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Methane Leaks from Natural Gas Systems Follow Extreme Distributions

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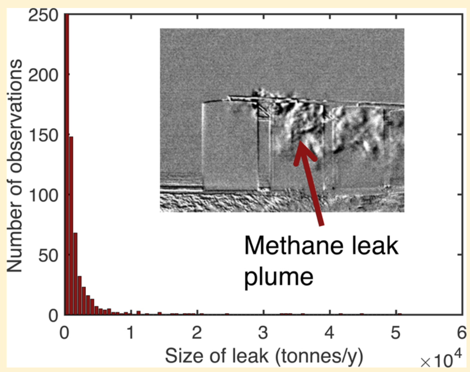
Supporting Information

ABSTRACT: Future energy systems may rely on natural gas as a low-cost fuel to support variable renewable power. However, leaking natural gas causes climate damage because methane (CH_4) has a high global warming potential. In this study, we use extreme-value theory to explore the distribution of natural gas leak sizes. By analyzing ~15 000 measurements from 18 prior studies, we show that all available natural gas leakage data sets are statistically heavy-tailed, and that gas leaks are more extremely distributed than other natural and social phenomena. A unifying result is that the largest 5% of leaks typically contribute over 50% of the total leakage volume. While prior studies used log-normal model distributions, we show that log-normal functions poorly represent tail behavior. Our results suggest that published uncertainty ranges of CH_4 emissions are too narrow, and that larger sample sizes are required in future studies to achieve targeted confidence intervals. Additionally, we find that cross-study aggregation of data sets to increase sample size is not recommended due to apparent deviation between sampled populations. Understanding the nature of leak distributions can improve emission estimates, better illustrate their uncertainty, allow prioritization of source categories, and improve sampling design. Also, these data can be used for more effective design of leak detection technologies.



INTRODUCTION

Some have argued that natural gas can play a key role in the future U.S. and global energy system as part of an "all of the above" energy strategy.[1] This is because natural gas is abundant, environmentally preferable to coal in many respects, and useful in complimenting flexible power systems under scenarios of rapid and high renewables penetration. However, even relatively small leaks from the natural gas system can create large climate concerns because natural gas is comprised mostly of methane (CH_4), a gas with high global warming potential (GWP, ~34 times that of CO_2 over 100 years, ~86 times on a 20-year basis).[2]

The U.S. Environmental Protection Agency (EPA) constructs an estimate of the volumes of methane emitted by the natural gas industry as part of its greenhouse gas inventory (GHGI).[3] A suite of evidence from many studies suggests that natural gas CH_4 leakage rates in the U.S. are higher than these official estimates,[4,5] which can create challenges for meeting climate stabilization goals.[6,7] Little is known about global natural gas system leakage rates, although a recent strong rise in global CH_4 concentrations raises concern about unknown or undercounted global CH_4 sources.[7] Some large studies have found high emissions from oil and gas systems in particular, including those using satellites,[8] and those analyzing historical air samples.[9]

All engineered systems have imperfections, and some loss of product is unavoidable. For example, electricity grids typically lose 5% or more of transmitted power.[10] The natural gas system is similar: upsets, malfunctions and errors can result in gas escaping to the air. In addition, some natural gas devices—like certain pneumatic valves—emit gas as a matter of their engineering design. The sum of the former (so-called fugitive emissions) and the latter (vented) we will refer to collectively as leaks.

One posited reason for this consistent underestimation of emissions is the "heavy tailed" distribution of emissions rates.[4] A number of early experimental studies of methane emissions from natural gas facilities found that emissions rates from natural gas leaks are highly heterogeneous: a small fraction of leaking sources (so-called "super-emitters") often account for large fraction of the total volume of leakage.[11−19] In addition, a suite of recent studies funded by the Environmental Defense Fund (EDF) have also found similar behavior.[5,11,20−30] Other studies by academic researchers[31−34] and consultants[35,36] found similar results. While this heavy-tailed behavior has been

