Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2018, 52, 12915−12925

pubs.acs.org/est

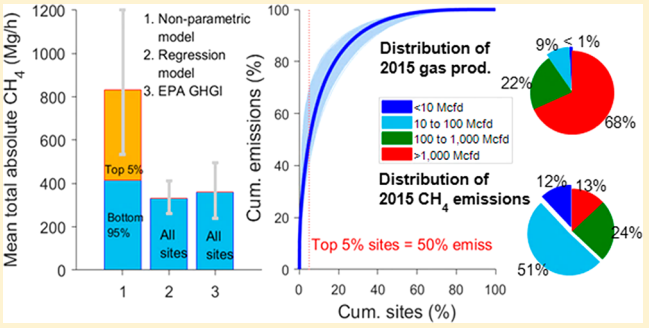
Methane Emissions from Natural Gas Production Sites in the United States: Data Synthesis and National Estimate

Mark Omara,*,† Naomi Zimmerman,‡ Melissa R. Sullivan, Xiang Li,§ Aja Ellis, Rebecca Cesa, R. Subramanian, Albert A. Presto, and Allen L. Robinson

Center for Atmospheric Particle Studies, Department of Mechanical Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

Supporting Information

ABSTRACT: We used site-level methane (CH_4) emissions data from over 1000 natural gas (NG) production sites in eight basins, including 92 new site-level CH_4 measurements in the Uinta, northeastern Marcellus, and Denver-Julesburg basins, to investigate CH_4 emissions characteristics and develop a new national CH_4 emission estimate for the NG production sector. The distribution of site-level emissions is highly skewed, with the top 5% of sites accounting for 50% of cumulative emissions. High emitting sites are predominantly also high producing (>10 Mcfd). However, low NG production sites emit a larger fraction of their CH_4 production. When combined with activity data, we predict that this creates substantial variability in the basin-level CH_4 emissions which, as a fraction of basin-level CH_4 production, range from 0.90% for the Appalachian and Greater Green River to >4.5% in the San Juan and San Joaquin. This suggests that much of the basin-level differences in production-normalized CH_4 emissions reported by aircraft studies can be explained by differences in site size and distribution of site-level production rates. We estimate that NG production sites emit total CH_4 emissions of 830 Mg/h (95% CI: 530−1200), 63% of which come from the sites producing <100 Mcfd that account for only 10% of total NG production. Our total CH_4 emissions estimate is 2.3 times higher than the U.S. Environmental Protection Agency's estimate and likely attributable to the disproportionate influence of high emitting sites.



INTRODUCTION

Natural gas (NG) extracted from shale and tight oil reservoirs has transformed the U.S. energy landscape resulting in rapid increases in total NG production and consumption.[1] While NG combustion emits less than half the carbon dioxide (CO_2) of other fossil fuels,[2] it is primarily composed of methane (CH_4), which produces 86 times more radiative forcing than CO_2 over a 20-year time frame.[3] Therefore, CH_4 emitted from the NG system represents wasted resources, lost revenue, and erodes the potential climate benefits of NG relative to other fossil fuels.

There has been a major effort over the last five years to quantify CH_4 emissions from the oil and NG supply chain. Dozens of recent measurement-based studies[4−32] have exposed the magnitude and scope of the CH_4 emissions problem, highlighting the following common themes: (i) Government inventories often significantly underestimate CH_4 emissions, (ii) a small fraction of high-emitting sites or sources account for a disproportionately large fraction of total CH_4 emissions, and (iii) there are significant basin-to-basin differences in production-normalized CH_4 emissions (i.e., CH_4 emissions expressed as a fraction of CH_4 produced).

We focus on CH_4 emissions from NG production sites. The U.S. EPA[33] attributes two-thirds of the 6.5 Tg of total CH_4 emissions from the NG supply chain to the NG production sector, which includes 2 Tg of CH_4 emissions associated with NG production from more than 400 000 NG wells. Herein, we define NG production sites to include any NG-producing well pad with one or more wellheads and ancillary surface equipment (e.g., NG separators, pneumatic pumps/controllers, and/or storage vessels). Such onsite processing equipment are often significant sources of elevated CH_4 emissions.[4,8,29] These high emissions are often the result of abnormal process conditions (e.g., equipment malfunctions); they can be persistent or episodic and are difficult to predict.[4,27−29] The stochastic characteristics of high-emitting sites appear to contribute, at least in part, to the orders-of-magnitude variability in measured absolute site-level CH_4 emissions (Figure 1). Furthermore, top-down aircraft studies report widely varying estimates of basin-level, production-normalized CH_4 emissions.[19−24] The causative factors for site- and basin-level variability in CH_4 emissions are not well-understood. It has been suggested that differences in the composition of the

Received: June 27, 2018
Revised: August 29, 2018
Accepted: September 26, 2018
Published: September 26, 2018

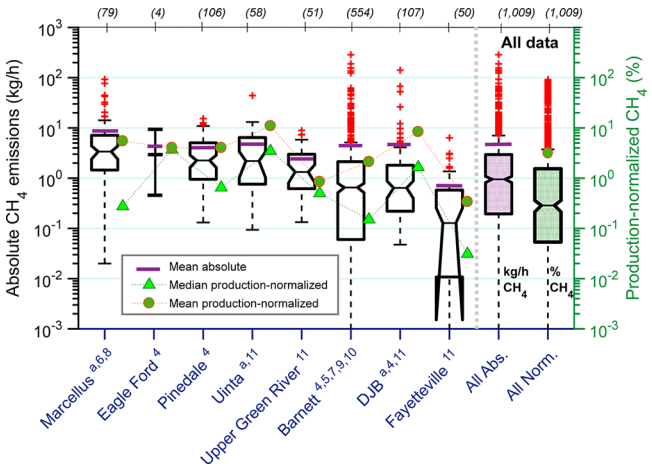


Figure 1. Site-level measurement data synthesized in this study. Numbers in parentheses indicate the number of sites with emissions data for each basin; the citations to the original studies are indicated as superscripts after basin names. New measurements are indicated with an (a) in the Denver-Julesburg (DJB; n = 18, or 17% of all DJB sites), Marcellus (NE PA unconventional sites, n = 45, or 57% of all Marcellus data), and Uinta (n = 29, or 50% of all Uinta sites). The boxes represent the 25th and 75th percentiles, while the whiskers extend to 1.5× the interquartile range, and values outside this range are the outliers, marked with red crosses. The black horizontal line inside each box represents the median while means are shown in purple. The notches visually depict the 95% confidence interval on the median. For Eagle Ford, measurement data for the four sites are represented with an error bar indicating the minimum and maximum. For Fayetteville, the notch extends beyond the 25th percentile as a result of the sample size and the data spread in this basin. "All Abs." and "All Norm." represent combined data set for all absolute and production-normalized CH_4 emission rates (n = 1009), respectively.

extracted NG (e.g., dry versus wet gas), operator practices, and/or differences in NG production rates may be important.[11,24,29] Additionally, several states have recently proposed or enacted oil and NG CH_4 regulations,[34−38] which may yield pronounced differences in future regional/basin-level CH_4 emissions when compared against regions/basins without similar regulatory actions.

To better understand CH_4 emissions among NG production sites and across multiple basins, we compiled and analyzed recently measured site-level CH_4 emissions data for more than 1000 NG production sites in eight U.S. basins[4−11] (Figure 1). We use this large data set of site-level CH_4 emissions (both absolute and production-normalized emissions) and site-level NG production to test the hypothesis that there are no significant basin-to-basin differences in the distribution of site-level CH_4 emissions and that, on average, site-level emissions correlate with their NG production characteristics. We then combine these site-level CH_4 emissions data with a national database on NG production site characteristics (i.e., site-level NG production rate) to estimate (i) total CH_4 emissions from U.S. NG production sites, (ii) major sources and distributions of CH_4 emissions, including CH_4 from high-emitting sites, and (iii) variability in CH_4 emissions among basins.

MATERIALS AND METHODS

Overview of Site-Level Measurement Data. We analyzed measured site-level CH_4 emissions data from 1009 NG production sites located in eight different basins. This includes recently published data from eight independent studies,[4−11] supplemented with new data for 92 additional sites sampled in the Denver-Julesburg (DJB), Uinta, and Marcellus (northeastern PA, Figure 1, Supporting Information (SI) Section S1). These new measurements targeted production regions with unique site-level production characteristics, that is, unconventional dry gas production sites with high site-level production rates in northeastern Marcellus and low-producing, mixed oil and gas sites in Uinta and DJB. The new measurement data help diversify site-level production characteristics and measured production regions/basins in the consolidated data set.

We focus on routinely producing sites with known NG production and assumed that measured CH_4 emissions resulted from routine operations (e.g., equipment leaks, venting from pneumatic controllers and storage tanks) or were unplanned (e.g., unintended emissions from malfunctioning equipment). Thus, the combined data set does not include CH_4 emissions from completion flowback[8] or liquids unloadings.[11] Additionally, site-level CH_4 emissions rates were unavailable for storage or coalbed CH_4 well sites, and emissions from these sites were not assessed in the present study. For measured sites with reported NG production rates, the CH_4 measurements were performed between 2010 and 2016 and used a variety of onsite and downwind ground-based site-level CH_4 measurement techniques that can be broadly grouped into three categories:

(a) Direct onsite measurements (henceforth, "onsite measurements"), which involved optical gas imaging for leak identification followed by direct quantification of all identified leaks.[5] These component-specific measurements are then summed to estimate site-level emission rate. Onsite measurements accounted for 28% of all site-level measurement data.

