiguity in the few Parker County water wells still the object of discussion at the national level (EPA SAB 2016).

Acknowledgments:

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. Sample locations and water quality results

Table S2. Dissolved gas characterization results

Table S3. Selected gas analytical results from gas wells

Appendix SI-1. General Geology and Hydrogeology

Appendix SI-2. Sampling and Chemical Analyses

Appendix SI-3. Summary of Previous Studies

Appendix SI-4. Additional Results

Appendix SI-5. Evidence of Natural Methane in the Barnett Shale Footprint

Please note: “Supporting Information” is generally *not* peer reviewed. Wiley is not responsible for the content or functionality of any supporting information supplied by the authors. Any queries (other than missing materials) should be directed to the corresponding author.

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Figure captions

Figure 1. Distribution of dissolved methane across the Barnett Shale play. Thin black line represents the eastern and northern structural boundaries of the Barnett Shale. Square with thick black line delimits the boundaries of Figure 2 domain. Each small red dot represents a Barnett Shale gas well; map includes 18,022 Barnett Shale horizontal and vertical wells that were drilled by the date the sampling ended. Core area is visible thanks to the high well density. A total of 457 unique sample locations are shown, some overlapping at this scale. County names are shown. Trinity Aquifer outcrop is shown in solid light green (that is, when at least one of the fresh water-bearing strata crops out); the fully confined section is depicted in stippled green (when older strata from the Trinity Aquifer are confined farther to the west of the displayed unconfined-confined line).

Figure 2. The spatial distribution of groundwater wells sampled for methane in the Parker–Hood cluster area as well as vertical (many plugged and abandoned) and horizontal gas well locations and traces of the well laterals. Note that the cluster of elevated methane is not co-located with the highest density of horizontal wells.

Figure 3. Bernard plot showing BEG water samples (purple dots). Symbol size is related to dissolved methane concentration. As indicated by the colored areas, attributes of thermogenic gas are low C1/C2+C3 ratio and isotopically heavy carbon and it plots on the lower right quadrant of the Bernard plot. On the other hand microbial gas is characterized by a high C1/C2+C3 ratio (i.e., very little ethane and higher alkanes) and isotopically lighter carbon and it plots on the upper left quadrant of the Bernard plot. Mixing lines between thermogenic and

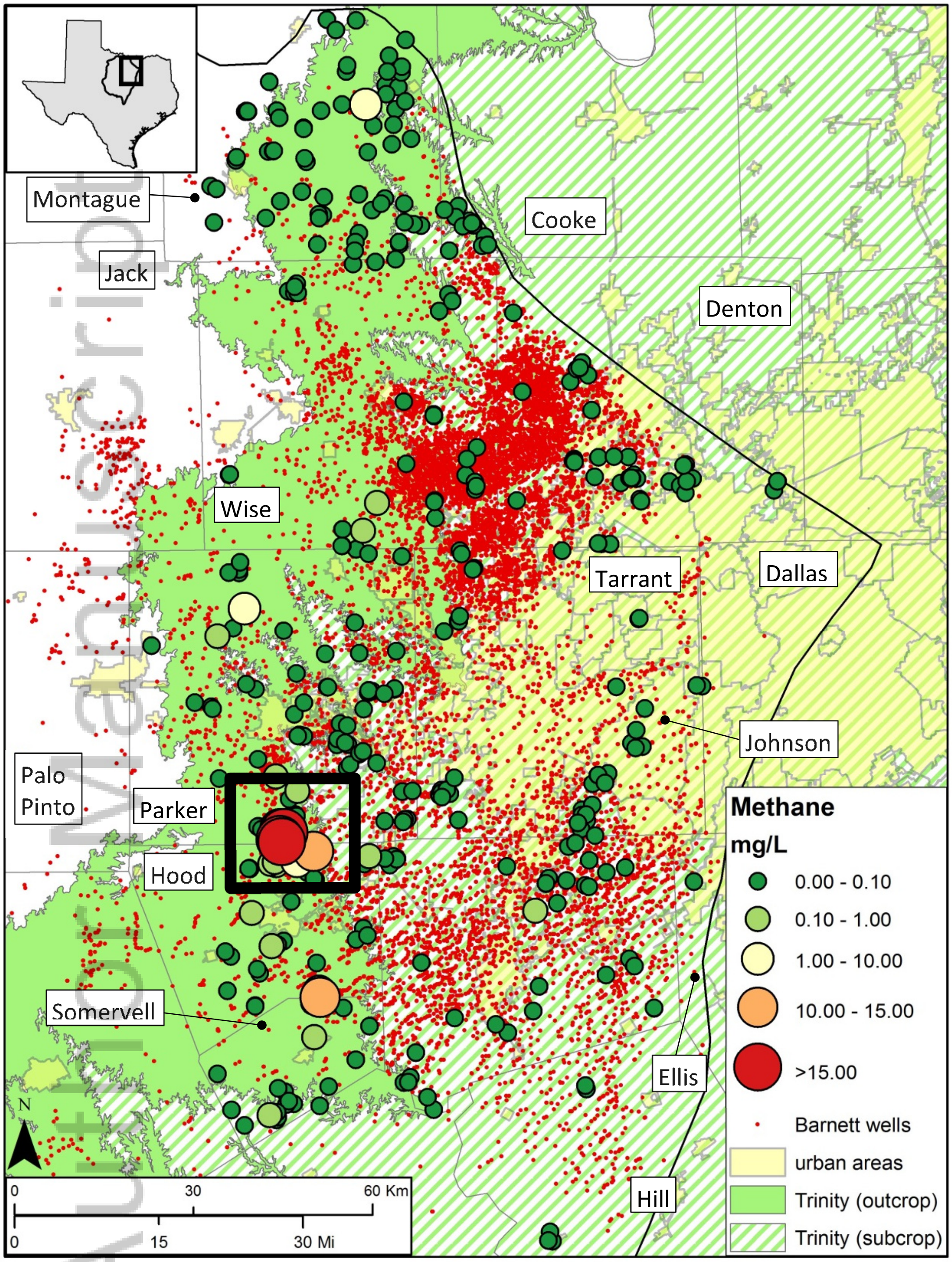
microbial endmembers go through the lower left quadrant whereas gas samples that underwent more complex processes such as migration and (bio) degradation map on the upper right quadrant. Parameters of gas wells are indicated by "+" (Strawn) and "×" (Barnett). Various sources are BEG (SI tables), Darrah et al. (2014), and RRC (2014) for the Teal and Butler wells, which were at the center of the RRC investigation. Figures S1 and S2 complement this plot with additional data taken from other sources.