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Table 1. General Study Characteristics for Included Studies (And Source of Underlying Measurements)

study	location	facilities studied	total sampled or screened components	emission volumes quantified
Allen et al. 2013	U.S. (various)	production facilities and drilling/completions activities	150 sites, 2030 listed components, unclear total component count[a]	769
Allen et al. 2014a	U.S. (various)	production facilities, pneumatic devices	377 measured devices	377
Allen et al. 2014b	U.S. (various)	production facilities, liquids unloading	107 wells	105
ERG et al. 2011	Texas (Barnett shale)	production (w/inclusion of few compressor stations and processing facilities)[b]	388 sites containing: 1138 wells, 1209 tanks, 188 compressors. 736,659 estimated valves and connectors.	2147
GHGRP 2015	U.S. (various)	all reporting facilities with reciprocating compressors, less categories with small numbers of reporting facilities	16 480 possible reported values	5048 reported values
Harrison et al. 2011	Texas, New Mexico	compressors, focus on transmission with some processing and gathering/boosting	84 compressors, over 5800 sources	176[e]
Hendrick et al. 2016	Massachusetts	distribution mains	100	100
Kang et al. 2014	Pennsylvania	abandoned wells	19 wells	19
Kuo 2012	California	all stages (production, processing, storage, transmission, and distribution)	972 devices,[c] 92 157 components screened	337
Lamb et al. 2015	U.S. (various)	metering and regulation, distribution	22 participating distribution companies	257 pipe leakage measurements, 693 metering and reg. measurements
Lan et al. 2015	Texas (Barnett shale)	wellpads, compressor stations, gas processing plants	152 facilities	24 wellpads, 7 compressor station measurements at 6 compressor stations, 2 gas processing plants
Mitchell et al. 2015	Texas (Barnett shale)	gathering facilities and processing plants	114 gathering facilities, 16 processing plants	131 reported observations[f]
NGML et al. 2006	U.S. (various)	gas processing plants	5 gas plants, 74 438 components screened	1629 to 1641[g]
Omara et al.	Pennsylvania	production wellpads	35 wellpads	4 flowback events, 31 other general Wellpad plumes
Rella et al. 2015	Texas (Barnett shale)	well pads	182 wellpads	115 nonzero measurements
Subramanian et al. 2015	U.S. (various)	compressor stations	47 compressor stations	327 extracted for this study, some are composite[h]
Yakovitch et al. 2015	Texas (Barnett shale)	various facility-scale plumes	170 sites	169 reported measurements
Zimmerle et al. 2015	U.S. (various)	compressors and other components in transmission and storage sector	Measurements at 677 facilities	2292 new onsite measurements reported, 2685 extracted for this study[j]

[a]Listed components include pneumatic controllers and chemical injection pumps. Does not include valves, flanges, etc. which are generally included in other study source counts. [b]Table 3.1-1 in study lists 375 well sites, 8 compressor stations, 1 proc. facility, 1 water treatment, 1 drilling, 1 fracking, 1 completion flowback. [c]"Equipment/systems screened included 172 wellheads, 131 separators, 17 dehydrators, 145 piping segments, 66 compressors (51 reciprocating, 9 centrifugal, 6 rotary), 374 pneumatic devices, 19 metering and regulating stations, 34 hatches, 2 pumps, and 12 customer meters" (Kuo 2012 p. 5). [d]Number of compressors across 11 sites from Table 2-1. Total components screened not presented, but averages across 5 transmission stations are presented in Table 3-1. [e]231 total possible sources are reported in Harrison et al. appendix tables, but some sources are reported as "-" (likely not measured, as distinct from reported values of 0 scfd). [f]The paper cites 130 G&P facilities, 114 gathering and 16 processing. Supplemental data sets include 131 observations. [g]Different numbers of leaks were reported in text and in tabular results (e.g., Appendix I from which data were extracted). [h]Each site can (and does) report multiple measurements for different types of equipment. In addition, each type of equipment at a given facility could report emissions summed across multiple instances of that equipment. For example, site "g" may report emissions from pneumatic devices as the sum of emissions from 4 leaking pneumatic devices. [j]This total for our study includes all sources in the document "CDFmaster.xlsx", excepting combustion related sources on the following tabs: *CombustionLean2Stroke, CombustionLean4Stroke, CombustionRich4-Stroke, CombustionTurbine.* This totals 2685 measurements.

observed in the literature many times, it has not been analyzed in a comprehensive fashion.

