Methane Emissions from Conventional and Unconventional Natural Gas Production Sites in the Marcellus Shale Basin

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Supporting Information

ABSTRACT: There is a need for continued assessment of methane (CH$_4$) emissions associated with natural gas (NG) production, especially as recent advancements in horizontal drilling combined with staged hydraulic fracturing technologies have dramatically increased NG production (we refer to these wells as “unconventional” NG wells). In this study, we measured facility-level CH$_4$ emissions rates from the NG production sector in the Marcellus region, and compared CH$_4$ emissions between unconventional NG (UNG) well pad sites and the relatively smaller and older “conventional” NG (C$_n$NG) sites that consist of wells drilled vertically into permeable geologic formations. A top-down tracer-flux CH$_4$ measurement approach utilizing mobile downwind intercepts of CH$_4$, ethane, and tracer (nitrous oxide and acetylene) plumes was performed at 18 C$_n$NG sites (19 individual wells) and 17 UNG sites (88 individual wells). The 17 UNG sites included four sites undergoing completion flowback (FB). The mean facility-level CH$_4$ emission rate among UNG well pad sites in routine production (18.8 kg/h (95% confidence interval (CI) on the mean of 12.0—26.8 kg/h)) was 23 times greater than the mean CH$_4$ emissions from C$_n$NG sites. These differences were attributed, in part, to the large size (based on number of wells and ancillary NG production equipment) and the significantly higher production rate of UNG sites. However, C$_n$NG sites generally had much higher production-normalized CH$_4$ emission rates (median: 11%; range: 0.35—91%) compared to UNG sites (median: 0.13%; range: 0.01—1.2%), likely resulting from a greater prevalence of avoidable process operating conditions (e.g., unresolved equipment maintenance issues). At the regional scale, we estimate that total annual CH$_4$ emissions from 88 500 combined C$_n$NG well pads in Pennsylvania and West Virginia (660 Gg (95% CI: 500 to 800 Gg)) exceeded that from 3390 UNG well pads by 170 Gg, reflecting the large number of C$_n$NG wells and the comparably large fraction of CH$_4$ lost per unit production. The new emissions data suggest that the recently instituted Pennsylvania CH$_4$ emissions inventory substantially underestimates measured facility-level CH$_4$ emissions by >10—40 times for five UNG sites in this study.

INTRODUCTION

Methane (CH$_4$) emissions from the natural gas (NG) supply chain have attracted significant interest in recent years because CH$_4$, the principal component of NG (e.g., 76% to 92% CH$_4$ in produced NG$^5$), produces 30 times more radiative forcing than CO$_2$ over a 100-year time frame.$^2$ These CH$_4$ emissions may offset potential benefits of NG as a transition fuel between more carbon-intensive fossil fuels (e.g., coal) and renewable energy systems.$^3$—$^5$ Methane emissions from the NG production sector are of particular importance because of the large and increasing count of NG production wells which has yielded dramatic increases in the daily volumes of NG produced from NG shale basins in the U.S. in recent years.$^6$

Recent studies have focused on CH$_4$ emissions from unconventional NG (UNG) well pads.$^7$—$^{10}$ These UNG well pads produce NG from wells developed through horizontal drilling combined with staged hydraulic fracturing of tight, low permeability shale reservoirs. The focus on UNG wells (or well pads) reflects their rapidly growing importance in augmenting total NG production in several U.S. shale basins. For example, in the Marcellus Shale Basin, currently the largest producing shale basin in the U.S.,$^1$ UNG production reached 15.1 BCFD (billion cubic feet per day) in June, 2015,$^6$ representing a 99% increase from June, 2008.$^1$ A second category of NG production well pads that has attracted comparably little scrutiny is the “conventional” NG well pads (C$_n$NG—we use the $v$ subscript here to avoid confusion with the CNG abbreviation widely used to refer to compressed natural gas). These C$_n$NG well pads produce NG from wells developed through conventional, vertical drilling of more permeable reservoirs (e.g., conventional sandstone). In the Marcellus region, these C$_n$NG well pads exhibit markedly different characteristics compared to UNG well pads. First, each C$_n$NG well pad has, on average, one well per well pad.$^1$ In contrast, UNG well pads have between one to 11 active wells.
per well pad (average: 3 wells/well pad). The larger count of wells on UNG well pads allows for much higher rate of NG production volumes per well pad (e.g., an annual average of ∼1.5 billion cubic feet per UNG well pad versus ∼2.6 million cubic feet per CNG well pad in 2014). The larger rates of NG production require more ancillary NG production equipment (e.g., pneumatic controllers, condensate/produced water tank batteries), which are often significant sources of CH₄ emissions.⁷,⁸,¹²

CNG well pads are generally much older and produce NG at a much lower rate than UNG well pads. For example, in 2014, CNG wells in Pennsylvania were, on average, 16 years older than UNG wells. Finally, in 2014, the total count of routinely producing CNG well pads in Pennsylvania and West Virginia was 15 times and 70 times greater than the total count of routinely producing UNG well pads, respectively. These differences in the count of routinely producing well pads likely amplify differences in cumulative CH₄ emissions between the CNG and UNG well pads in the Marcellus region.