Figure 4. Plots showing, as a function of the vertical distance to the Cretaceous unconformity (negative numbers mean distance below the unconformity): (a) dissolved methane concentration, (b) methane $\delta^{13}C$; and (c) dissolved gas C1/C2+C3 molar ratio. Circle size is proportional to methane concentrations. Note the different vertical scale in plot (a). A total of 242 water samples in Parker, Hood, and Somervell counties (that is larger than the Parker–Hood cluster) are plotted including 90 water samples with isotope analyses.

Figure 5. Dissolved methane concentration vs. (a) distance to closest horizontal Barnett, (b) distance to closest vertical non-Barnett wells, (c) gas well density, and (d) lateral length density in Parker, Hood, and Somervell counties.

Figure 6. Isotope plots of (a) methane δD vs. $\delta^{13}C$ and (b) $\delta^{13}C$ of propane vs. $\delta^{13}C$ of ethane (data in Tables S4 and S6 including repeat samples). Most samples but not all show an isotope shift of dissolved methane, ethane and propane towards heavy values. Dots of dissolved water samples are scaled by their methane concentration, whereas gas samples are not, with all samples

with methane <1.5 mg/l set a 1.5 mg/l to improve readability. Single-size black circles represent gas samples recently taken by BEG and earlier by RRC. Palo Pinto County Barnett Shale gas samples map separately from the Barnett Shale gas sampled in the Parker-Hood cluster area. BG7 and BG8 gas wells (neighboring wells) map away from the other gas well samples and show a higher methane fraction and decrease higher alkane fraction suggesting impact of biodegraded gas maybe coming from the bradenhead. Strawn gas sample is represented by the red circle. A single water well (#200) show $\delta^{13}C$ lighter than the source gas suggesting some mixing with minor microbial methane; the sample also shows degradation of ethane and propane. Note that low dissolved methane samples are more biodegraded than higher methane samples.


Montague
Jack
Cooke
Denton
Wise
Tarrant
Dallas
Johnson
Palo Pinto
Parker
Hood
Somervell
Ellis
Hill
Methane
mg/L
0.00 - 0.10
0.10 - 1.00
1.00 - 10.00
10.00 - 15.00
>15.00
Barnett wells
urban areas
Trinity (outcrop)
Trinity (subcrop)
N
0
30
60 Km
0
15
30 Mi