These superemitting sources represent profitable "low hanging fruit" for methane reduction efforts. Reducing emissions from these sources is claimed to be profitable by a number of sources.[37,38] Recent work in the Environmental Defense Fund "Barnett Coordinated Campaign" created a defined class of emitters called "functional super-emitters", based not only on the magnitude of the emissions source, but also on the throughput of the emitting facility.[39]

These superemitting sources may affect the uncertainty quantification for emissions inventories. EPA inventory methods take activity factors (AF), such as number of wells in a region, and multiply these by emissions factors (EFs), typically construed as mean emissions per activity unit (e.g., kg/well-yr). To account for large emitters, uncertainty was modeled in inventory methods using log-normal emissions distributions. However, if sampling efforts used to construct EFs missed large emitting "outlier" sources due to their infrequency, then their arithmetic mean could underestimate the true population mean. Poor understanding of source size distributions also affects scientific efforts to better understand emissions rates: since the distributions of populations of emitters are poorly understood, it is unclear what sample sizes are required for accurate representation of the underlying populations. Note that the issues of activity factor uncertainty can be significant, but are not addressed here.

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In this paper, we explore the statistical behavior of existing emissions data sets. We then explore the implications of these results for inventory methodologies and for designing new methane studies. We first collect data from a total of 18 different sources. We then create within-study and cross-study subsets of similar emissions sources. We then perform a variety of statistical and simulation-based studies to examine the potential for meta-analysis and cross-study aggregation, as well as study the impacts of assuming log-normal functional forms for emissions distributions. Lastly, we discuss the implications of our results for solving the leakage problem.

■ MATERIALS AND METHODS

We collect data from a screened set of 17 measurement-based studies and one regulatory data set (Supporting Information, SI, section S3), which include over 15 000 reported emissions rates. These data sets are summarized in Table 1.

The screening criteria for measurement-based studies require that underlying direct measurements be reported by the study authors, rather than summary statistics (e.g., mean) or plots (e.g, histograms of emissions distributions). The included studies are the only known studies in the public domain where the full set of underlying emissions measurements are reported by study authors. In addition, we include one set of emissions rates reported by natural gas operators to the EPA Greenhouse Gas Reporting Program (GHGRP), as these data in particular are required to be measured as part of the emissions reporting process (see SI for more discussion).

Some studies report emissions per site (e.g., wellpad) or facility (e.g., gas processing plant). In some cases, site-wide estimates are made via remote measurement. Our screening process separates these results from device-level measurements.

These studies cover a range of years, industry segments, and geographical locations. Sample sizes range from tens to thousands (see Table S1). In addition, the methods used to measure and classify emissions differ, at least slightly, between studies (see Table S2 for the emissions source classification schemes by source).

While there is measurement uncertainty any time an emissions rate is quantified, we neglect measurement uncertainty in this study. For example, direct measurement techniques such as the Bachrach Hi-Flow Sampler (BHFS) are often estimated to be accurate to ±10%.[16] We consider all emissions at their reported levels and study the effect of distributions of reported emissions.

An important note is that recent work[40,41] has suggested that there may be downward bias in the widely used BHFS, especially in cases where methane concentrations are low. The above work calls into question the results of the Allen et al. studies,[11,23,24] but the issues noted could affect other studies as well. It is not clear at this time either how widespread such problems are, nor the resulting degree of underestimation. Note that if the BHFS does indeed systematically underestimate the size of large leaks, then results here about the importance of superemitters would only be strengthened, not weakened.

A summary description of the methods and results of each study, as well as any caveats about the use of the data, are presented in SI section S2.