Most recent studies that have addressed CH₄ emissions in the Marcellus Shale region were based on airborne measurements and a first approximation (mass balance approach) that provided area or regional estimates of CH₄ emission fluxes. A challenge with these top-down studies is apportioning CH₄ emission estimates to the different sectors and sources. Facility-level data can be especially useful for understanding the sources of CH₄ emissions, such as characterizing differences in emissions between CNG and UNG well pads. However, few studies have measured per-well or facility-level production emissions in the Marcellus region. When combined with onsite surveys of potential CH₄ emissions sources (e.g., using forward-looking infrared camera), facility-level CH₄ emissions estimates can provide important details on site-specific CH₄ emissions characteristics that are often unavailable to top-down regional aircraft observations. Furthermore, measured facility-level CH₄ emissions data from NG production sites check bottom-up component-specific CH₄ emission measurements (e.g., Allen et al.) that are often used to develop CH₄ emission factors useful for estimating CH₄ emissions in statewide or national inventories. Thus, onsite observations of CH₄ emissions sources coupled with actual measured facility-level CH₄ emissions data can provide a benchmark for assessing the representativeness of inventory CH₄ emission factors for estimating total CH₄ emissions.¹⁷

This paper describes data from dual tracer flux measurements of facility-level CH₄ emission rates made at 18 CNG (19 individual wells) and 17 UNG (88 individual wells) NG production sites (including four completion flowback sites) in southwestern Pennsylvania and northern West Virginia (Supporting Information, SI, Figure S1). The main goals of this study were 3-fold: First, to investigate facility-level differences in (i) absolute CH₄ emissions and (ii) production-normalized CH₄ emissions (i.e., CH₄ emitted as a fraction of total CH₄ produced) between the CNG and UNG well pad sites. Second, using a probabilistic modeling scheme, we assess these CH₄ emissions differences at the regional scale to estimate the relative contribution of CNG production sites to total CH₄ emissions associated with NG production in the Marcellus region. Finally, we compare the new site-specific CH₄ emissions data with the official state of Pennsylvania CH₄ emissions inventory.

### METHODS

We used the downwind tracer flux measurements approach to measure facility-level CH₄ emissions. This is a well-established, top-down CH₄ measurement technique that utilizes atmospheric tracer(s) released at a controlled rate within close proximity to the CH₄ source.¹⁸,¹⁹ The approach used here is described in detail by Roscioli et al. and in the SI. Briefly, nitrous oxide (N₂O) and acetylene (C₂H₂) were emitted from single points and at known emission rates either onsite or at the fenceline of the target facility. Plumes of the two tracers and the target analytes (CH₄ and C₂H₆) were then measured 100 m to 1.2 km downwind using a mobile laboratory equipped with high time-resolution measurement instruments (1 Hz or faster, Aerodyne QC-TILDAS and Picarro cavity ring-down spectrometer). Controlled CH₄ release experiments conducted in a local park showed that the dual tracer flux measurements efficiently reproduced actual CH₄ emission rates, especially when the tracers were placed within 50 m of the CH₄ emission source(s) (Section S2).

At each site, an onsite observer used a forward-looking infrared (FLIR) camera to identify potential CH₄ sources. The results of these onsite assessments of CH₄ leak sources are presented in Table S6.

**Site Selection.** This study focuses on NG production well pad sites that were in either routine production or in the completion flowback (FB). Before routine UNG production commences, a drilled and hydraulically fractured UNG well must be cleaned of sand, water, and chemical additives previously injected to fracture the shale and liberate trapped hydrocarbons. During this “well completion” stage, water, sand, and chemical additives flow back to the surface, along with CH₄, C₂H₆, and other hydrocarbons entrained in the flowback liquids. After this FB period, the well typically enters routine NG production. We performed measurements of facility-level CH₄ emission rates at four UNG sites undergoing FB, 13 UNG sites in routine production, and 18 CNG sites in routine production. In total, 18 sites (3 FB, 9 UNG, 6 CNG) were sampled from four southwestern Pennsylvania counties (Beaver, Allegheny, Washington, and Greene; Figure S1), while 17 sites (1 FB, 5 UNG, 11 CNG) were sampled from Doddridge County in West Virginia (Figure S1).

A partner company provided onsite access to nine sites (3 FB, 6 UNG). The other 26 sites, owned by 17 operators in West Virginia and Pennsylvania, were characterized without company knowledge. Seventeen of these sites were located on property owned by volunteer members of the West Virginia Host Farms Program. The remaining nine sites were identified from the Pennsylvania Department of Environmental Protection (DEP) oil and gas reporting database.¹¹ All nine sites were located either in state parks or were within 50 m of a public road.