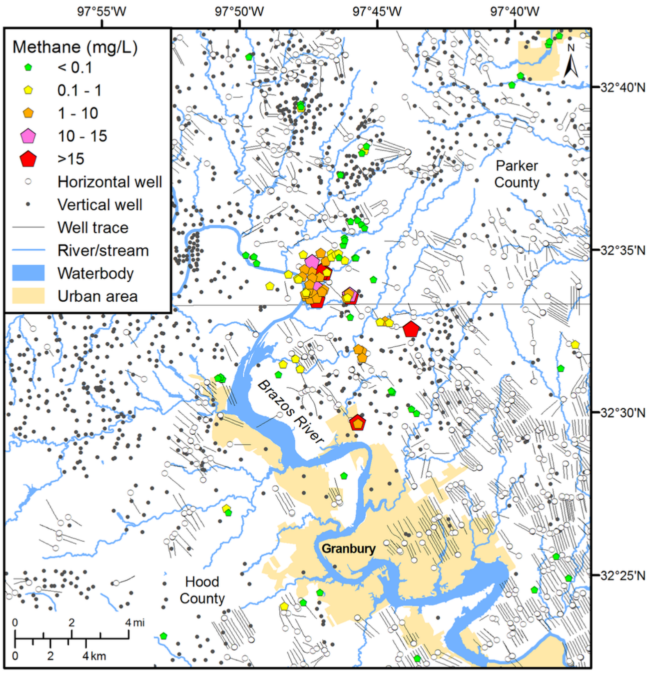


Fig. 2 BrazosRiver_Methane_08032016_300dpi.tif

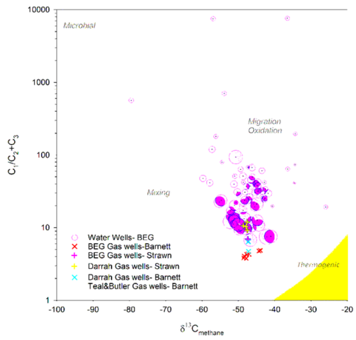