In order to further analyze data at a more granular level, we create two sets of categorized "source level" data sets. The first data set creates groups of like components within a given study. The second data set aggregates similar components across studies (e.g., all reported "flange" leaks). These will henceforth be called "single-study" and "cross-study" data sets, respectively. Single-study data sets have smaller sample sizes than cross-study data sets, but do not suffer from concerns about fitting single distributions to aggregate categories (see below). The data sets used rely on previously published studies and include or exclude types of sources as performed in the original study (e.g., for example, exhaust emissions of CH_4 due to incomplete combustion do not appear in any of the source data sets, though can be an important source).

Source categories were used wherever possible from those defined in original studies. Each study is given a leak classification scheme that includes up to three possible levels of classification ("sources", "sub-sources", and "sub-sub-sources"). Selecting categories for single-study data sets was done as follows:

- By default, the source-level categories are preferred (see SI Table S5).
- The resulting categorizations are reviewed by hand, and some studies are further disaggregated into "sub-source" categories where engineering judgment suggests appropriate (see SI for individual exceptions)
- An illustrative sample size cutoff of $n \geq 100$ is applied to ensure that there are sufficient measurements in each studied category.

A total of 52 single-study data sets exist after steps 1 and 2 (see SI). Of these categories, 34 had more than 100 observations. These 34 categories are shown in SI Table S4.

For creation of cross-study data sets, engineering judgment and discussion with original study authors was used to create a set of 26 cross-study component- or device level data sets, and 5 whole-facility data sets. Aggregation rules use "or" logic to allow inclusion of broader membership (no double counting). SI Tables S6 and S7 list these aggregation rules based on study category names outlined in SI Table S5. The statistical validity of grouping similarly named measurements from different studies was performed using two-sample Kolmogorov–Smirnov (KS) tests (null hypothesis: like-named data sets were sampled from the same underlying population).

For data sets passing screening tests, a number of additional statistical analyses were performed, including: finding the best-fitting log-normal distribution using method of moments (MOM), assessing log-normal fits using KS tests and properties of residuals in tail observations, and computing tail indices for weight of tails (large data sets only). We focus here on log-normal distributions because they are widely used, although we note that some studies have fitted other distributions as well.[26] See SI section S4 for more details.

Lastly, we performed simulation studies to examine the impacts of assuming that emissions rates are log-normally distributed. We explore including breadth and skew of mean estimate confidence intervals (CIs), reduction in CI breadth with increasing sample size, and expected contributions of superemitters to the leakage problem (see SI section S5). We conclude with some discussions about best practices as alternatives to using log-normal distributions.

■ RESULTS AND DISCUSSION

Our synthesis results show that (1) heavy-tailed distributions are a pervasive characteristic of natural gas leak size distributions; (2) natural gas leaks are more heavy-tailed than other natural and social phenomena, (3) the largest 5% of leaks