All sites were selected based on (i) downwind road access within 100 m to 1.2 km and (ii) absence of potentially interfering CH₄ sources and/or collocated nonpartner assets based on aerial imagery as seen on Google Earth. Final site selection was made on the day of measurement and was determined by local terrain and meteorology. Final site selection was not based on a measurable downwind CH₄ plume. Measurements at selected sites were performed between June 2014 and February 2015.

**Site Characteristics and Representativeness.** The selected UNG and CNG well pad sites exhibited a wide...
range in site-specific total gas production, facility age, and the count of total onsite equipment associated with NG production. Total UNG production per well for the day of measurement was provided by the study partner company for nine sites in Pennsylvania (3 FB, 6 UNG; Table S4). For these sites, the study partner company also provided gas composition for NG produced on the day of measurement, which averaged approximately 77% \( \text{CH}_4 \) and 14% \( \text{C}_2\text{H}_6 \) (Table S4). For all other sites, the rate of daily NG production was estimated from (i) publicly available monthly UNG and C\(_2\)NG production data for West Virginia NG wells,\(^5\) or (ii) publicly available monthly (2015) UNG production data and annual C\(_2\)NG production data for Pennsylvania NG wells.\(^11\) It was assumed the daily rate of NG production did not vary over the reporting period. For these sites, the production-normalized \( \text{CH}_4 \) emissions (i.e., \( \text{CH}_4 \) emitted as a fraction of total \( \text{CH}_4 \) produced) were estimated assuming 83.1% and 81.0% \( \text{CH}_4 \) content in UNG (2015) UNG production data and annual C\(_2\)NG and Gas databases for West Virginia\(^13\) and Pennsylvania.\(^11\) The reported spud dates of the producing NG wells found in the Oil storage tank (Table S5).

Consisted of one wellhead, one separator, and one liquids burner units (Table S5). In contrast, the \( \text{CH}_4 \) emissions from other sites included, on average, approximately 55% of total UNG produced in 2014 (Figure S3).\(^11\)

For each site, the average \( \text{CH}_4 \) emission rate was calculated by averaging results from each plume weighted by its plume-type uncertainty (1/$\sigma^2$, additional details in the SI). The uncertainty associated with the weighted average facility-level \( \text{CH}_4 \) emission rate was calculated as the unbiased sample variance of the mean using Bessel’s correction. All measured \( \text{CH}_4 \) emissions results are expressed in kg \( \text{CH}_4 \)/h (1 kg/h \( \text{CH}_4 \) = 0.866 SCFM (standard cubic feet per minute) \( \text{CH}_4 \) at 15.6 °C and 1 atm).

**Statistical Methods.** To develop an estimate of the mean \( \text{CH}_4 \) emission rate and regional \( \text{CH}_4 \) emissions, \( \text{CH}_4 \) emissions probabilistic distribution models that adequately reproduce the skewness in the \( \text{CH}_4 \) emissions distribution profiles were used. These models were constructed by fitting emissions data from individual plumes (\( n = 79 \) and \( n = 67 \) accepted plumes for C\(_2\)NG and UNG sites, respectively) to a suite of probabilistic distribution models (Lognormal, Weibull, Inverse Gaussian, Exponential, Generalized Extreme Value, and Generalized Pareto) in MATLAB. These models were sorted using the Bayesian Information Criterion (BIC) and Akaike Information Criterion (AIC) and further assessed by examining the quantile-quantile plots (Section S4). A log-normal distribution (BIC = 124.1; AIC = 119.3; "log location" = −0.975; "log scale" = 1.33) and an inverse Gaussian distribution (BIC = 483.9; AIC = 479.5; "scale (\( \mu \))" = 18.7; "shape (\( \lambda \))" = 3.95) provided the best fit to \( \text{CH}_4 \) emissions data for the C\(_2\)NG and UNG sites, respectively (additional details in the SI). The best-fit probability distribution models were used to estimate the mean facility-level \( \text{CH}_4 \) emission rate and associated uncertainty bounds (95% confidence interval (CI) on the mean). For each production category (i.e., C\(_2\)NG or UNG), data drawn from the fitted distribution were resampled, with replacement, to yield 10\(^4\) bootstrap samples, each of the same size as the empirical data set. The mean facility-level \( \text{CH}_4 \) emission rate was then calculated as the average of averages obtained from 10\(^4\) samples and the 95% CI on the mean was calculated from the respective 2.5\(^{\text{th}}\) and 97.5\(^{\text{th}}\) percentiles.