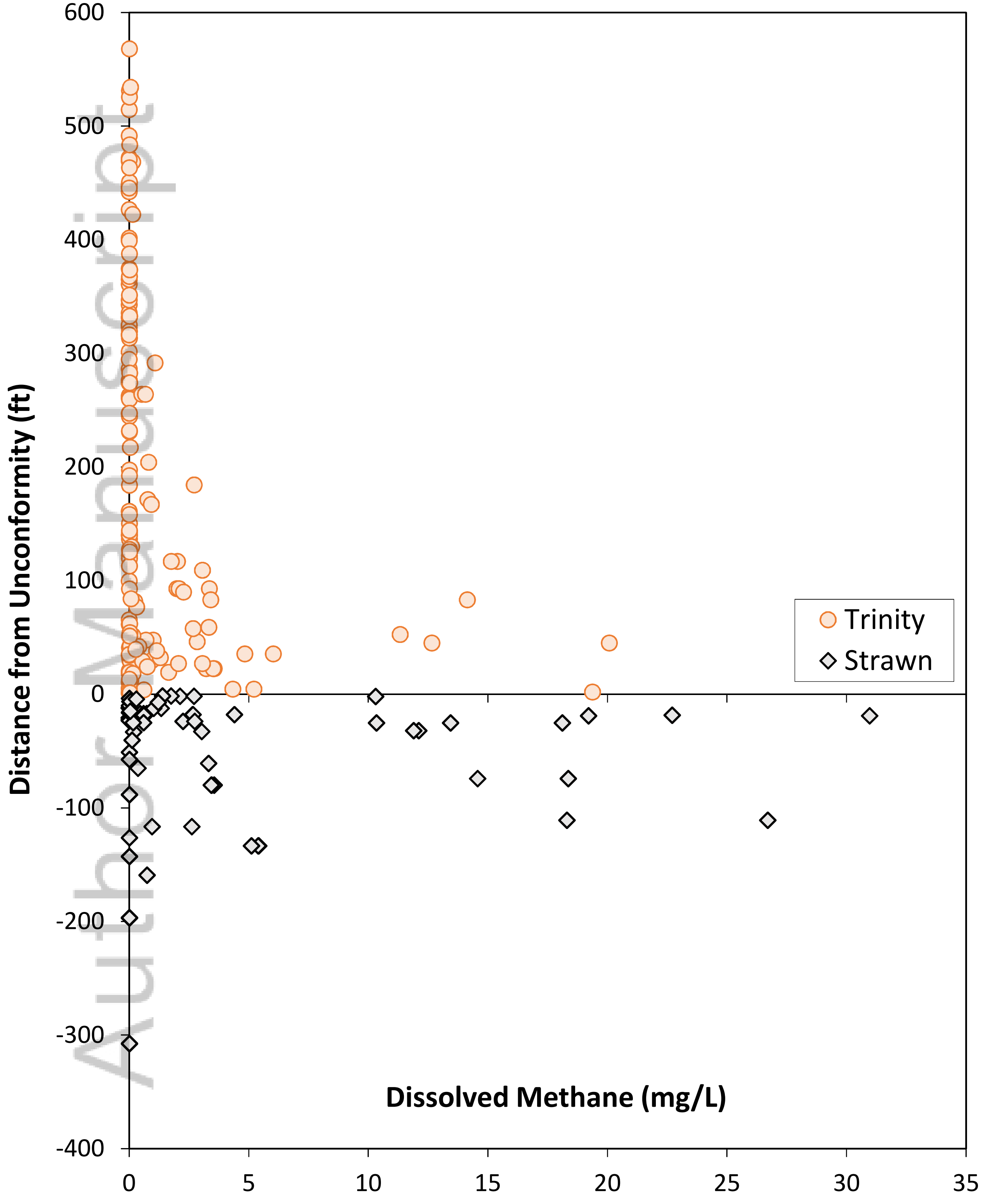
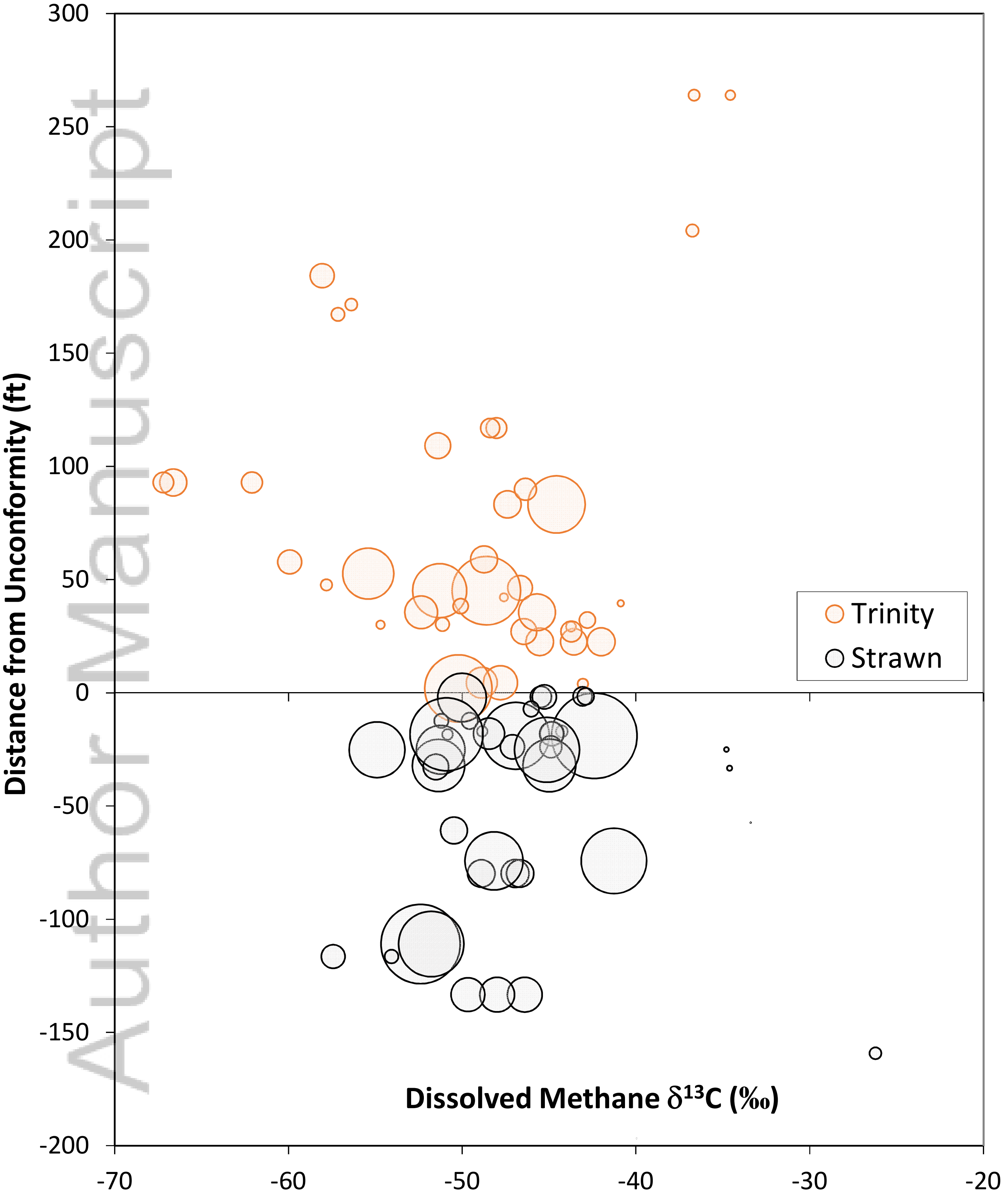
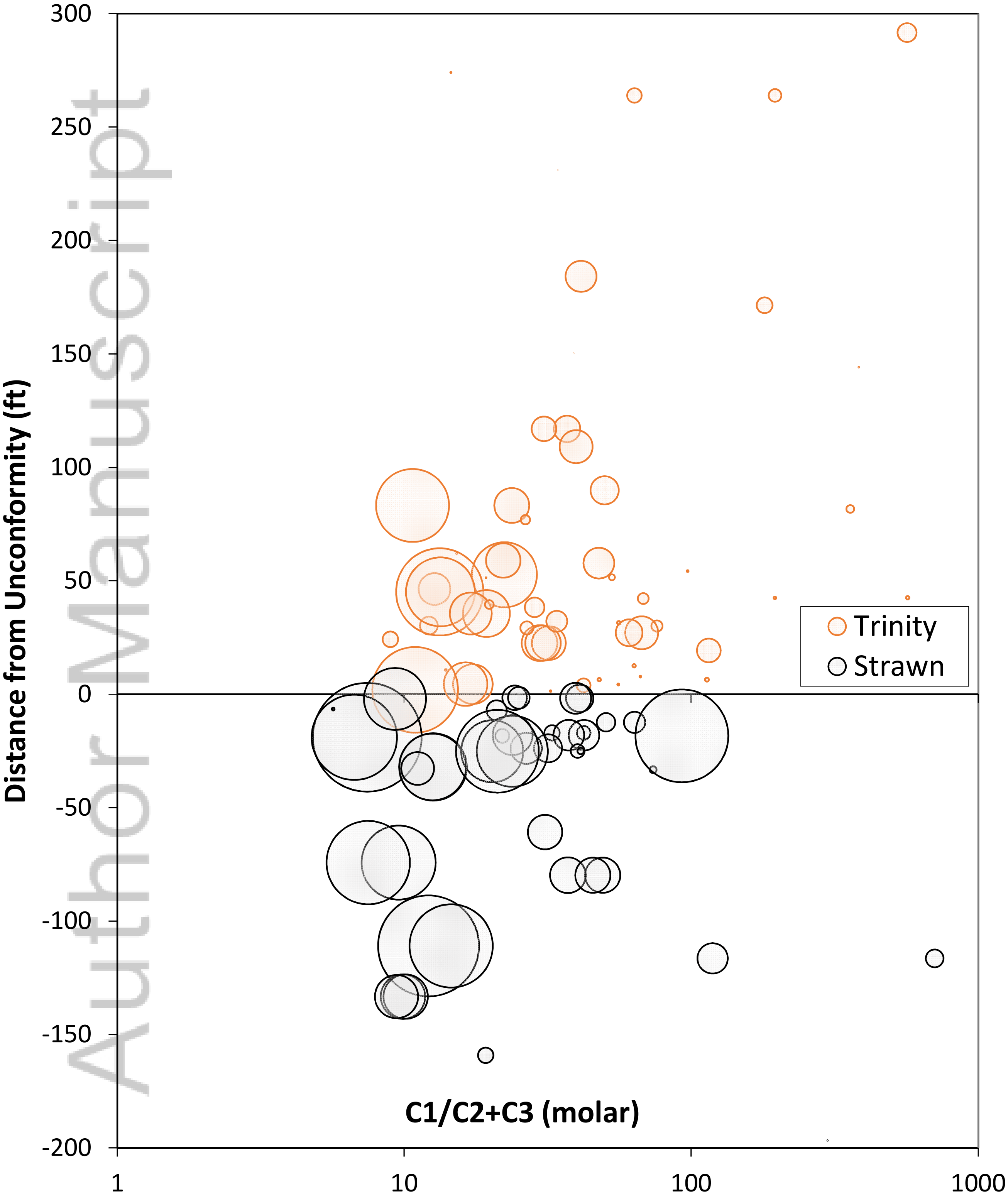