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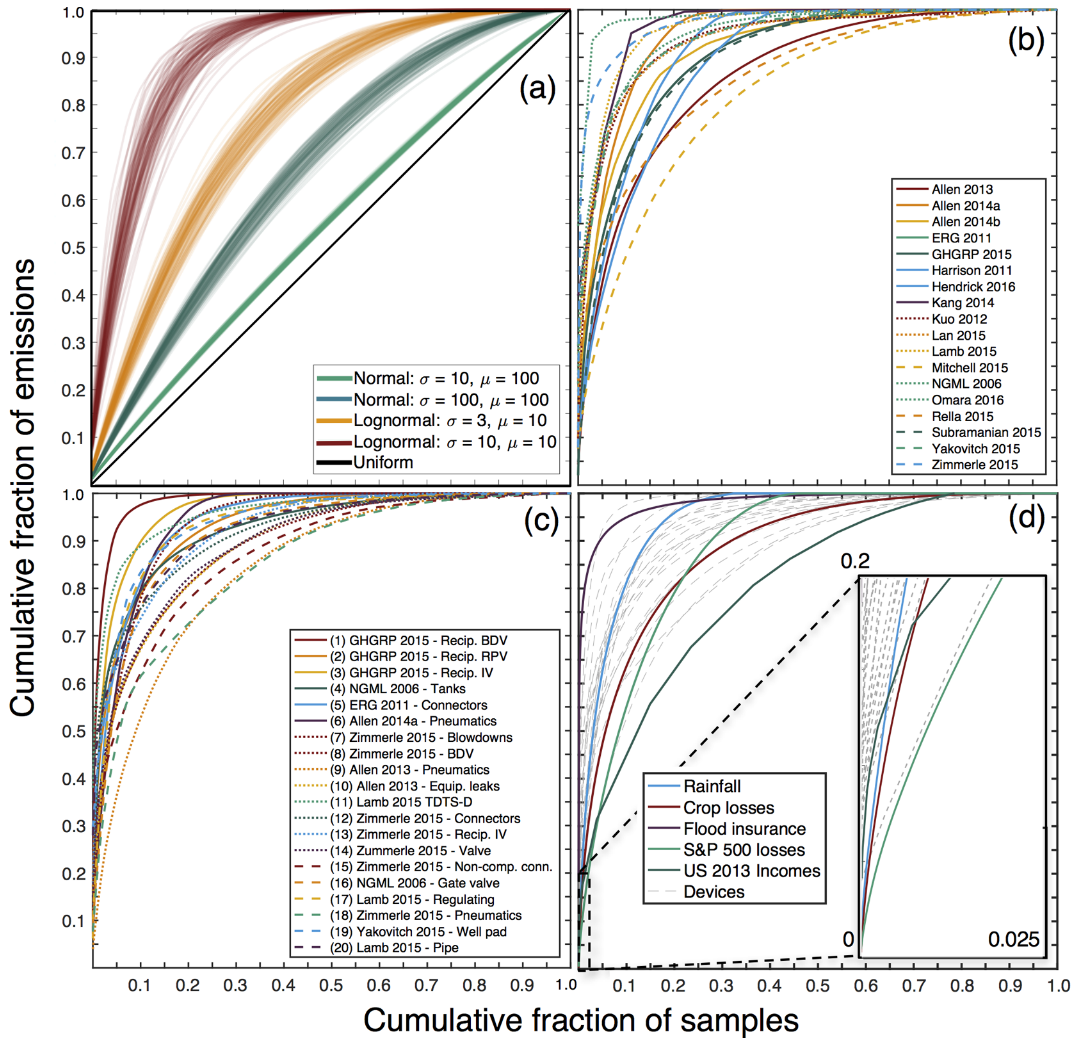

Figure 1. Normalized cumulative distributions showing the cumulative fraction of measurement samples (x-axis) and the cumulative fraction of emissions (y-axis), ordered from largest to smallest leaks. (a) shows envelopes of cumulative plots of n = 100 samples drawn from listed uniform, Gaussian and log-normal distributions. (b) shows cumulative contributions normalized for each study (18 total) in the analysis. (c) shows results for 20 largest source-specific data sets (see SI for abbreviations). And (d) compares those source-specific data sets (light gray) to heavy-tailed distributions from other natural and social phenomena. Inset to (d) focuses on the top 2.5% of samples, showing that emissions distributions for natural gas data sets are more extreme than other known heavy-tailed phenomena. See SI for additional discussion of methods and full lists of included data sets.

are (by median expectation) responsible for over 50% of the leaked methane from a given source category; (4) the recent use of log-normal distributions to model the distribution of leaks within a source category is not supported and systematically underestimates the importance of large emitters; (5) heavier-than-log-normal distributions lead to larger uncertainty than currently included in official estimates; (6) robustly characterizing heavy-tailed distributions will require sample sizes much larger than currently used in most studies; (7) aggregating results across studies to improve accuracy and robustness is statistically challenging. We discuss these results sequentially, and then we last discuss technology and policy implications of the synthesized evidence.