The 10\(^4\) bootstrap samples represent a large data set of resampled facility-level \( \text{CH}_4 \) emissions distribution with a 95% confidence bound that captures the uncertainties in the sampling methodology and variabilities in site-specific \( \text{CH}_4 \) emissions. From this large resampled data set, bootstrap samples with distributions representative of the mean, the 2.5\(^{\text{th}}\)
and the 97.5th percentiles were fitted to appropriate parameterized CH₄ emissions distribution models as previously described (Table S7, Figure S20). To estimate regional CH₄ emissions, facility-level CH₄ emission rates were randomly drawn from these distributions for n NG well pad sites in each production category, where n represents the total count of well pad sites in the region (Section S4). The simulation was repeated 10⁸ times, and the results were averaged to give a central estimate of total CH₄ emissions and uncertainty bounds for each category of production sites. The total count of sites was obtained by grouping individual NG wells (C,NG or UNG wells) in the Pennsylvania¹¹ and West Virginia¹³ databases based on operator-provided geospatial and production information. Multwell pads were accounted for by assuming a cluster of wells within 75 m of each other originated from one well pad (additional information in the SI). In Pennsylvania, 2760 UNG and 43,900 C,NG sites were identified. In West Virginia, 630 UNG and 44,600 C,NG sites were identified.

### RESULTS AND DISCUSSION

**Facility-Level Methane Emission Rates.** Absolute facility-level CH₄ emission rates were highest among the FB and UNG sites and lowest among the C,NG sites. Among the FB sites, absolute facility-level CH₄ emission rates ranged from 5.6 ± 1.1 (1σ) kg/h to 46 ± 8.5 (1σ) kg/h (Figure 1). Among the routinely producing well pad sites, absolute facility-level CH₄ emission rates varied by more than 3 orders of magnitude, with UNG sites exhibiting generally higher CH₄ emissions (range: 0.85 ± 0.40 (1σ) to 92.9 ± 47.5 (1σ) kg/h) compared to C,NG sites (range: 0.02 ± 0.01 (1σ) to 4.48 ± 1.33 (1σ) kg/h; Figure 1). Approximately two-thirds (61%) of C,NG sites emitted less than 1.0 kg/h CH₄. In contrast, average CH₄ emissions greater than 20 kg/h were observed at three (23%) of the 13 UNG sites (Figure 1). At most sites, plume-to-plume variability in individual estimates of CH₄ emissions was defined by a median coefficient of variation (CV) of 36%, in which approximately two-thirds (63%) of all sites had CVs < 50%.

A one-way ANOVA evaluation of the log₁₀-transformed CH₄ emission rates showed significant differences in facility-level CH₄ emissions between the C,NG and UNG sites (p < 0.0001). UNG sites (mean: 18.8 kg/h/site; 95% CI on the mean: 12.0—26.8 kg/h/site) emitted approximately 23 times more CH₄ than C,NG sites (mean: 0.82 kg/h/site; 95% CI on the mean: 0.59—1.1 kg/h/site). However, on a production-normalized basis (i.e., CH₄ emitted as a fraction of total CH₄ produced), C,NG sites generally had higher production-normalized CH₄ emission rates (median: 10.5%; range: 0.35—91%) compared to UNG sites (median: 0.13%, range: 0.01—1.2%; Figure 1). These CH₄ emission differences are likely attributable to a variety of factors, including (i) variability in the rate of total NG production, (ii) facility age, (iii) the engineering design of the facility (e.g., utilization of emission capture/control devices), and/or (iv) well operator practices (e.g., the level and frequency of site inspection and maintenance).

**Variability in Emissions with Site-Specific Total Gas Production.** Sites with larger rates of NG production (UNG sites) exhibited generally higher absolute CH₄ emissions. Approximately 31% of the variability in absolute CH₄ emissions among routinely producing UNG sites was explained by linear regression with site-specific total NG production (slope = 0.57, r² = 0.31). Among C,NG sites, the variability in site-specific total NG production explained only 6% of the variability in CH₄ emissions (linear regression, slope = 0.31, r² = 0.055). However, when all the sites were combined, approximately 55% of absolute CH₄ emissions were correlated with site-specific total NG production (slope = 0.38, r² = 0.55; Figure 2A). Additionally, an inverse relationship between production
normalized \( \text{CH}_4 \) emissions and total NG production was observed \((r^2_{adj} = 0.77)\), but with large scatter within each production category (Figure 2B). These relationships between \( \text{CH}_4 \) emissions and production (or NG throughput) have also been reported in recent studies.\(^8,20\)

The stronger relationship between absolute \( \text{CH}_4 \) emissions (or production-normalized \( \text{CH}_4 \) emissions) and site-specific total NG production for all study sites \((\text{C}_\text{NG} \text{ and UNG})\) reflects the wide range in site-specific total NG production \((0.68 - 78,024 \text{MSCF/D})\) for a small set of selected NG sites \((n = 35)\). It also suggests that, within each production category \((\text{C}_\text{NG} \text{ or UNG})\), there are many sources of \( \text{CH}_4 \) emissions that are independent of site-specific rates of total NG production. For example, emissions from continuous high (or low) bleed pneumatic controllers that result from the normal functioning of the NG equipment are likely to be relatively consistent regardless of the site-specific rate of NG production. Also, as discussed below, there likely are site-specific operating conditions \((e.g., \text{avoidable equipment maintenance issues})\) that may yield higher measured \( \text{CH}_4 \) emissions, regardless of the site-specific rate of NG production.