(b) Downwind tracer flux (TF) measurements of downwind plumes of CH_4 and intentionally released tracers (e.g., acetylene and nitrous oxide).[6,8] TF sites accounted for 6.7% of the total data.

(c) Downwind CH_4 plume measurements combined with inverse Gaussian modeling. This includes both downwind stationary measurements using EPA's Other Test Method (OTM-33A[4,11]), and downwind mobile measurements followed by Gaussian modeling (MM-Gaussian[7,9,10]). Sites sampled using these techniques accounted for 65% of the total sites.

There are limitations with each method. For example, onsite measurement (method (a)) requires site access and proper operation and performance of both the plume imaging (for leaks survey) and leak rate measurement devices.[5,39] Even with site access, some onsite emission sources may be present at locations that are not safely accessible for leak rate quantification (e.g., see Subramanian et al.[16]). Additionally, all stationary and mobile downwind measurements require sites with downwind road access and favorable meteorological conditions. These measurement methods have different uncertainties, which range from approximately ±20% to ±60% (TF and OTM-33A) to a factor of 3 for the MM−Gaussian approach.[4−11]

We use the site-level production-normalized CH_4 emissions as reported by Robertson et al.[11] and Omara et al.[8] For Rella et al.,[10] Yacovitch et al.,[9] and Lan et al.[7] we use the site-level CH_4 emissions, NG production, and production-normalized CH_4 emissions as consolidated and reported by Zavala-Araiza et

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

Table 1. Ten NG Production Bins Used in the Nonparametric Model (Developed Based on Deciles of NG Production for the Measured Sites) And Their Estimated Mean Site-Level Production-Normalized CH_4 Emissions

production bin (Mcfd)	<0.4−31	31−73	73−147	147−254	254−390	390−616	616−1047	1047−1699	1699−3342	>3342
no. measured sites[a]	101	101	101	101	101	101	101	101	101	100
national sites (%)[b]	65%	15%	8.3%	3.9%	2.1%	1.7%	1.4%	0.90%	0.83%	0.81%
national prod. (%)[c]	3.2%	4.2%	5.2%	4.5%	3.97%	4.9%	6.7%	7.2%	11.7%	48.4%
mean (% CH_4)[d]	20	5.4	2.8	1.6	1.9	1.4	0.89	1.2	0.23	0.17
lower bound on mean (% CH_4)	16	3.3	1.6	1.1	0.96	0.7	0.38	0.45	0.14	0.12
upper bound on mean (% CH_4)	25	7.9	4.4	2.2	3.3	2.5	1.7	2.2	0.34	0.24

[a]Denotes the number of measured sites in each production bin (total = 1009). [b]Total U.S. NG production sites = 498 000. [c]NG production for these 498 000 sites was 83 billion cubic feet per day (Bcfd). [d]The mean production-normalized CH_4 emission rate in each bin was obtained by randomly drawing, with replacement, an emission rate from the empirical distribution until a randomly sampled emission rate was assigned to each of the sampled sites. This was repeated 10 000 times and the mean obtained from the average of averages of each simulation, while the 2.5th and 97.5th percentiles characterized the lower and upper bounds on the mean, respectively (SI Figure S18).

al.[29] For onsite measurements in the Barnett,[5] we calculated site-level production-normalized CH_4 emissions based on the study's reported site-specific CH_4 mole fraction in NG and site-level NG production; sites without NG production rates were excluded from this analysis. For Brantley et al.[4] and measurements performed as part of the present study, we estimated site-specific production-normalized CH_4 emissions based on the average county-specific or region-specific CH_4 mole fractions from the EPA's Oil and Gas Tool.[40]

We excluded data for eight sites with production-normalized CH_4 emissions >100%. These eight sites were sampled offsite using the downwind plume measurements approaches utilizing Gaussian plume inverse modeling. It is possible that the measured CH_4 emissions exceeding 100% of CH_4 production was due to offsite CH_4 sources (e.g., biogenic CH_4 source, CH_4 from collocated equipment such as abandoned well, etc.). The exclusion of these eight sites from the consolidated data set does not change our results: if we include them in our analysis, the total production CH_4 emissions increases by <7%, well within the overall 95% confidence interval.

Overall, the 1009 measured sites were located in the Barnett (n = 554 sites), Denver-Julesburg (DJB, n = 107), Pinedale (n = 106), Marcellus (n = 79), Uinta (n = 58), Upper Green River (n = 51), Fayetteville (n = 50), and Eagle Ford (n = 4) basins (Figure 1). Site-specific NG production rates ranged from 0.4 Mcfd (1 Mcfd = 1000 cubic feet per day) to 78 000 Mcfd. Analysis of production data from Drillinginfo[41] (further description below) indicates that in 2015, 94% of U.S. NG production sites had site-level NG production rates that fell within this range. Additional site information (e.g., number of wells onsite, gas processing and emissions control equipment in use, conventional or unconventional well type, and site age) were generally unavailable or not reported.

National Activity Data. We used well-level NG production data reported by Drillinginfo (DI Desktop[41]), a commercial platform that aggregates publicly available and proprietary well-level data, including monthly NG production, first reported production date, drilling configuration, operator name, and location. Using geospatial analysis with ArcGIS, we aggregated well-level information into site-level (well-pad) information (see SI Section S2). In total, 498 000 NG producing well pad sites were identified, with total 2015 NG production of approximately 27 Tcf (trillion cubic feet). As of March 2017, Drillinginfo did not report 2015 well-level production data for wells in Kentucky, Tennessee, Missouri, Oregon, Illinois, and Indiana. These states were not included in our analyses. The EIA[42] estimates that these states contributed <0.5% of total national NG production. Using the EPA's county-specific and basin-specific estimates of mean CH_4 content in NG,[40] we estimated total CH_4 production of 23 Tcf from these sites in 2015. The distribution of sites based on their NG production characteristics is shown in Table 1.

Extrapolation of Measured Site-Level Emissions to Total Population of Sites. We used two methods for extrapolating the measured site-level CH_4 emissions to the total population of sites: (i) a robust regression model, and (ii) a nonparametric model. These two approaches allow us to explore the influence of high-emitting sites on predicted total CH_4 emissions; whereas the first approach downweights their contribution, the second approach fully incorporates them. As described further in detail below, both of these approaches utilize the site-level production-normalized CH_4 emissions data. In the first approach, we estimated site-level CH_4 emissions for each of the 498 000 NG production sites in 2015 by fitting a robust weighted least-squares quadratic regression model of the production-normalized CH_4 emission as a function of NG production. The robust fit was performed using a MATLAB Statistics Toolbox algorithm that uses an iteratively reweighted least-squares approach with a bisquare weighting function,[43] wfun (wfun = $(\mathrm{abs}(r) < 1) \times (1 - r^2)^2$; r = resid/(tune × s × $(1 - h)^{0.5}$); $s = \frac{1}{0.6745} \times$ median absolute deviation of the residuals (resid) from the median; h is a vector of leverage values for the least-squares fit and tune is a tuning constant = 4.685). Thus, for each site, its production-normalized CH_4 emission rate (%) was estimated based on the fit obtained from the robust regression, which is a function of the site's NG production rate. The site's absolute CH_4 emission rate (kg/h) was then calculated by multiplying its production-normalized CH_4 emission rate with its CH_4 production rate.

In the second approach, we estimate site-level CH_4 emissions using nonparametric bootstrap resampling methods in order to adequately characterize the asymmetrical distributions of the empirical data. We first developed 10 empirical production-normalized CH_4 emissions distributions by grouping measured emissions into 10 bins based on deciles of NG production for the 1009 sites with emissions data (Table 1). We then grouped all 498 000 U.S. NG production sites into the same 10 bins based on the measured site-level NG production deciles. Among sites with emissions data, the site-level NG production rates ranged from 0.4 Mcfd to 78 000 Mcfd; however, among the total population of U.S. NG production sites, site-level NG production ranged from 0.001 Mcfd to 138 000 Mcfd (SI Figure S21). In grouping the

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

national population of sites, the 28 900 sites (5.8% of all sites) producing <0.4 Mcfd were placed in the same bin as the sites producing 0.4 to 31 Mcfd, which describes the first decile. Similarly, the six sites (0.0012% of all sites) that produced >78 000 Mcfd were placed in the last bin as the sites producing 3342 to 78 000 Mcfd. As shown in Table 1, the mean production-normalized CH_4 emissions in each bin decreases consistently with increases in site-level NG production. Our analysis shows that this grouping for national sites with NG production outside of the measured production is robust: if, for example, sites producing <0.4 Mcfd were assigned a production-normalized CH_4 emissions of 100%, the resulting national CH_4 emissions would increase by only 0.33%. Furthermore, we find that the distribution of site-level NG production rates for the sampled sites is statistically similar to that for the national population of sites across all production bins, except for the low production sites in the first bin which are undersampled (SI Figure S17).