First, heavy-tailed distributions of emissions sources are ubiquitous across all available data sets. By ordering emission data sets from largest to smallest we create a set of cumulative normalized distributions (Figure 1). Each plot shows the increase in contribution to total emissions (y-axis) when cumulating ranked leaks (x-axis). Note that emissions distributions plotted by study (Figure 1b) show more contribution from large sources than a wide range of illustrative normal and log-normal distributions (Figure 1a). Similar plots of the 20 largest single-study data sets (Figure 1c) also show skewed distributions.

Second, Figure 1d shows that the tails of these distributions are extremely heavy compared to other heavy-tailed phenomena. Methane emissions are more extremely distributed than other natural and social phenomena known to exhibit heavy tails: precipitation events, investment losses, United States crop insurance claims, and United States personal incomes[42−45] (see especially 1d inset for top 2.5% of observations). Natural gas emissions distributions are less heavy-tailed than United States flood insurance claims. See SI section S2 for description of data gathering methods.

Third, from these results we propose a rule of thumb which we call the "5−50 rule": for a given source category, the largest 5% of leaks should be expected to account for at least 50% of total emissions on a median basis. As in prior studies,[27] we use

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the top 5% as our working definition for "super-emitters". Figure 2 plots the contribution of superemitters to total leakage

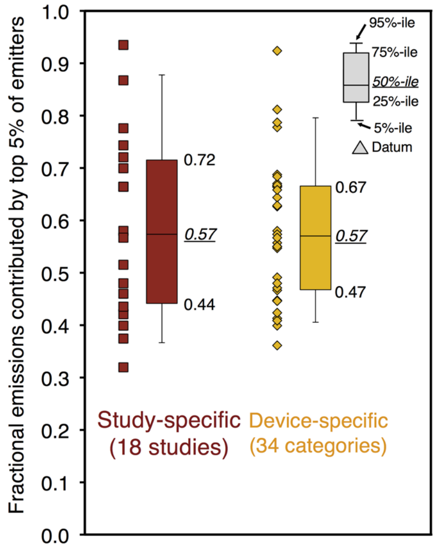

Figure 2. Fractional contribution of top 5% of emitters in each of 18 studies (red) and 34 device-specific categories of data from single studies (orange). Median results across both groupings are above 50% contribution from top 5% of emitters. Similar results were found for multistudy data sets (not plotted here, see SI).

for study-specific and device-specific data sets from Figure 1. Note that the median contribution of the largest 5% of leaks is above 50%. When reported, studies have tended to find between 0.5% and 2% of all operating components to be leaking a measurable amount,[13,16,32] suggesting that these superemitters will typically represent fewer than 1-in-1000 operating components.

Fourth, we show that the use of log-normal fits to data systematically underestimates the importance of the largest emitters. EPA has used log-normal distributions in modeling uncertainty and log-normal curves have been recently suggested as useful in modeling heavy-tailed emissions sources.[26,46] For each device-specific data set we use method of moments (MOM) to generate the best-fitting log-normal distribution. We then use the Kolmogorov–Smirnov (KS) test to examine whether the data were statistically likely to have been derived from the best-fitting log-normal distribution. 31 out of 34 data sets reject this hypothesis at $p < 0.0001$ level, while 33 of 34 reject this hypothesis at $p < 0.05$. These single-study data set measurements therefore do not appear to be drawn from log-normal distributions. Further, the residuals between log-normal fit and data in the tail are overwhelmingly positive (see Table S21). The implication of positive residuals is that fitted log-normal distributions will underpredict the importance of the largest sources. Graphical examples of positive residuals are shown in SI Figures S1 and S2.

The extent of this mis-alignment is illustrated in Figure 3. For the 20 largest single-study data sets, we draw from each best-