There are other \( \text{CH}_4 \) emissions sources that vary with facility size. Sites with large rates of NG production typically have larger count of wells and ancillary equipment \((\text{e.g., gas production units, condensate tank batteries, emission control equipment, and pneumatics; Table S5})\), each of which is a potential source of \( \text{CH}_4 \) emission (Table S6).

The onsite infrared camera surveys suggest that venting/off-gassing from liquids storage tanks were an important source of emissions. Substantial emissions were observed from condensate/produced water tank batteries at 19 sites (Table S6). Other important emissions were from pneumatic controllers \((\text{Table S6})\) and leaks from onsite NG production and emissions capture/control equipment \((e.g., \text{gas production units, enclosed burner, and vapor recovery units})\). These results are consistent with \( \text{CH}_4 \) emission sources observed in recent studies of the NG production and gathering and processing sectors.\(^7,8,20,21\)

**Variability in Emissions with Facility Age.** We found that for all the selected sites, both the rate of NG production \((\text{slope} = -2.5; r^2_{adj} = 0.77)\) and absolute \( \text{CH}_4 \) emissions \((\text{slope} = -0.98; r^2_{adj} = 0.44)\) were negatively correlated with facility age \((\text{Figure S17})\). That is, the newer \((\text{UNG})\) sites are larger in size and produce NG at a greater rate than the relatively older and smaller \((\text{C}_\text{NG})\) sites, with comparably higher associated \( \text{CH}_4 \) emissions. However, a multilinear regression using log\(_{10}\) normalized production and facility age as independent variables revealed that production was the significant variable \((p = 0.01)\), while facility age was not significant \((p = 0.99)\) in predicting site-level \( \text{CH}_4 \) emissions.

Some of the \( \text{C}_\text{NG} \) well pad components appeared decrepit \((e.g., \text{Figure S16})\) and poorly inspected and maintained relative to the UNG well pad infrastructure. Equipment inspection and maintenance are regularly performed at UNG well pads \((e.g., \text{daily, Personal communication with well attendant at site #6})\), which increases the likelihood of promptly identifying and resolving issues pertaining to equipment integrity and performance. However, well inspection and maintenance at \( \text{C}_\text{NG} \) well pads is much less frequent. Mechanical integrity assessments are required on a quarterly basis for \( \text{C}_\text{NG} \) wells in Pennsylvania, while West Virginia mandates an annual assessment, with particular emphasis on mitigating “significant leakages” and “casing integrity failure” \((\text{WV Title 35 Legislative Rule, § 35-4-11.6})\).

\( \text{C}_\text{NG} \) sites that exhibited signs of aging infrastructure and had known maintenance issues were among the highest emitting \( \text{C}_\text{NG} \) sites \((\text{Table S6})\). Some examples of specific sources of \( \text{CH}_4 \) losses at these \( \text{C}_\text{NG} \) sites included fugitive leaks from loose fittings on an aging field piping junction \((\text{facility #20})\), malfunctioning pressure regulator \((\text{#25})\), and leaks from rusted piping at a wellhead base \((\text{#29}; \text{Table S6})\). In general, the \( \text{CH}_4 \) emissions from these \( \text{C}_\text{NG} \) sites were greater than 5% of the site-specific total \( \text{CH}_4 \) production \((\text{Figures 1 and 2}; \text{Table S6})\). These results suggest that well operator practices \((e.g., \text{the frequency of well inspection and maintenance})\) may exert a significant impact on facility-specific \( \text{CH}_4 \) emissions, and support the observation that a potentially substantial fraction of observed \( \text{CH}_4 \) emissions is linked to avoidable maintenance issues.\(^8,20,22,23\) Finally, the \( \text{CH}_4 \) emissions resulting from equipment maintenance issues that can be resolved through operator interventions would not necessarily be linked to the site-specific rate of NG production, and likely explains some of the scatter within each production category in Figure 2.

To the best of our knowledge, this study presents the first comprehensive assessment of facility-scale \( \text{CH}_4 \) emissions from \( \text{C}_\text{NG} \) well pad sites in the Marcellus region. Precise comparisons of site-specific UNG \( \text{CH}_4 \) emission rates with literature data are limited by differences in measurement methodologies \((e.g., \text{ground-based mobile measurements versus airborne measurements})\), sample population, and characteristics of sampled sites \((\text{Table S8})\).\(^7,9,14-16\) Nevertheless, \( \text{CH}_4 \) emissions rates for routinely producing UNG sites in this study are within the wide range of results obtained in previous studies in the Marcellus region \((\text{Table S8})\). For example, at the facility scale, Goetz et al.\(^7\) reported \( \text{CH}_4 \) emissions from three UNG sites that ranged from 3.4 ± 3.3 \((1\sigma)\) to 14.2 ± 20.4 \((1\sigma)\) kg/h/site and are comparable to facility-level UNG \( \text{CH}_4 \) emissions in this study \((\text{Table S8})\).