For each site in each production bin, we estimate its site-level CH_4 emissions (kg/h/site) by randomly drawing, with replacement, a production-normalized CH_4 emission rate from the bin-specific empirical distribution. We then multiply this randomly sampled production-normalized CH_4 emission rate with the site-specific CH_4 production rate, repeat this process for every site, and then sum across all sites. We repeat this simulation 5000 times for each site in order to estimate the mean total CH_4 emissions; the 2.5th and the 97.5th percentiles were then used to characterize the 95% confidence interval on mean total CH_4 emissions.

Our overall estimated uncertainty on mean total CH_4 emissions, obtained from the 2.5th and 97.5th percentiles based on the nonparametric resampling, was +40%/ −36% and was dominated by variability in mean site-level CH_4 emissions. These are influenced by study-specific sample sizes, site representativeness, and/or method accuracy. There are also uncertainties associated with activity data from Drillinginfo[41] but they are difficult to quantify as these data are aggregated from publicly available sources that may be subject to reporting errors. These uncertainties include uncertainties in well location and production data. All Drillinginfo data were used as reported without any modifications. Finally, there are uncertainties associated with county/basin-level CH_4 mole fractions from the EPA's Oil and Gas Tool.[40] However, the impact of these uncertainties on estimated total CH_4 emissions are expected to be small. For example, in the Appalachian Basin, we used an average CH_4 content of 83%.[40] Increasing this to 95% or decreasing it to 75% yields results that are within 15% of the mean estimated total CH_4 for this basin, well within the overall method uncertainty of +40%/−36%.

Two-Sample Kolmogorov−Smirnov Tests. We compared the distributions of site-level absolute and production-normalized CH_4 emissions among different basins using the two-sample Kolmogorov−Smirnov (K−S) test, with significance established at $p < 0.01$. These statistical comparisons were performed using MATLAB.

RESULTS AND DISCUSSION

Variability in Empirical Site-Level and Basin-Level Methane Emission Rates. Figure 1 shows that both the absolute and production-normalized CH_4 emission rates are highly variable. Nearly three-quarters (74%) of sites exhibited site-level CH_4 emissions between 0.1 and 10 kg/h but, overall, site-specific absolute CH_4 emission rates varied by more than 5 orders of magnitude, ranging from 0 to 300 kg/h. There are basin-to-basin differences in emissions with mean basin-specific absolute CH_4 emission rate ranging from 0.61 kg/h/site (95% confidence interval, henceforth CI: 0.33−0.95) to 7.9 kg/h/site (CI: 4.9−12) in the Fayetteville and Marcellus basins, respectively. The overlap, or lack thereof, in the length of the boxplot notches in Figure 1 suggests basins cluster into three groups with statistically different measured median absolute CH_4 emission rates: (i) A group of basins with high site-level emissions: Marcellus (median = 3.4 kg/h/site), Pinedale (2.3 kg/h/site), Uinta (2.2 kg/h/site); (ii) A group of basins with moderate site-level emissions: Barnett (0.65 kg/h/site) and Denver-Julesburg (DJB) (0.64 kg/h/site); and (iii) Fayetteville, with low site-level emissions (0.13 kg/h/site). The Upper Green River basin falls between the high and moderate emissions groups with a median emissions of 1.3 kg/h/site.

Site-specific production-normalized CH_4 emission rates ranged from 0% to 91%, while the mean basin-specific production-normalized CH_4 emission rates ranged from 0.34% (CI: 0.07−0.74%) to 11% (CI: 6.9−16%) in the Fayetteville and Uinta, respectively (SI Table S8). Within 95% confidence intervals, four groups of basins have measured median production-normalized CH_4 emissions that are statistically different (SI Figure S19): (i) DJB (median = 1.6%) and Uinta (3.5%) have high production-normalized emissions; (ii) Marcellus (0.27%), Pinedale (0.65%), and Upper Green River (0.50%) have moderate production-normalized emissions; (iii) Barnett (0.15%) and (iv) Fayetteville (0.031%) both have low emissions. Thus, at the basin level, the measured mean or median site-level production-normalized CH_4 emissions vary by one to 2 orders of magnitude, while the measured mean or median site-level absolute CH_4 emissions vary by at least an order of magnitude.

Comparison of Empirical Site-Level Methane Emissions Distributions among Basins. Figure 2 shows the empirical cumulative distributions of both the absolute and production-normalized CH_4 emissions sorted by basins. The site-level emissions are highly skewed; for example, among all sampled sites in the Barnett, the top 5% of high-emitting sites accounted for 66% of cumulative absolute CH_4 emissions. The skewness of CH_4 emissions distributions are determined, in part, by the sample size.[18] A concern is representativeness of the sample population, including the magnitude and frequency of extreme emitters.[44] Representative distributions are difficult to capture in part because of the stochastic characteristics of site-level CH_4 emissions and the logistical limitations of common site-level measurement techniques (see Materials and Methods). To compare CH_4 emissions distributions among basins, we attempted to control for these potential sampling artifacts by stratifying basin-specific CH_4 emissions based on the median site-level NG production rate (390 Mcfd) and, in each group, limiting our comparison to only include basins with $n \geq 50$.

We used the two-sample Kolmogorov−Smirnov test (i.e., six paired tests for the <390 Mcfd group and three paired tests for the >390 Mcfd group) to compare the different basin-specific emissions distributions shown in Figure 2 (SI Table S13). The absolute CH_4 emissions distributions are generally statistically different among basins at the 1% significance level (Figure 2a). Indeed, the two-sample K−S test suggests only the absolute site-level CH_4 emissions distributions for the <390 Mcfd sites in the Pinedale and Uinta basins came from similar continuous distributions ($p = 0.24$).

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

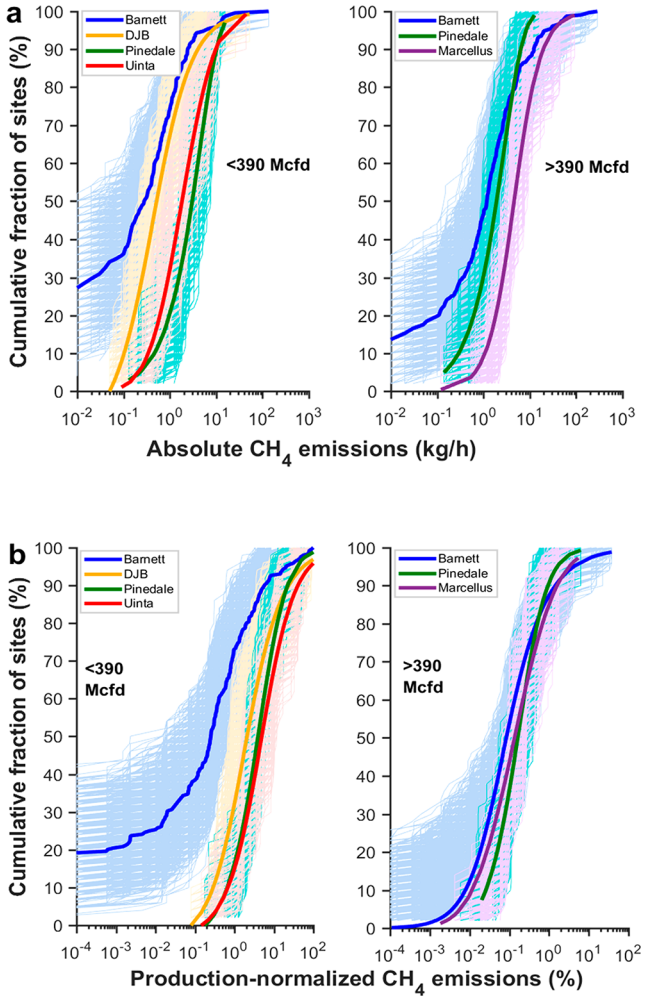


Figure 2. Comparison of CH_4 emissions distributions among basins. (a) absolute and (b) production-normalized emissions. Only basins with $n \geq 50$ sites were evaluated. For the <390 Mcfd bin, comparisons were made among the Barnett (n = 245), DJB (n = 95), Pinedale (n = 50), and Uinta (n = 50) Basins. For the >390 Mcfd bin, comparisons were made among the Barnett (n = 309), Pinedale (n = 56), and the Marcellus (n = 57) Basins. The lightly colored lines indicate the 10 000 bootstrap distributions obtained by randomly sampling 50 sites, with replacement, from the empirical distributions (shown in bold solid lines). Differences in distributions were assessed using the 2-sample Kolmogorov–Smirnov test with significance established at $p < 0.01$.

In contrast, the distributions of production-normalized CH_4 emissions were generally statistically similar among all paired basins ($p > 0.01$, SI Table S13), except for the Barnett sites producing <390 Mcfd (Figure 2b). The Barnett data for the <390 Mcfd sites are skewed low compared to the other basins partly because 20% of all the sampled sites in this bin had nondetectable emissions,[10] and nearly one-third were obtained from short-term onsite measurements.[5] The sites with reported zero emissions were sampled using mobile downwind plume measurements but had no independent measure to verify sites with undetectable plumes (e.g., the use of an intentionally released tracer from the site). Additionally, component- level measurements,[5] which are typically completed in minutes, may be biased low as periodic emission events (e.g., tank flashing) may be missed. Given this uncertainty, it is possible that high-emitting sites are underrepresented among sites producing <390 Mcfd in the Barnett, thus increasing the uncertainty in the scaled-up CH_4 emissions. This potential sampling artifact was not observed among sites producing >390 Mcfd (Figure 2b). However, the 10 000 bootstrap distributions (recreated from the empirical distribution) for the Barnett indicate overlap with the Denver-Julesburg (DJB), Pinedale, and Uinta CH_4 distributions, particularly at the high end of the distribution (Figure 2).