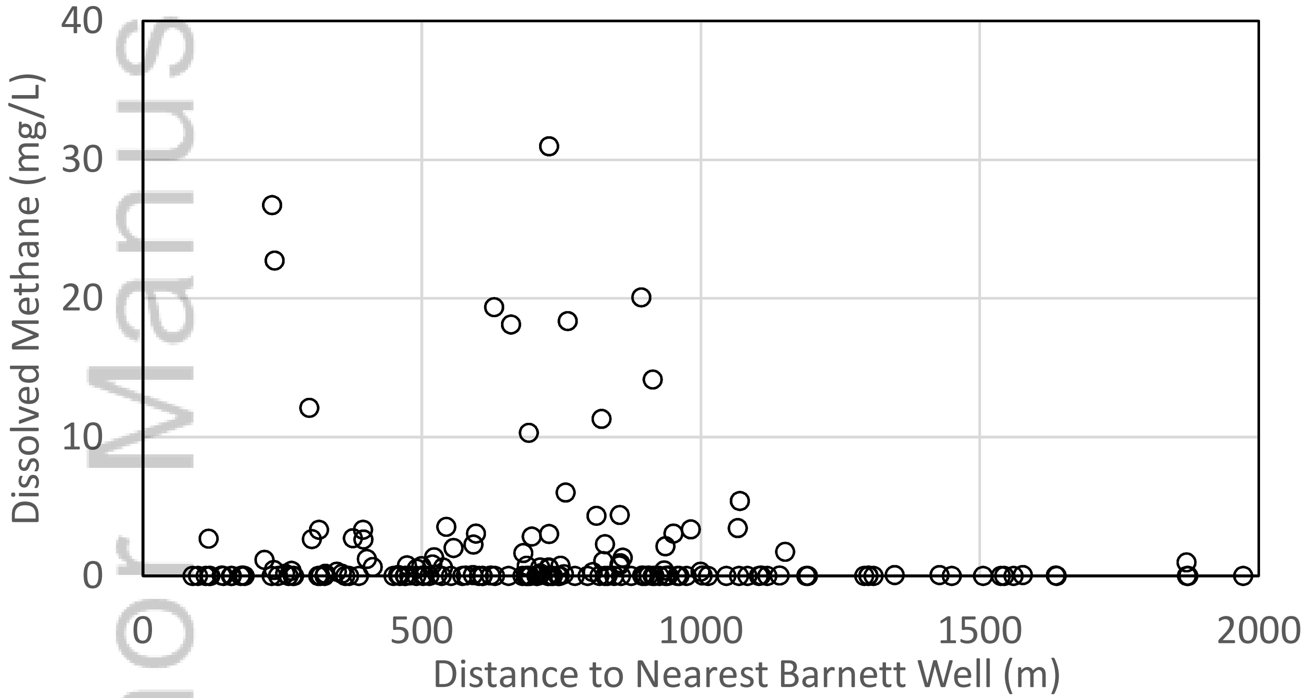
Fig. 3 bernardplot_Barnett.TIF


600
500
400
300
200
100
0
-100
-200
-300
-400
Distance from Unconformity (ft)
0
5
10
15
20
25
30
35
Dissolved Methane (mg/L)
Trinity
Strawn