**Emissions from Flowback Sites.** Measurements at the four UNG sites undergoing completion FB were conducted between June 2014 and October 2014 before the implementation of the New Source Performance Standard \((40 \text{ CFR Part 60, Subpart OOOO})\). Subpart OOOO went into effect on January 1, 2015, and requires “green completions.” In “green completions,” FB gases and condensates from hydraulically fractured wells must be separated from FB fluids and delivered to storage equipment or pipeline for productive use or sale, thereby eliminating direct venting and minimizing flaring. Three of the four FB sites \((\text{#2, #3, and #4})\) were “green completion” sites. These three sites also utilized vapor recovery units \((\text{VRUs})\) on condensate tanks and recovery units to recover flash losses and/or vapor losses associated with normal tank usage. Measured site-level \( \text{CH}_4 \) emission rates at these “green completion” sites ranged from 5.6 ± 1.0 \((1\sigma)\) to 15.2 ± 5.2 \((1\sigma)\) kg/h \((\text{Table S4})\). FLIR camera surveys indicated that \( \text{CH}_4 \) emission sources at these sites originated primarily from pneumatic controllers on VRUs.

FB site #1 exhibited the largest observed \( \text{CH}_4 \) emission rate of 46.4 ± 8.5 \((1\sigma)\) kg/h \((\text{among FB sites; Table S4})\) that resulted from substantial gas flaring on the day of measurement. Site #1 differed from the other three FB sites in that the FB configuration involved direct flaring of FB gases. Although our sample size is small \((n = 4)\), these results suggest that “green completions,” in which FB gases are separated from fluids, metered and sent to sales, can substantially reduce FB \( \text{CH}_4 \) emissions. These results are consistent with observations by Allen et al.\(^7\) who found that the lowest per-well \( \text{CH}_4 \) emissions \((e.g., \sim 3 \text{ kg/h for a well in Appalachia})\) were associated with
green completions.” Both Allen et al.7 and Goetz et al.9 also reported high FB CH₄ emissions (>50 kg/h) that were associated with wells or FB sites that directly flared or vented FB gases.

**Distribution of Methane Emissions.** The facility-level CH₄ emissions data collected here were highly skewed, with a subset of sites contributing the majority of emissions. For example, we found that three (or 17% of) CNG sites (>2.8 kg/h/site) accounted for 50% of aggregate CH₄ emissions (Figure 3). Even more asymmetry was observed for the routinely occurring or vented FB gases.

The facility-level CH₄ emissions distribution was a highly skewed fat tail with a long tail, which is indicative of a distribution with a small number of large contributors. This is consistent with previous studies that have shown that a small fraction of sites contribute a disproportionately large fraction of cumulative CH₄ emissions.8,10,24

Recent studies have also shown that CH₄ emissions from NG production sites are highly skewed, with a small fraction of sites contributing a disproportionately large fraction of cumulative CH₄ emissions.8,10,24 However, small sample sizes may not fully capture the “fat tail” of the CH₄ emissions distribution. We compared the UNG site-level CH₄ emissions distribution in the present study with the distribution reported by Rella et al.10 who sampled 115 well pad sites with detectable CH₄ emissions in the Barnett Shale region. The well pad sites from both studies showed similarities in the distribution of site-specific NG production and site-level CH₄ emissions. First, the top 20% of sites in both studies accounted for roughly 60% of cumulative NG production. Second, the CH₄ emissions distributions in the present study were similar to the distribution from a much larger data set reported by Rella et al.10 (Figure 3). For example, the top 20% of the sites contributed approximately 74% and 78% of aggregate CH₄ emissions from sites in the Rella et al.10 and present study, respectively (Figure 3). However, as further discussed below, there are potential methodological biases that contribute to additional uncertainties, especially when total regional CH₄ emissions are estimated from a limited sample of measured facility-level CH₄ emissions.

**Estimation of Total Methane Emissions from NG Production Sites in the Marcellus Region.** In this section,

On a production-normalized basis, two UNG sites (#6 and #15) and three CNG sites (#s 19, 28, and 31; Table S4) exhibited production-normalized CH₄ emissions that were greater than the 85th percentile within each production category (i.e., > 45% and 0.62% CH₄ emissions for CNG and UNG, respectively). These sites can be described as functional superemitters, following the criterion suggested by Zavala-Araiza et al.24 for NG production sites.

These functional superemitters did not necessarily have the highest absolute CH₄ emission rates. For example, only one (#6) of the three highest emitting UNG sites was characterized as a functional superemitter. These functional superemitters contribute approximately 18% and 35% of aggregate absolute CH₄ emissions among the sampled CNG and UNG sites, respectively. When these results are combined with onsite infrared camera surveys (Table S6), the excess CH₄ emissions from the functional superemitters appeared to be mainly associated with avoidable process operating conditions. Examples of these emissions include well casing vents (UNG #15 and CNG #28) and open venting from condensate tank at CNG site #31.