Relationship between Measured Site-Level Methane Emissions and NG Production. Recent studies report weak relationships between absolute CH_4 emissions and site-level characteristics, including NG production, oil production, water production, and/or site age.[4,8,11,29] Given the limited information for individual sites, we can only examine the relationship between site-level CH_4 emissions and NG production.

Figure 3 shows the site-level absolute and production-normalized CH_4 emissions as functions of NG production. Figure 3b shows a strong trend of decreasing production-normalized CH_4 emissions with increases in site-level NG production. To quantify the trend, we fit the entire data set with quadratic robust weighted least-squares regression with bisquare weighting (see Materials and Methods):

$$\log_{10}\left[\%CH_4\left(\frac{kg/h}{kg/h}\right)\right] = 0.072 \pm 0.056(95\%CI) \times \log_{10}[Prod(Mcfd)]^2 - 1.1 \pm 0.28 \times \log_{10}[Prod(Mcfd)] + 1.96 \pm 0.34;\ r^2_{adj} = 0.74.$$

On average, low NG producing sites emit a larger fraction of their CH_4 production than high NG producing sites and up to 74% of the variability is explained by variability in NG production rates (Figure 3). This implies that basins in which total NG production are dominated by high NG production sites are likely to have lower production-normalized CH_4 emissions and vice versa.

Figure 3 also shows modest increases in absolute CH_4 emissions with site-level NG production (quadratic robust weighted least-squares regression with bisquare weighting:

$$\log_{10}[CH_4(kg/h)] = 0.071 \pm 0.056(95\%CI) \times \log_{10}[Prod(Mcfd)]^2 - 0.097 \pm 0.28 \times \log_{10}[Prod(Mcfd)] - 0.23 \pm 0.33;\ r^2_{adj} = 0.74)$$

High NG production sites (e.g., > 1000 Mcfd/site) are generally newer facilities (SI Figure S3); they may have optimally performing equipment and components, and are likely subjected to more frequent on-site inspection and maintenance than old, low producing sites.[8] Because of their high NG production rates, exceptionally high CH_4 emissions (e.g., > 10% of site-level CH_4 production) at these sites would likely be audible and/or visible, increasing the possibility for detection and repair if routine inspections are performed.

Both Figure 1 and Figure 3 highlight the significant scatter in CH_4 emissions within basins and within NG production bins; this underscores the stochastic character of emissions at any given site, which may result from sources that include malfunctions (e.g., separator dump valve stuck open), operational errors (e.g., storage tank venting from thief hatch accidentally left open), and/or process and design issues (e.g., overpressurized separators).[27−29] Therefore, the fits in Figure 3 predict the emissions of an average site as a function of production but do not predict the emissions for any specific site. Fortunately, trends in average emissions are what is needed to develop national or basin-level emission estimates,

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

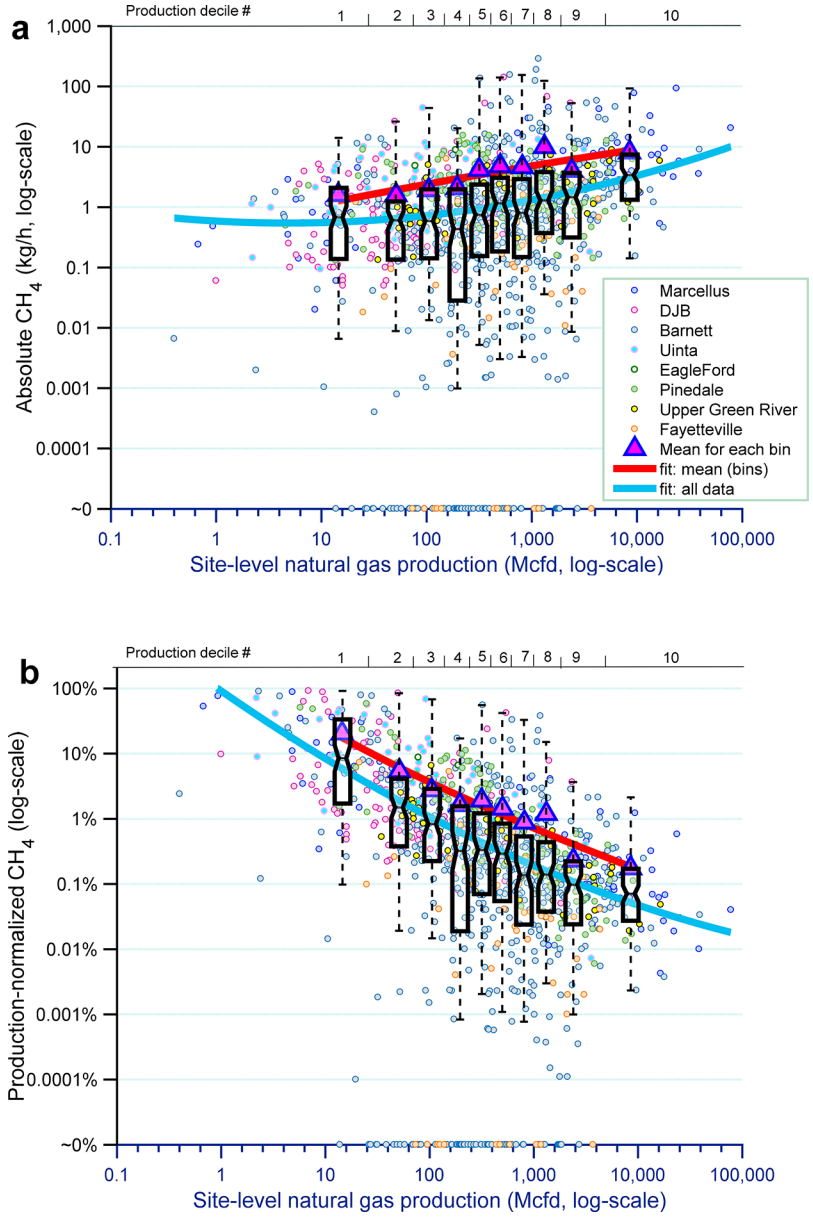


Figure 3. Relationship between site-level CH_4 emissions and NG production. (a) absolute and (b) production-normalized CH_4 emissions. Solid cyan lines show quadratic robust weighted least-squares regressions with bisquare weighting (see Materials and Methods) performed on the entire data set. Measured site-level CH_4 emissions were also binned by deciles of their site-level NG production, which are numbered sequentially on the top x axis. The notched box plots (outliers not shown) visually depict the data spread in each production decile. The black horizontal line in each notched box shows the median. The triangular purple symbols show the mean CH_4 emission rate in each production decile and the solid red lines show the polynomial fit through the mean CH_4 emission rate in each decile. These regression equations are (a) $\log_{10}[CH_4\ (kg/h)] = 0.30 \pm 0.14 \times \log_{10}[Prod\ (Mcfd)] - 0.23 \pm 0.38$; $r^2_{adj} = 0.72$) and (b) $\log_{10}[\%CH_4(^{kg/h}/_{kg/h})] = -0.71 \pm 0.15 \times \log_{10}[Prod(Mcfd)] + 2.0 \pm 0.41$; $r^2_{adj} = 0.93$) for the absolute and production-normalized CH_4 emissions, respectively.

which integrate an average emission factor with activity data reflecting the total number of well sites.

Influence of High-Emitting Sites on Total Methane Emissions. Within each basin (Figure 1) and production bin (Figure 3, notched box plots), the mean CH_4 emission rate is higher than the median because of the disproportionate influence of low frequency, high emitting sites. The high CH_4 emitters are commonly referred to as "super emitters"; since we lack information on the site-level CH_4 sources, we denote them simply as "high emitters" and identify them as the top 5% of sites based on the cumulative fraction of CH_4 emissions. Figure 4a shows, empirically, that the top 5% of high-emitting sites account for 57% (CI: 40−70%) of cumulative CH_4 emissions, with each of these sites having site-level CH_4 emissions >13 kg/h/site. Furthermore, their cumulative CH_4 emissions are equivalent to 1.6% (CI: 1.1−2.2%) of their total CH_4 production. This result is consistent with the observation by Brandt et al.[44] that the largest 5% of leaks from NG systems typically contribute over 50% of total leakage volume. Overall, our results suggest that CH_4 emission models (or CH_4 emission factors) that do not adequately capture the disproportionate contribution of high emitters may significantly underestimate total emissions.