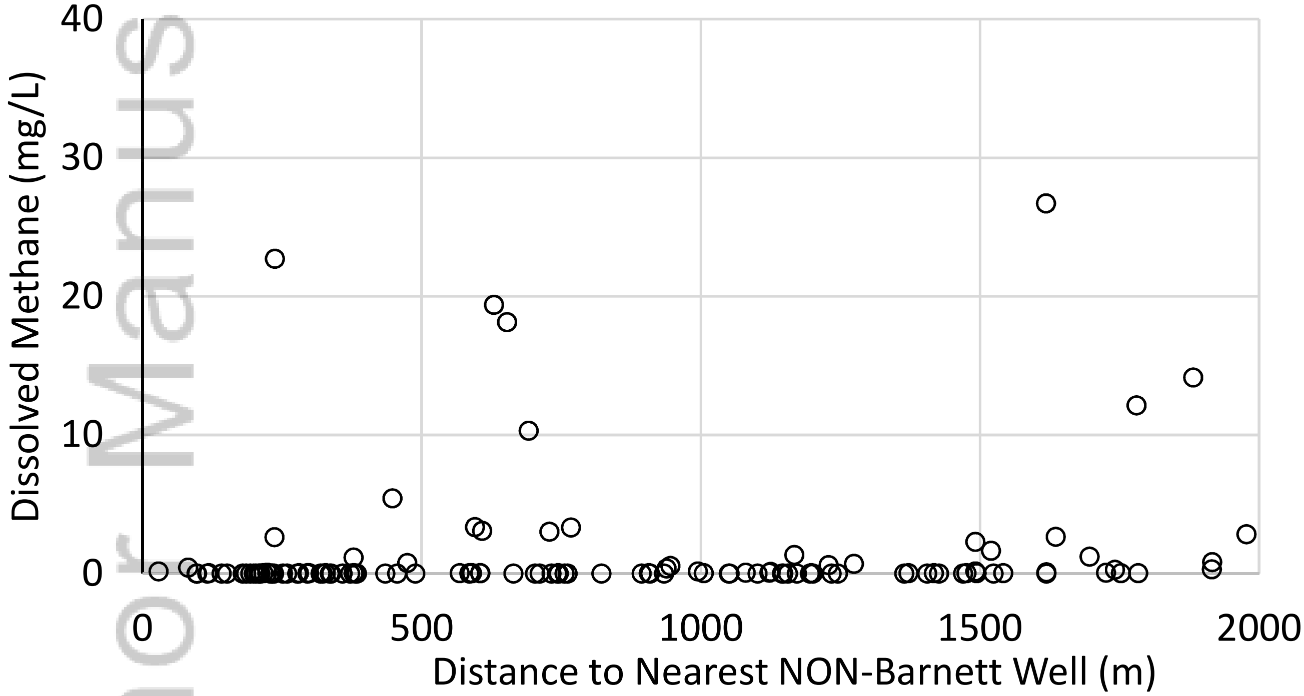

300
250
200
150
100
50
0
-50
-100
-150
-200
Distance from Unconformity (ft)
-70
-60
-50
-40
-30
-20
Dissolved Methane δ13C (‰)
Trinity
Strawn