Figure 3. Distribution of mean site-specific CH₄ emissions (ranked by descending order) for UNG sites (red circles) and CNG sites (blue circles) plotted on the left y-axis. The red and blue lines represent distributions obtained from the best-fit probabilistic models for UNG and CNG, respectively. The green line shows CH₄ emissions distributions reported by Rella et al.10 for 115 sites with detectable emissions in the Barnett Shale. The right y-axes show cumulative CH₄ emissions from all selected sites in each production category.

**Table 1. Estimation of 2014 Total CH₄ Emission from All CNG and UNG Sites in PA and WV**

<table>
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<th>West Virginia</th>
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<th>Pennsylvania</th>
<th>West Virginia</th>
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<tr>
<td>estimated total CH₄ emissions (kg/h)</td>
<td>51 600</td>
<td>11 800</td>
<td>63 400</td>
<td>40 000</td>
<td>40 600</td>
<td>80 600</td>
</tr>
<tr>
<td>CH₄ emissions from top 5% of sites (kg/h)</td>
<td>32 000—73 000</td>
<td>7 400—16 700</td>
<td>40 000—90 000</td>
<td>29 400—54 000</td>
<td>29 900—54 800</td>
<td>59 000—100 000</td>
</tr>
<tr>
<td>CH₄ emissions from top 15% of sites (kg/h)</td>
<td>21 800 (42%)</td>
<td>4950 (42%)</td>
<td>26 750 (42%)</td>
<td>14 700 (37%)</td>
<td>15 200 (37%)</td>
<td>29 900 (37%)</td>
</tr>
<tr>
<td>estimated total CH₄ emissions (Gg)</td>
<td>34 900 (68%)</td>
<td>7800 (67%)</td>
<td>42 700 (67%)</td>
<td>24 400 (61%)</td>
<td>25 000 (62%)</td>
<td>49 400 (61%)</td>
</tr>
</tbody>
</table>

a Average number of NG production days was 340 days/year and 322 days/year for CNG and UNG well pad sites, respectively. One MSCF CH₄ = 19.17 kg CH₄ at 15.6 °C and 1 atm. The 2014 site count, average production days, and production data were obtained from the PA DEP11 and WV DEP13 oil and gas reporting Web sites. b Numbers in parentheses represent the 95% confidence interval on estimated total regional CH₄ emissions. c Numbers in parentheses represent the fraction of total emissions contributed by the top 5% and 15% of well pad sites.
we estimate the CH₄ emissions from routinely producing NG production well pad sites in Pennsylvania and West Virginia in 2014. These estimates were performed by randomly drawing from selected distribution models of facility-level CH₄ emission rates taking into account the total number of routinely producing well pad sites in the Marcellus region. Figure 3 shows that the selected models efficiently reproduced empirical mean CH₄ emissions distributions. The fraction of regional CH₄ emissions associated with functional superemitters were not assessed because of the small number of sites identified as functional superemitters. Instead, results are presented for total regional CH₄ emission estimates by production category together with the respective contribution of the top 5% and 15% of sites (Table 1).

In Pennsylvania and West Virginia, there were an estimated 88,500 routinely producing CᵥNG well pad sites, which are estimated to have emitted 660 Gg of CH₄ (95% CI: 480 to 800 Gg CH₄) in 2014. In comparison, 3390 UNG well pad sites in both states emitted 490 Gg of CH₄ (95% CI: 310 to 690 Gg) in 2014 (Table 1). Thus, while facility-specific CH₄ emissions were dominated by the UNG well pads, the 2014 total CH₄ emissions in the Marcellus region were dominated by emissions from CᵥNG well pads because of their much larger number despite their much lower NG production volume per site.

CᵥNG well pads also dominated total CH₄ emissions on a production-normalized basis (i.e., ((total CH₄ emissions from all well pad sites)/(total CH₄ production from all well pad sites)) × 100). Total CH₄ production were estimated assuming 83.1% and 81.0% CH₄ in UNG and CᵥNG, respectively. The CH₄ emissions from all CᵥNG sites in Pennsylvania and West Virginia are estimated to be 16% (95% CI: 11.4 to 19.3%) of total CᵥNG CH₄ produced in 2014 (Table 1). In contrast, UNG well pads emitted 0.64% (95% CI: 0.40 to 0.91%) of total 2014 UNG CH₄ production in Pennsylvania and West Virginia (Table 1).