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

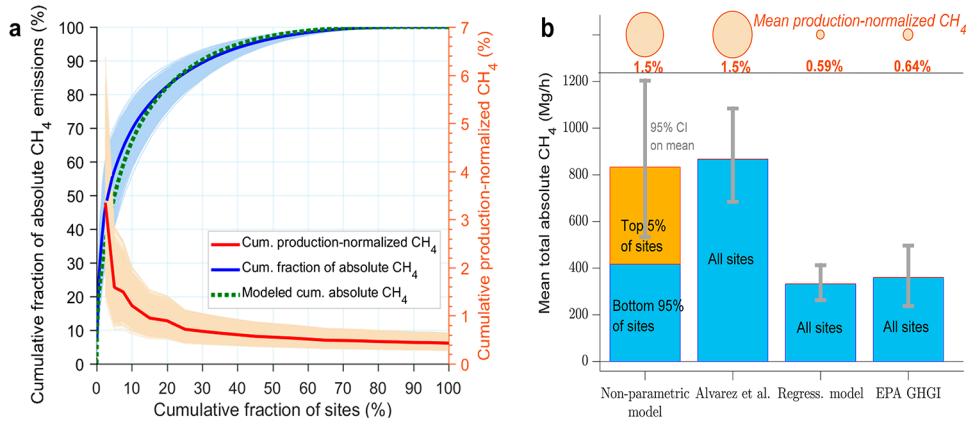


Figure 4. Total CH_4 emissions are dominated by a small fraction of high-emitting sites. (a) Site-level absolute CH_4 emissions distribution plotted in descending rank-order. Empirically (n = 1009), the top 5% of sites contribute 57% of total absolute CH_4 emissions (solid blue line); their cumulative CH_4 emissions are equivalent to 1.6% of their total CH_4 production (solid red line). The light blue and orange bands visually depict the 95% confidence intervals on the cumulative fraction of absolute and production-normalized CH_4 emissions, respectively. The dotted green line shows the predicted CH_4 distribution for all 498 000 U.S. onshore NG production sites as obtained from the nonparametric model—the top 5% of sites account for 50% of total CH_4 and have mean site-level CH_4 emissions of 17 kg/h/site (CI: 10−25). (b) Comparison of estimated total U.S. production CH_4 emissions based on (i) nonparametric model, (ii) total CH_4 emission estimate for all production sources reported by Alvarez et al.,[45] (iii) a regression model approach, and (iv) total onshore CH_4 emissions from the 2017 EPA GHGI (see Main Text). The top bubble plots visually depict the differences in production-normalized CH_4 emissions (see SI Section 2.2).

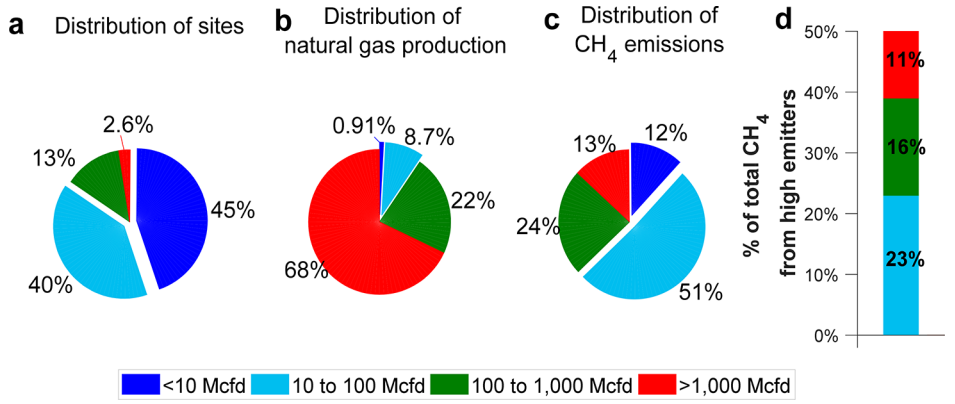


Figure 5. Distribution of sites, NG production, and CH_4 emissions based on four cohorts of site-level NG production. (a) Distribution of U.S. NG production sites in 2015 (n = 498 000). (b) Distribution of their NG production (total = 83 Bcfd). (c) Distribution of their estimated CH_4 emissions (total = 830 Mg/h). (d) CH_4 emissions from the high-emitting sites (none of the 220 000 sites producing <10 Mcfd was estimated to be a high emitter). High-emitting sites are defined as the top 5% of U.S. sites (based on the cumulative fraction of site-level CH_4 emissions (n = 25 000)) and that emit >7.2 kg/h/site. Total CH_4 from high-emitting sites were estimated to be 420 Mg/h (95% CI: 260−630 Mg/h).

To quantify the importance of accurate accounting of high-emitters on national emission estimates such as the EPA GHGI,[33] we estimated, for the year 2015, the total U.S. CH_4 emissions from NG production using the two approaches previously described (see Materials and Methods). In the first approach, we use a robust regression model that captures the average site-level CH_4 emissions behavior and simulates a bottom-up inventory approach in which the full effect of extreme CH_4 emitters are not accounted for. Second, we use a nonparametric model that fully incorporates the disproportionate influence of high-emitting sites. For this analysis, we use the combined production-normalized CH_4 emissions data given the strong similarities in basin-specific distributions (Figure 2b) and robust trend with site-level NG production (Figure 3b). We include site-level production-normalized CH_4 data from all basins, including those where small sample sizes precluded a comparative assessment of their CH_4 distribution. We acknowledge that this and other potential sampling artifacts discussed above likely increase the overall uncertainty in total estimated CH_4 emissions.

When combined with activity data from Drillinginfo's DI Desktop,[41] the regression model approach estimates total CH_4 emissions of 330 Mg/h (95% CI on mean: 260−410; or 0.67 kg/h/site and equivalent to production-normalized emissions of 0.59%; Figure 4b) in 2015. In contrast, the nonparametric model yields an estimate that is more than two times the regression model results, that is, total CH_4 emissions of 830 Mg/h (CI: 530−1200; or 1.7 kg/h/site and equivalent to production-normalized emissions of 1.5%).

The regression model approach is similar, in principle, to the bottom-up inventory methods in which an average CH_4 emission factor is applied to activity data, which may include count of wells, components, and/or equipment at a site or region. This is the approach typically used in government inventories such as the EPA GHGI.[33] Our estimated total CH_4 emissions based on the regression model (330 Mg/h) is similar to the 360 Mg/h of total CH_4 emissions for onshore oil and

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

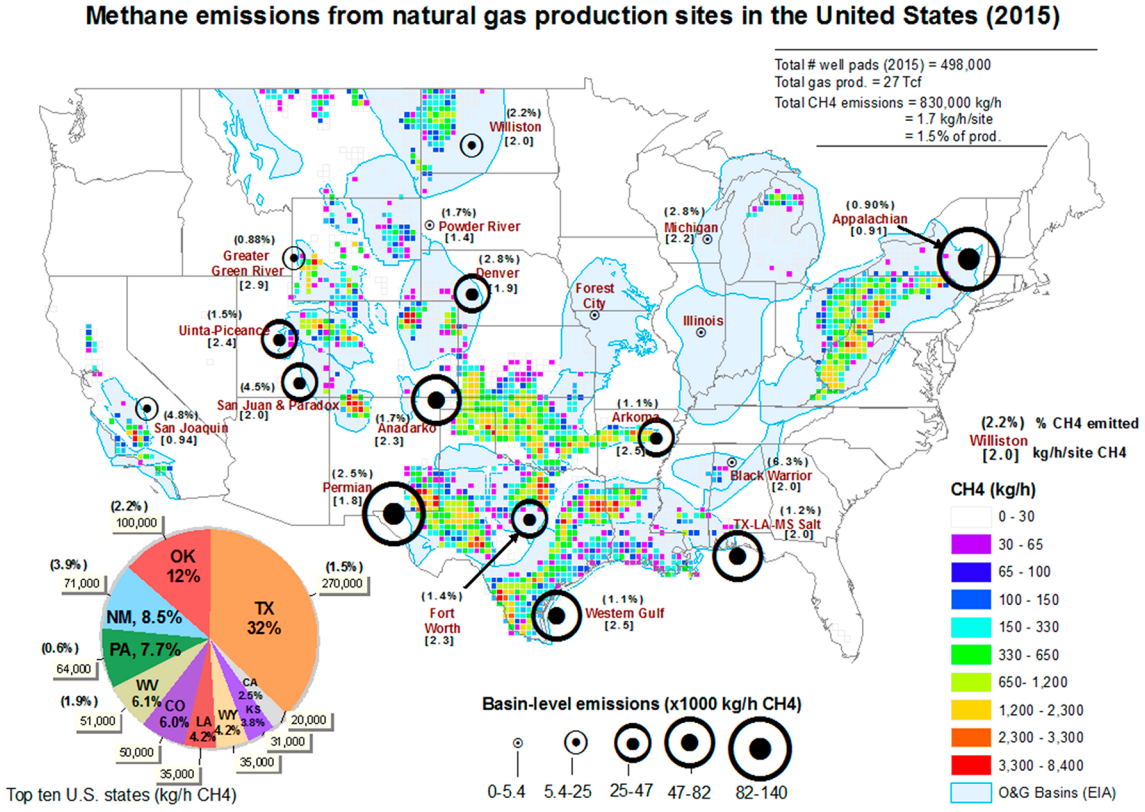


Figure 6. Spatial distribution of CH_4 emissions, plotted on 35km × 35km grid cells. Percentages and numbers in parentheses above and below basin names indicate the basin-level production-normalized and average site-level CH_4 emission rates, respectively. Pie chart labels indicate the predicted mean total CH_4 emissions (kg/h); percentages above the labels indicate the production-normalized CH_4 emissions for the top five states, while percentages inside each pie indicate the predicted fraction of total U.S. CH_4 contributed by that state. Additional data can be found in SI Tables S7, S9, and S11 and in the provided Google Earth kmz file. The oil and gas basin boundaries are from the U.S. EIA.[46] Map data source: ArcUSA, U.S. Census, and ESRI. The map was created using ArcGIS software by ESRI (www.esri.com) and used herein under license.