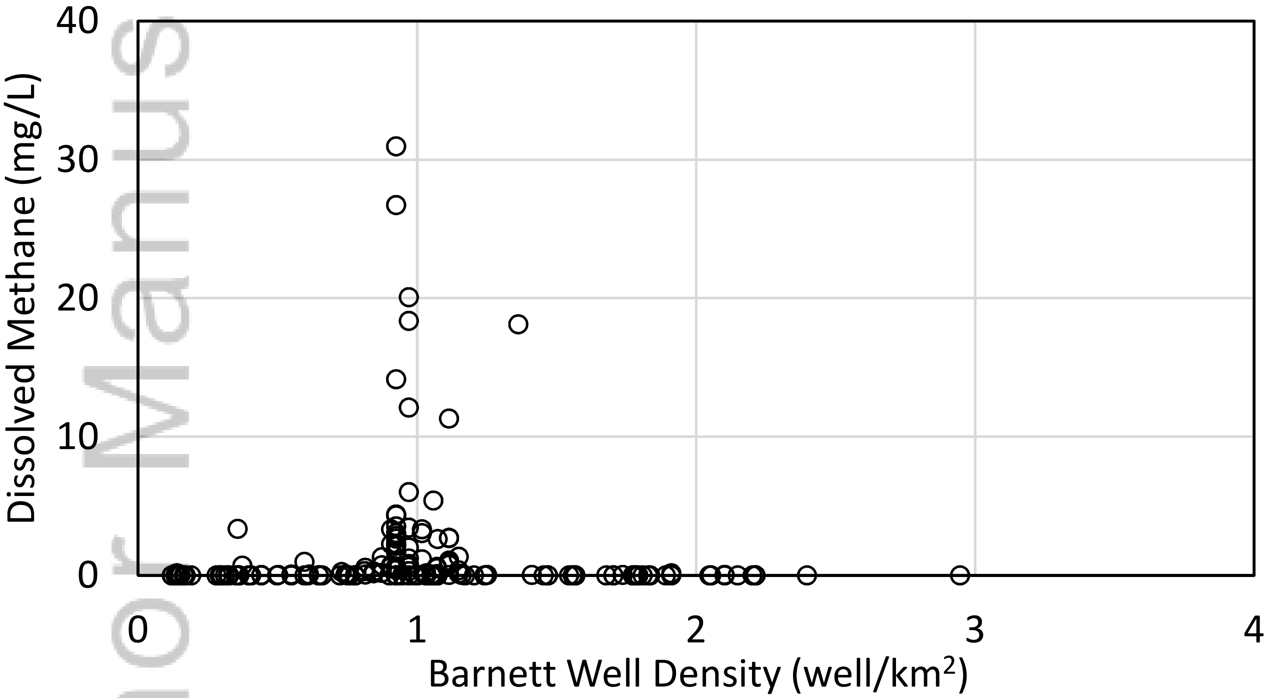


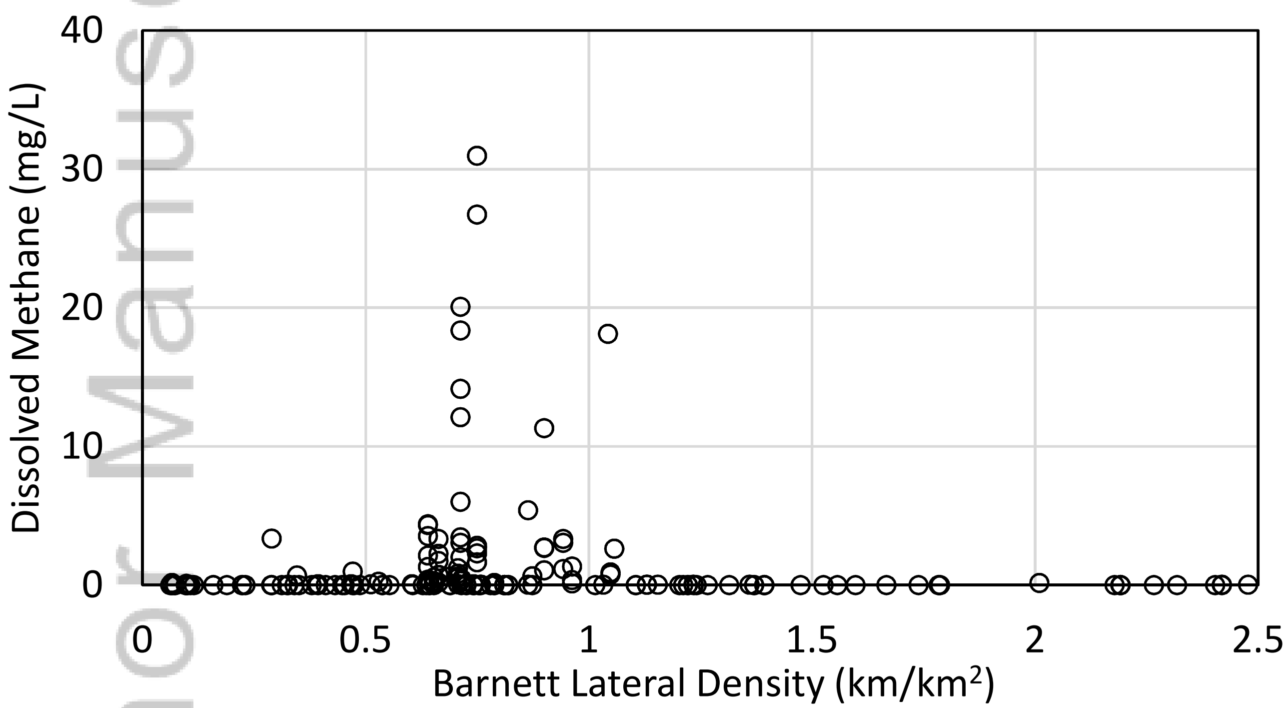
Distance from Unconformity (ft)
300
250
200
150
100
50
0
-50
-100
-150
-200
C1/C2+C3 (molar)
1
10
100
1000
Trinity
Strawn

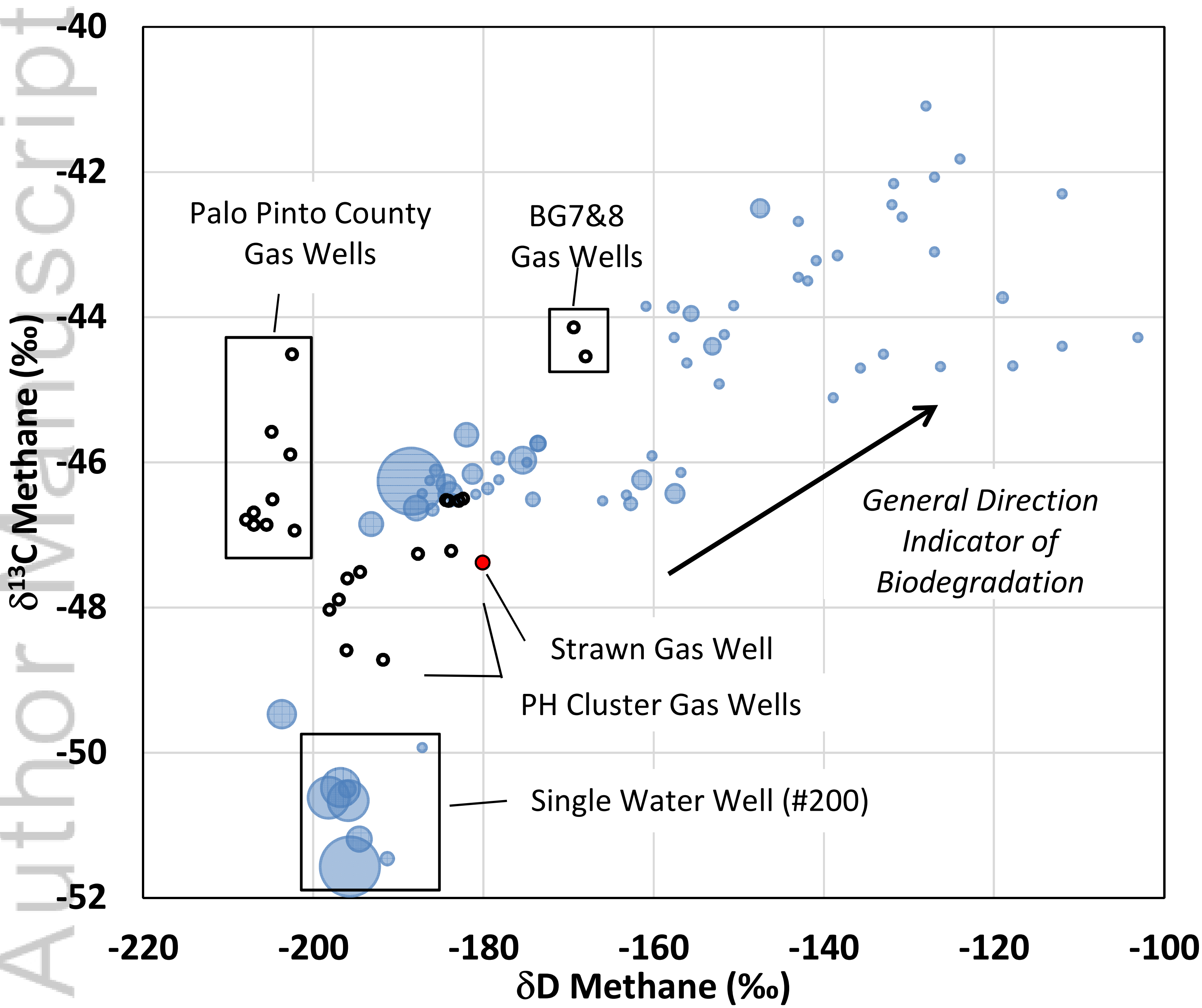


40
30
20
10
0
Dissolved Methane (mg/L)
0
500
1000
1500
2000
Distance to Nearest Barnett Well (m)