Based on our results, the estimated 2014 CH₄ leakage from all routinely producing NG well pad sites, as a fraction of statewide CH₄ production, was 1.0% in Pennsylvania (95% CI: 0.7 to 1.5%) and 3.0% in West Virginia (95% CI: 2.2 to 4.1%). The combined regional CH₄ emissions (1150 Gg, Table 1) represented approximately 1.4% (95% CI: 0.98 to 2.0%) of total Marcellus CH₄ production (i.e., production from all routinely producing UNG and CᵥNG sites in PA and WV combined) in 2014. Recent top-down airborne studies in northeastern Pennsylvania (2013 measurements) and southwestern Pennsylvania (2012 measurements) reported regional fractional CH₄ loss rates of 0.18 to 0.41% and 2.8 to 17.3%, respectively. It is important to note that these results are limited to the study region and include CH₄ emissions from other sources not measured in the present study (e.g., emissions from oil wells and NG well pads in the drilling stage).

We expect that in the future CH₄ emissions from UNG well pad sites will become increasingly important in the Marcellus region, especially if the number of new UNG wells continue to increase concomitantly with declines in the number of routinely producing CᵥNG wells (Figures S4 and S5). Our results showed that total CH₄ emissions from UNG well pad sites have already exceeded total CH₄ emissions from CᵥNG sites in Pennsylvania (Table 1).

**Uncertainties in Estimates of Regional Methane Emissions.** Overall, uncertainties associated with total regional estimates of CH₄ emissions were estimated at +49%/−18% and +42%/−37% for CᵥNG and UNG well pad emissions, respectively. These uncertainties are dominated by the uncertainty of the dual tracer flux methodology (±29% (Section S2)) and the impact of variability in measured facility-level CH₄ emissions and parametrized CH₄ emissions models obtained from a small sample size. Following, we discuss additional sources of uncertainties that were difficult to quantify and are not included in the overall uncertainty estimate.

The sample size in this study, while small, is comparable or greater than similar recent studies on per-well or facility-level CH₄ emissions in the Marcellus or Appalachian region. However, when empirical CH₄ emissions from small data sets are extrapolated to the regional scale, there is an increased likelihood of under-representing or over-representing the actual CH₄ emissions distribution from total sites in the region. Although the UNG CH₄ emissions distribution in the present study compare well with distributions from a recently published larger data set (Figure 3), there still are uncertainties inherent in the sampling methodologies that are difficult to quantify. For example, sampling of sites were not entirely random. That is, sites were sampled based on downwind road access. This quasi-random sampling of sites yield distributions that may not fully capture actual CH₄ emissions distributions from overall well pad sites. Further studies targeting larger numbers of randomly sampled sites are required.

Other uncertainties that are difficult to quantify were associated with the utilization of publicly available, industry-reported geospatial well location, and production data. The Pennsylvania DEP provide annual CᵥNG production reports as opposed to monthly reports provided by the West Virginia DEP. Site-specific NG production can vary substantially month-to-month, and will generally taper off over the lifetime of the well (Figure S14). Similarly, we assumed facility-level emissions to be constant throughout the year. Some routine emissions (e.g., intermittent leakages from pneumatic controllers) result from the normal functioning of the NG equipment, and may therefore be relatively consistent throughout the course of a year. However, as previously discussed, there are likely episodic emission events (e.g., maintenance issues) that could be curtailed by operator interventions, but may increase total site-level CH₄ emissions in a given year.

**Comparison of Total Methane Emissions with the Pennsylvania Natural Gas Emissions Inventory.** The Pennsylvania DEP began collection of air quality emissions data from UNG sources in 2011. The 2013 data (most recent year for which data are available) include annual CH₄ emissions from UNG sources broken down by source category (e.g., fugitives, storage tanks, pneumatic devices, dehydration units, etc.). The publicly available inventory data contain information for facility-level emissions, emissions totals by company, and county-level totals. We compared facility-level UNG CH₄ emissions and total Pennsylvania emissions estimated in the present study with the Pennsylvania inventory data.

Five of the UNG sites sampled in this study were in routine NG production in 2013 (the remainder of this study’s PA UNG sites were not in routine production). The CH₄ emissions measured by this study at these five sites were 10−37 times greater than the PA DEP inventory facility-level CH₄ emissions (Table S9). It is important to note that these results are limited to these five UNG sites, which exhibited total 2014 production
of 0.8 to 2.1 billion cubic feet NG and measured annual CH₄ emissions of 24 to 36 t. The total 2013 CH₄ emissions from all UNG sources in the inventory (which also includes compressor station emissions) were reported to be 108 Gg, which is four times less than the 2014 Pennsylvania UNG well pad CH₄ emissions estimated here (400 Gg; Table 1). Large discrepancies between inventory and actual measured CH₄ emissions have been widely documented. These discrepancies likely result from the uncertainties in the representativeness of emission factors used to estimate inventory CH₄ emissions. Because of the cost of performing measurements required to construct emissions factors, sample sizes may be limited and may not fully capture the often skewed distribution of CH₄ emissions.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05503. Additional site information, discussion of tracer flux methodology, and data analyses, and supplementary Tables and Figures (PDF)

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A.A.P., A.L.R., and R.S. designed research. M.O., M.R.S., X.L., and A.A.P. performed research; M.O. and M.R.S. analyzed data. The manuscript was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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## REFERENCES