NG production sites as reported in the 2017 EPA GHGI for 2015 emissions (Figure 4b). Furthermore, the EPA GHGI estimate is similar to our mean estimate of 420 Mg/h (CI: 300−570; or 0.88 kg/h/site (CI: 0.61−1.2)) for the lowest-emitting 95% of all U.S. sites (based on cumulative fraction of emissions) as obtained from the nonparametric model (Figure 4b). The robust regression fit (cyan line in Figure 3b) essentially passes through the median CH_4 emission rate in each production bin as the effect of extreme CH_4 outliers are downweighed in favor of tracing the underlying trend through the bulk of the data. Thus, total emissions estimates based on the robust regression model and the results for the lowest-emitting 95% of sites do not fully account for the CH_4 emissions from the exceptionally high emitters.

Our nonparametric model incorporates high emitters (i.e., the top 5% of sites). Its estimate of the total CH_4 emissions is 2.3 times higher than the EPA GHGI's estimate for total CH_4 from the oil and NG production sites (Figure 4b). Similar discrepancies between bottom-up inventories and measurements have been reported in recent studies.[17,18,25,26,30,45] Herein, our results suggest that CH_4 emissions from the high emitters (national mean: 17 kg/h/site (CI: 10−25); range: 7.2−1100), which account for 50% (CI: 32−75%) of cumulative emissions (Figure 4a), are primarily responsible for the discrepancy between our predicted total CH_4 and the EPA GHGI estimate. That is, the nonparametric model results match the EPA GHGI only when we exclude the contribution of the top 5% of high emitting sites. As reported in the 2017 GHGI,[33] the 2015 national CH_4 emissions for the NG gathering and processing (2.8 Tg), transmission and storage (1.3 Tg), and distribution (0.44 Tg) sectors already incorporate data from skewed emissions distributions obtained in recent sector-specific measurement-based campaigns.[14,17,18] Our analysis supports a similar adjustment of CH_4 emissions for the NG production sector.

Distribution of Methane Emissions among Natural Gas Production Sites. Figure 5 summarizes the total CH_4 predictions stratified by production level. We define low, intermediate, and high NG production sites as sites producing <100 Mcfd, 100 to 1000 Mcfd, and >1000 Mcfd, respectively. Low NG production sites account for 85% of the total number of sites but only 9.6% of total NG production (Figure 5a,b). Although their mean site-level CH_4 emissions are low (0.46 and 2.1 kg/h/site for the <10 Mcfd and 10 to 100 Mcfd sites, respectively; SI Table S10), their very large number makes them an important source of CH_4 emissions nationally, contributing nearly two-thirds (63% (CI: 45−83%) of the total CH_4 emissions. In contrast, high NG production sites (>1000 Mcfd/site) contribute two-thirds of total U.S. NG production and have higher mean site-level CH_4 emissions (8.3 kg/h/site; SI Table S10). However, they are few in number (i.e., they account for only 2.6% of the total number of sites) and contribute only 13% (CI: 7−21%) of the total CH_4 emissions.

We estimate that none of the 220 000 sites (45% of all sites) producing <10 Mcfd/site are high emitters; these low-

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

production sites had mean site-level CH_4 emission estimate of 0.46 kg/h/site (CI: 0.35−0.58; SI Table S10). In contrast, we estimate that 47% of the total CH_4 from high-emitting sites came from 8.3% of sites producing 10−100 Mcfd/site. High emitters in this cohort accounted for 23% of the total CH_4 from all sites (Figure 5d, SI Table S10). The remainder of the emissions from high emitters are contributed by sites with intermediate (16% of total CH_4 from all sites) and high NG production (11% of total CH_4 from all sites, Figure 5d).

Spatial Distribution of Methane Emissions. Figure 6 shows the estimated spatial distribution of site-level CH_4 emissions calculated from the nonparametric model, as previously discussed (i.e., the site-level CH_4 emissions distributions for all 498 000 NG production sites plotted in Figure 6 is the same distribution shown in Figure 4a (dotted green line)). Using site-specific location data from Drillinginfo,[41] the estimated emissions were then geo-spatially joined to 35 km × 35 km grid cells and summed to give the grid-specific total CH_4 (Figure 6).

We predict production CH_4 hotspots in the liquids-rich fairway of the Appalachian Basin (southwestern Pennsylvania and northern West Virginia), and in northwestern (San Juan Basin) and southeastern (Permian Basin) New Mexico, and in Weld County, Colorado (Denver Basin; Figure 6). Methane hotspots are not necessarily areas with high NG production. For example, Weld County (CO) was the eighth largest NG producing county in 2015 but is predicted to be the highest CH_4 emitting county in 2015 (26 Mg/h (CI: 16−34 Mg/h)). The emissions in Weld County are four times greater than that from Susquehanna (PA), the highest NG producing county. This is due to the very large number of sites with relatively low NG production in Weld County (13 000 sites) compared to Susquehanna (400 high producing sites).

Our analysis predicts wide variability in CH_4 emissions among states and among basins. For example, we predict that Texas contributes approximately one-third (32% (95% CI: 20−48%); Figure 6, SI Table S11) of total CH_4 emissions from NG production sites, roughly equivalent to the contribution of the combined CH_4 emissions from NG production sites in Oklahoma, New Mexico, and Pennsylvania (28% (95% CI: 19−39%)). Additionally, predicted basin-specific mean absolute CH_4 emissions per site ranged from 0.91 kg/h/site (CI: 0.62−1.2) in the Appalachian to 2.9 kg/h/site (CI: 1.6−3.9) in the Greater Green River Basin (SI Table S9). Mean production-normalized CH_4 emissions ranged from 0.88% (CI: 0.48−1.2%) in the Greater Green River Basin to 4.5% (CI: 3.3−6.6%) in the San Juan Basin (Figure 6; Table S9). These trends are caused by differences in the distributions of both the number of sites and their NG production characteristics. For example, the Appalachian Basin has the highest basin-level CH_4 emissions (140 Mg/h (CI: 95−180 Mg/h) or 17% of total CH_4 emissions (Figure 6). However, the Appalachian and Greater Green River Basins have the lowest estimated production-normalized CH_4 emissions of approximately 0.90% (Figure 6). NG production in both of these basins are dominated by high-producing sites with relatively low estimated production-normalized emission rates. These sites account for 94% and 72% of total NG production in the Appalachian and Greater Green River Basins, respectively. Similarly, the high estimated production- normalized CH_4 emissions of 4.5% (CI: 2.9−6.0%) in the San Juan Basin (Figure 6; SI Table S9) reflects the large contribution to total NG production (90%) from sites producing <1000 Mcfd/site in this basin.

Comparison with Previous Literature Estimates. Two previously published studies used site-level CH_4 emissions data that are part of the consolidated data set in the present study to estimate basin-level[26] or state-level CH_4 emissions.[8] Zavala-Araiza et al.[26] reported 2013 site-level CH_4 emissions of 1.8 (CI: 1.3−2.5) kg/h/site for the Barnett; the 2015 site-level CH_4 emissions estimates in the present study of 2.4 (CI: 1.4−3.6) kg/h/site for the Fort Worth Basin are in good agreement with their study. Similarly, our estimate of 115 Mg/h (CI: 78−150) for 2015 CH_4 emissions for NG producing sites in Pennsylvania and West Virginia overlaps with a previous estimate by Omara et al.[8] for these sources in 2014 (144 Mg/h (CI: 70−190)). Finally, our national estimate for total CH_4 emissions from NG production sites (830 Mg/h (CI: 530−1200)) compares well with recent estimates by Alvarez et al.[45] (870 Mg/h (CI: 680−1080, Figure 5b) that were based on site-level measurements but utilized a different extrapolation approach incorporating parametrized nonlinear models.[26]

Recent aircraft studies estimated the total CH_4 emissions from different NG production regions.[19−24,31,32] These studies report widely varying mean production-normalized CH_4 estimates, ranging from approximately 0.3−9% in northeastern PA (Marcellus) and Uinta Basin, respectively. Our analysis predicts that the distribution of sites and their NG production levels are important contributors to these trends. For example, basins in which low producing sites dominate site count and NG production (e.g., San Juan) have much higher production-normalized CH_4 emissions than basins where NG production are dominated by high NG producing sites (e.g., Greater Green River). We compared our new bottom-up estimates with these top-down studies (SI Section 3.6; Figure S20), which estimate CH_4 emissions from all oil and NG sources. Our predictions explain, on average, 58% of the airborne top-down CH_4 emissions (20−129% of basin-specific airborne CH_4 emissions (SI Table S12)). There are uncertainties in both estimates. For aircraft measurements, CH_4 source attribution and mass balance closure are uncertain, while the uncertainties in our bottom-up estimates were dominated by variability in study-specific mean site-level emissions.