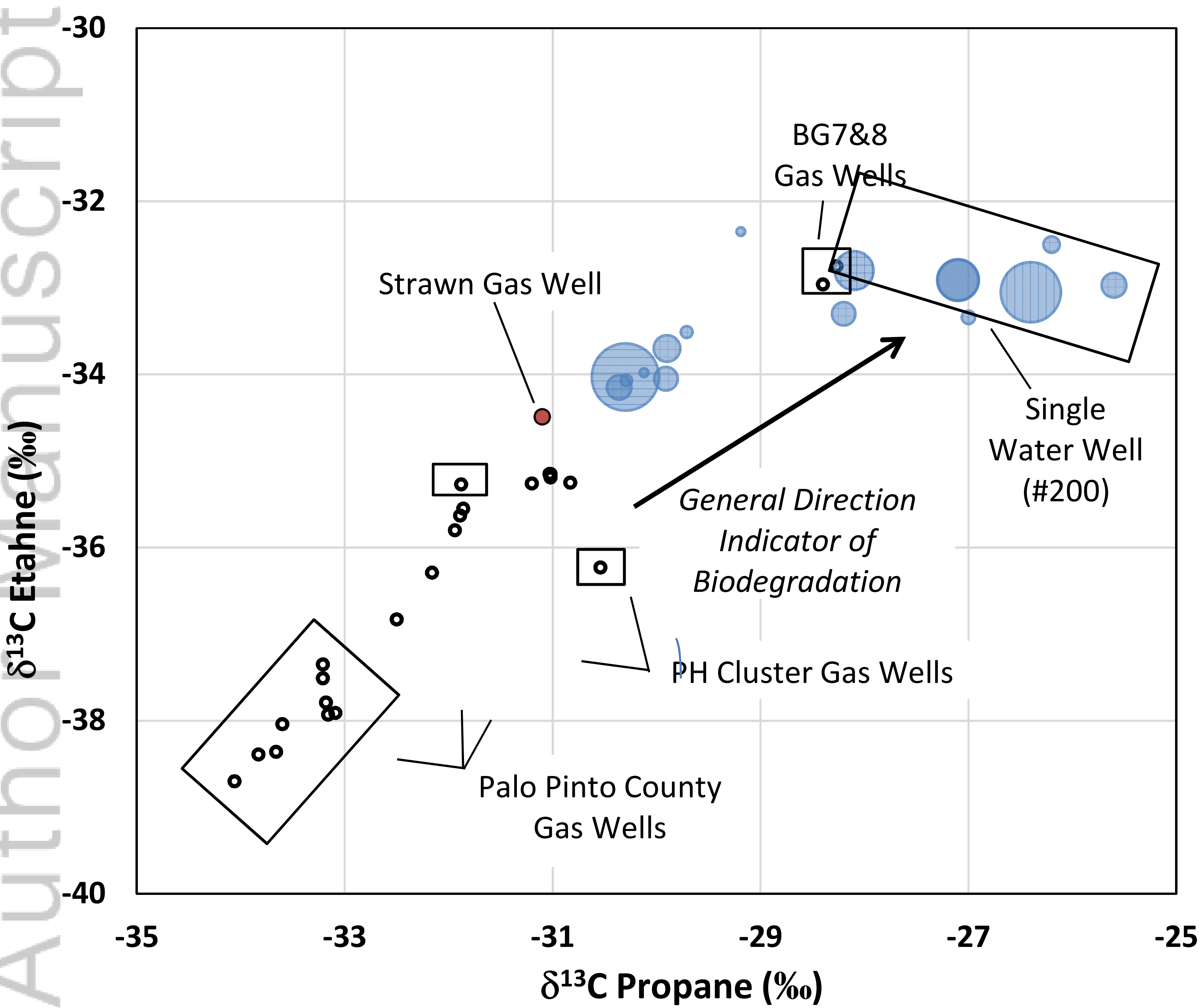

Dissolved Methane (mg/L)
40
30
20
10
0
0
500
1000
1500
2000
Distance to Nearest NON-Barnett Well (m)


40
30
20
10
0
Dissolved Methane (mg/L)
0
1
2
3
4
Barnett Well Density (well/km2)


40
30
20
10
0
Dissolved Methane (mg/L)
0
0.5
1
1.5
2
2.5
Barnett Lateral Density (km/km2)



Palo Pinto County Gas Wells
BG7&8 Gas Wells
General Direction Indicator of Biodegradation
Strawn Gas Well
PH Cluster Gas Wells
Single Water Well (#200)
-40
-42
-44
-46
-48
-50
-52
δ^{13}C Methane (‰)
-220
-200
-180
-160
-140
-120
-100
δD Methane (‰)



-30
-32
-34
-36
-38
-40
-35
-33
-31
-29
-27
-25
δ13C Etahne (‰)
δ13C Propane (‰)
BG7&8
Gas Wells
Strawn Gas Well
Single
Water Well
(#200)
General Direction
Indicator of
Biodegradation
PH Cluster Gas Wells
Palo Pinto County
Gas Wells