Other factors (beyond number of sites and site production characteristics) such as new state/local regulations[34−38] or voluntary emissions reductions programs performed by specific operators, likely also contribute to basin-to-basin variability, but we could not assess those factors in this analysis. Additionally, our approach assumes that the large and diverse ensemble of sites considered here reproduces the distribution of emissions across the NG production system at any given point in time. However, there are uncertainties on CH_4 emissions distributions that are difficult to quantify based on available data. Future studies are needed to specifically address these factors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b03535.

A Google Earth kmz file showing the data presented in Figure 6, and documentation that describes the measurement results obtained in the present study, characteristics and distribution of natural gas production

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

sites, and additional study results, figures, and tables (PDF, ZIP)

AUTHOR INFORMATION

Corresponding Author

*Phone: +1-512-691-3432; e-mail: momara@edf.org.

ORCID

Mark Omara: 0000-0002-8933-1927
Xiang Li: 0000-0001-6797-7340
Albert A. Presto: 0000-0002-9156-1094
Allen L. Robinson: 0000-0002-1819-083X

Present Addresses

[†]Environmental Defense Fund, 301 Congress Avenue, Austin, Texas 78701, United States.
[‡]Department of Mechanical Engineering, University of British Columbia, 2054−6250 Applied Science Lane, Vancouver, British Columbia, Canada, V6T 1Z4.
[§]Department of Soil, Water, and Climate, University of Minnesota, St Paul, Minnesota 55108, United States.

Author Contributions

A.L.R., R.S., and A.A.P. designed the research. M.O., N.Z., M.R.S., X.L., A.E., R.C., and R.S. performed the field measurements. M.O. and N.Z. analyzed data. M.O. prepared the manuscript with feedback from all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Funding for this study was provided by the National Oceanic Atmospheric Administration Climate Program Office, Award No. NA14OAR4310135 and by the Department of Energy, National Energy Technology Laboratory, funding opportunity #DE-FOA-0000894. N.Z.'s work was supported in part by the NSERC postdoctoral fellowship, No. PDF-487660-2016. X.L's work was supported in part by the NASA Earth and Space Science Fellowship Program, Grant 15-EARTH15F-181. We thank Dr. Eben Thoma for providing the OTM-33A site-level measurement data presented in Brantley et al.[4] The views expressed herein are solely those of the authors and do not necessarily reflect those of the project funders or Environmental Defense Fund.

REFERENCES

(1) U.S. Energy Information Administration. Annual Energy Outlook 2017. Available at: https://www.eia.gov/outlooks/aeo/pdf/0383(2017).pdf (accessed on August 29, 2018).

(2) U.S. Energy Information Administration. Carbon Dioxide Emissions Coefficients. Available at: https://www.eia.gov/environment/emissions/co2_vol_mass.php (accessed on August 29, 2018).

(3) IPCC. Intergovernmental Panel on Climate Change: *Fifth Assessment Report*; Geneva, 2014.

(4) Brantley, H. L.; Thoma, E. D.; Squier, W. C.; Guven, B. B.; Lyon, D. Assessment of methane emissions from oil and gas production pads using mobile measurements. *Environ. Sci. Technol.* **2014**, *48*, 14508−14515.

(5) ERG. Eastern Research Group, Inc. City of Fort Worth Natural Gas Air Quality Study. Final Report. July, 2011. Available at http://fortworthtexas.gov/gaswells/air-quality-study/final/ (accessed on August 29, 2018).

(6) Goetz, J. D.; Floerchinger, C.; Fortner, E. C.; Wormhoudt, J.; Massoli, P.; Knighton, W. B.; Herndon, S. C.; Kolb, C. E.; Knipping, E.; Shaw, S. L.; DeCarlo, P. F. Atmospheric emission characterization of Marcellus Shale natural gas development sites. *Environ. Sci. Technol.* **2015**, *49*, 7012−7020.

(7) Lan, X.; Talbot, R.; Laine, P.; Torres, A. Characterizing fugitive methane emissions in the Barnett Shale area using a mobile laboratory. *Environ. Sci. Technol.* **2015**, *49*, 8139−8146.

(8) Omara, M.; Sullivan, M.; Li, X.; Subramanian, R.; Robinson, A. L.; Presto, A. A. Methane emissions from conventional and unconventional natural gas production sites in the Marcellus Shale region. *Environ. Sci. Technol.* **2016**, *50*, 2099−2107.

(9) Yacovitch, T. I.; Herndon, S. C.; Petron, G.; Kofler, J.; Lyon, D.; Zahniser, M. S.; Kolb, C. E. Mobile laboratory observations of methane emissions in the Barnett Shale region. *Environ. Sci. Technol.* **2015**, *49*, 7889−7895.

(10) Rella, C. W.; Tsai, T. R.; Botkin, C. G.; Crosson, E. R.; Steele, D. Measuring emissions from oil and natural gas well pads using the mobile flux plane technique. *Environ. Sci. Technol.* **2015**, *49*, 4742−4748.

(11) Robertson, A. M.; Edie, R.; Snare, D.; Soltis, J.; Field, R. A.; Burkhart, M. D.; Bell, C. S.; Zimmerle, D.; Murphy, S. M. Variation in methane emission rates from well pads in four oil and gas basins with contrasting production volumes and composition. *Environ. Sci. Technol.* **2017**, *51*, 8832−8840.

(12) Allen, D. T.; Torres, V. M.; Thomas, J.; Sullivan, D. W.; Harrison, M.; Hendler, A.; Herndon, S. C.; Kolb, C. E.; Fraser, M. P.; Hill, A. D.; Lamb, B. K.; Miskimins, J.; Sawyer, R. F.; Seinfeld, J. H. Measurements of methane emissions at natural gas production sites in the United States. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 17768−17773.

(13) Allen, D. T.; Sullivan, D. W.; Zavala-Araiza, D.; Pacsi, A. P.; Harrison, M.; Keen, K.; Fraser, M. P.; Hill, A. D.; Lamb, B. K.; Sawyer, R. F.; Seinfeld, J. H. Methane emissions from process equipment at natural gas production sites in the United States: pneumatic controllers. *Environ. Sci. Technol.* **2015**, *49*, 633−640.

(14) Lamb, B. K.; Edburg, S. L.; Ferrara, W. W.; Howard, T.; Harrison, M. R.; Kolb, C. E.; Townsend-Small, A.; Dyck, W.; Possolo, A.; Whetstone, J. R. Direct measurements show decreasing methane emissions from natural gas local distribution systems in the United States. *Environ. Sci. Technol.* **2015**, *49*, 5161−5169.

(15) Mitchell, A. L.; Tkacik, D. S.; Roscioli, J. R.; Herndon, S. C.; Yacovitch, T. I.; Martinez, D. M.; Vaughn, T. L.; Williams, L. L.; Sullivan, M. R.; Floerchinger, C.; Omara, M.; Subramanian, R.; Zimmerle, D.; Marchese, A. J.; Robinson, A. L. Measurements of methane emissions from natural gas gathering facilities and processing plants: measurement results. *Environ. Sci. Technol.* **2015**, *49*, 3219−3227.

(16) Subramanian, R.; Williams, L. L.; Vaughn, T. L.; Zimmerle, D.; Roscioli, J. R.; Herndon, S. C.; Yacovitch, T. I.; Floerchinger, C.; Tkacik, D. S.; Mitchell, A. L.; Sullivan, M. R.; Dallmann, T. R.; Robinson, A. L. Methane emissions from natural gas compressor stations in the transmission and storage sector: measurements and comparisons with the EPA Greenhouse Gas Reporting Program protocol. *Environ. Sci. Technol.* **2015**, *49*, 3252−3261.

(17) Marchese, A. J.; Vaughn, T. L.; Zimmerle, D. J.; Martinez, D. M.; Williams, L. L.; Robinson, A. L.; Mitchell, A. L.; Subramanian, R.; Tkacik, D. S.; Roscioli, J. R.; Herndon, S. C. Methane emissions from United States natural gas gathering and processing. *Environ. Sci. Technol.* **2015**, *49*, 3219−3227.

(18) Zimmerle, D. J.; Williams, L. L.; Vaughn, T. L.; Quinn, C.; Subramanian, R.; Duggan, G. P.; Wilson, B.; Opsomer, J. D.; Marchese, A. J.; Martinez, D. M.; Robinson, A. L. Methane emissions from the natural gas transmission and storage system in the United States. *Environ. Sci. Technol.* **2015**, *49*, 9374−9383.

(19) Caulton, D. R.; Shepson, P. B.; Santoro, R. L.; Sparks, J. P.; Howarth, R. W.; Ingraffea, A. R.; Cambaliza, M. O. L.; Sweeney, C.; Karion, A.; Davis, K. J.; Stirm, B. H.; Montzka, S. A.; Miller, B. R. Toward a better understanding and quantification of methane emissions from shale gas development. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 6237−6242.

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925

(20) Petron, G.; Karion, A.; Sweeney, C.; Miller, B. R.; Montzka, S. A.; Frost, G. J.; Trainer, M.; Tans, P.; Andrew, A.; Kofler, J.; Helmig, D.; Guenther, D.; Dlugokencky, E.; Lang, P.; Newberger, T.; Wolter, S.; Hall, B.; Novelli, P.; Brewer, A.; Conley, S.; Hardesty, M.; Banta, R.; White, A.; Noone, D.; Wolfe, D.; Schnell, R. A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin: hydrocarbon emissions in oil & gas basin. *J. Geophys. Res. Atmospheres* **2014**, *119*, 6836−6852.
(21) Karion, A.; Sweeney, C.; Petron, G.; Frost, G.; Hardesty, R. M.; Kofler, J.; Miller, B. R.; Newberger, T.; Wolter, S.; Banta, R.; Brewer, A.; Dlugokencky, E.; Lang, P.; Montzka, S. A.; Schnell, R.; Tans, P.; Trainer, M.; Zamora, R.; Conley, S. Methane emissions estimate from airborne measurements over a western United States natural gas field. *J. Geophys. Res. Lett.* **2013**, *40*, 4393−4397.
(22) Karion, A.; Sweeney, C.; Kort, E. A.; Shepson, P. B.; Brewer, A.; Cambaliza, M.; Conley, S. A.; Davis, K.; Deng, A.; Hardesty, M.; Herndon, S. C.; Lauvaux, T.; Lavoie, T.; Lyon, D.; Newberger, T.; Petron, P.; Rella, C.; Smith, M.; Wolter, S.; Yacovitch, T. I.; Tans, P. Aircraft-based estimate of total methane emissions from the Barnett Shale region. *Environ. Sci. Technol.* **2015**, *49*, 8124−8131.
(23) Peischl, J.; Ryerson, T. B.; Aikin, K. C.; de Gouw, J. A.; Gilman, J. B.; Holloway, J. S.; Lerner, B. M.; Nadkarni, R.; Neuman, J. A.; Nowak, J. B.; Trainer, M.; Warneke, C.; Parrish, D. D. Quantifying atmospheric methane emissions from Haynesville, Fayetteville, and northeastern Marcellus shale gas production regions. *J. Geophys. Res. Atmospheres* **2015**, *120*, 2119−2139.
(24) Peischl, J.; Karion, A.; Sweeney, C.; Kort, E. A.; Smith, M. L.; Brandt, A. R.; Yeskoo, T.; Aikin, K. C.; Conley, S. A.; Gvakharia, A.; Trainer, M.; Wolter, S.; Ryerson, T. B. Quantifying atmospheric methane emissions from oil and natural gas production in the Bakken shale region of North Dakota. *J. Geophys. Res. Atmospheres* **2016**, *121*, 6101−6111.
(25) Lyon, D. R.; Zavala-Araiza, D.; Alvarez, R. A.; Harris, R.; Palacios, V.; Lan, X.; Talbot, R.; Lavoie, T.; Shepson, P.; Yacovitch, T. I.; Herndon, S. C.; Marchese, A. J.; Zimmerle, D.; Robinson, A. L.; Hamburg, S. P. Constructing a spatially resolved methane emission inventory for the Barnett Shale region. *Environ. Sci. Technol.* **2015**, *49*, 8147−8157.
(26) Zavala-Araiza, D.; Lyion, D. R.; Alvarez, R. A.; Davis, K. J.; Harris, R.; Herndon, S. C.; Karion, A.; Kort, E. A.; Lamb, B. K.; Lan, X.; Marchese, A. J.; Pacala, S. W.; Robinson, A. L.; Shepson, P. B.; Sweeney, C.; Talbot, R.; Townsend-Small, A.; Yacovitch, T. I.; Zimmerle, D. J.; Hamburg, S. P. Reconciling divergent estimates of oil and gas methane emissions. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 15597−15602.
(27) Zavala-Araiza, D.; Alvarez, R. A.; Lyon, D. R.; Allen, D. T.; Marchese, A. J.; Zimmerle, D. J.; Hamburg, S. P. Super-emitters in natural gas infrastructure are caused by abnormal process conditions. *Nat. Commun.* **2017**, *8*, 14012−1421.
(28) Zavala-Araiza, D.; Lyon, D.; Alvarez, R. A.; Palacios, V.; Harris, R.; Lan, X.; Talbot, R.; Hamburg, S. P. Toward a functional definition of methane super-emitters: application to natural gas production sites. *Environ. Sci. Technol.* **2015**, *49*, 8167−8174.
(29) Lyon, D. R.; Alvarez, R. A.; Zavala-Araiza, D.; Brandt, A. R.; Jackson, R. B.; Hamburg, S. P. Aerial surveys of elevated hydrocarbon emissions from oil and gas production sites. *Environ. Sci. Technol.* **2016**, *50*, 4877−4886.
(30) Brandt, A. R.; Heath, G. A.; Kort, E. A.; O'Sullivan, F.; Petron, G.; Jordaan, S. M.; Tans, P.; Wilcox, J.; Gopstein, A. M.; Arent, D.; Wofsy, S.; Brown, N. J.; Bradley, R.; Stucky, G. D.; Eardley, D.; Harris, R. Methane leaks from North American natural gas systems. *Science* **2014**, *343*, 733−735.
(31) Barkley, Z. R.; Lauvaux, T.; Davis, K. J.; Deng, A.; Miles, N. L.; Richardson, S. J.; Cao, Y.; Sweeney, C.; Karion, A.; Smith, M.; Kort, E. A.; Schwietzke, S.; Murphy, T.; Cervone, G.; Martins, D.; Maasakkers, J. D. Quantifying methane emissions from natural gas production in northeastern Pennsylvania. *Atmos. Chem. Phys.* **2017**, *17*, 13941−13966.
(32) Smith, M. L.; Gvakharia, A.; Kort, E. A.; Sweeney, C.; Conley, S. A.; Faloona, I.; Newberger, T.; Schnell, R.; Schwietzke, S.; Wolter, S. Airborne quantification of methane emissions over the Four Corners Region. *Environ. Sci. Technol.* **2017**, *51*, 5832−5837.
(33) U.S. Enivironmental Protection Agency. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990−2015 (2017). Available at https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2015 (accessed on August 29, 2018).
(34) California Air Resources Board, Oil and Gas Regulation (2017). Available at: https://www.arb.ca.gov/regact/2016/oilandgas2016/oilandgas2016.htm (accessed on August 29, 2018).
(35) Wyoming Oil and Gas Conservation Commission. Administrative Rules Chapter 3, Section 39. Authorization for Flaring and Venting of Gas (2016). Available at: https://rules.wyo.gov/ (accessed on August 29, 2018).
(36) Colorado Department of Public Health and Environment. Oil and gas emissions requirements (Regulation 7, Section XVII) (2016). Available at: https://www.colorado.gov/pacific/cdphe/summary-oil-and-gas-emissions-requirements (accessed on August 29, 2018).
(37) Pennsylvania Methane Reduction Strategy (2016). Available at: http://www.dep.pa.gov/business/air/pages/methane-reduction-strategy.aspx (accessed on August 29, 2018).
(38) Ohio Oil and Gas Laws (2016). Available at: http://oilandgas.ohiodnr.gov/laws-regulations/oil-gas-law-summary (accessed on August 29, 2018).
(39) Ravikumar, A. P.; Wang, J.; Brandt, A. R. Are optical gas imaging technologies effective for methane leak detection? *Environ. Sci. Technol.* **2017**, *51*, 718−724.
(40) U.S. Environmental Protection Agency. EPA Oil and Gas Tool, 2014 NEI Version 1.5−Production Activities Module. Updated July, 2016. Available at: ftp://ftp.epa.gov/EmisInventory/2011nei/doc/ (accessed on August 29, 2018).
(41) Drillinginfo DI Desktop; Austin, TX (2015). http://www.didesktop.com/ (accessed on August 29, 2018).
(42) U.S. Energy Information Administration. Natural Gas Gross Withdrawals and Production. Available at: https://www.eia.gov/dnav/ng/ng_prod_sum_dc_NUS_mmcf_a.htm (accessed on August 29, 2018).
(43) Street, J. O.; Carrol, R. J.; Ruppert, D. A note on computing robust regression estimates via iteratively reweighted least squares. *Am. Stat.* **1988**, *42*, 152−154.
(44) Brandt, A. R.; Heath, G. A.; Cooley, D. Methane leaks from natural gas systems follow extreme distributions. *Environ. Sci. Technol.* **2016**, *50*, 12512−12520.
(45) Alvarez, R. A.; Zavala-Araiza, D.; Lyon, D. R.; Allen, D. T.; Barkley, A. R.; Brandt, A. R.; Davis, K. J.; Herndon, S. C.; Jacob, D. J.; Karion, A.; Kort, E. A.; Lamb, B. K.; Lauvaux, T.; Maasakkers, J. D.; Marchese, A. J.; Omara, M.; Pacala, S. W.; Peischl, J.; Robinson, A. L.; Shepson, P. B.; Sweeney, C.; Townsend-Small, A.; Wofsy, S. C.; Hamburg, S. P. Assessment of methane emissions from the U.S. oil and gas supply chain. *Science* **2018**, *361*, 186−188.
(46) U.S. Energy Information Administration. Maps: Exploration, resources, reserves, and production. Available online at: https://www.eia.gov/maps/maps.htm (accessed August 29, 2018).

DOI: 10.1021/acs.est.8b03535
Environ. Sci. Technol. 2018, 52, 12915−12925