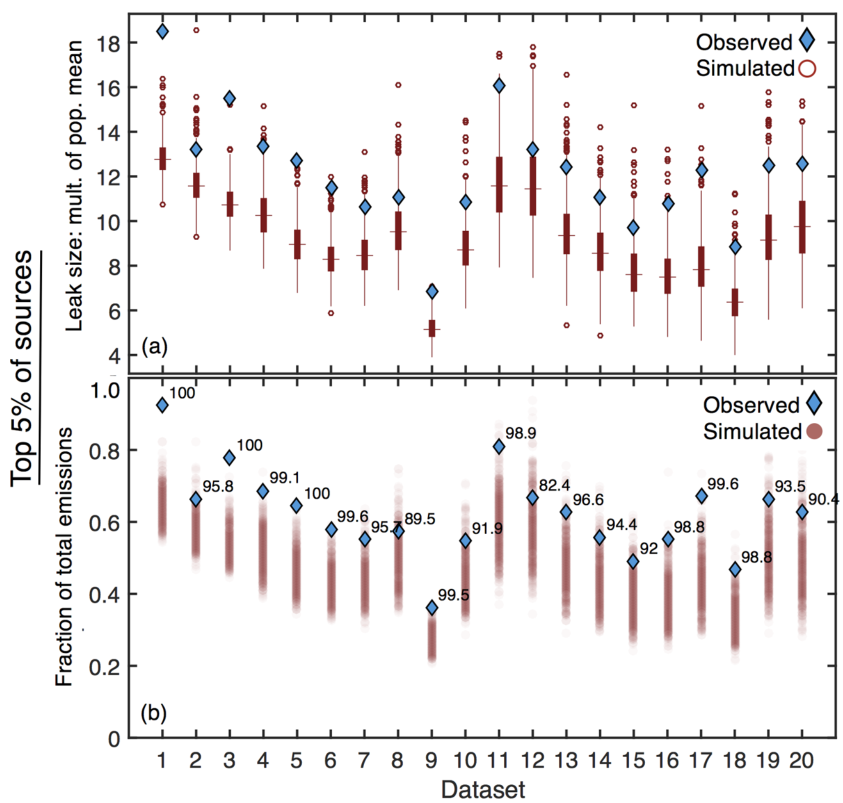

Figure 3. Results of using log-normal fits to estimate importance of superemitters (top 5% of sources). (a) Average size of leaks in top 5% expressed as multiple of population mean. Box plot shows interquartile range (box) and 1.5x IQR (whiskers) as well as outliers (dots) for 500 simulations. Empirically observed multiple of mean is shown as blue diamond. (b) Contribution of top 5% of sources as fraction of overall emissions. Empirical fractional contribution (blue diamonds) compared to 500 simulations based on best fitting log-normal distributions (semitransparent red circles). Percentiles of empirical observations are reported in (b). In both cases, drawing from a log-normal fit rarely recreates the empirical contribution of largest sources.

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fitting log-normal distribution a number of samples equal to the number of empirical samples. We repeat this process over 500 trials and each time compute two quantities: the average size of the top 5% of leaks expressed as multiple of the mean leak size (3a) and the fraction of all gas emitted by the top 5% of leaks (3b). Lognormal-derived results systematically underestimate both the size and relative contribution of the largest sources to empirical observations. Figure 3b lists numerical percentiles of empirical results, which are consistently high. In summary: while using a log-normal fit may recreate mean emitter behavior, it systematically underestimates the contribution of superemitters to the problem.

Fifth, heavy-tailed distributions result in wider and more asymmetric confidence intervals (CIs) around estimates of mean emissions than is currently appreciated. Estimated tail indices for some of these data are so extreme that standard CI approaches may be inappropriate and may lead to overly narrow and downwardly biased estimates of uncertainty. Current EPA methods[47] use this the AF-EF approach along with uncertainty analysis based on sampling from log-normal modeling approaches (SI section S2.3). This results in an EPA GHG inventory sector-wide uncertainty of −19% to +30%. Our analysis in SI (section S5) shows that a more robust uncertainty approach for heavy-tailed distributions (i.e., nonparametric bootstrap resampling) increases the width of CIs, generally by increasing the upper bound. Via simulation from a heavier-tailed-than-log-normal distribution (SI Section 6), we assess the coverage rates of *m*-out-of-*n* nonparametric bootstrap, *n*-out-of-*n* nonparametric bootstrap, and log-normal-based parametric bootstrap and find them to be 94.5%, 94.7%, and 90.7% respectively (S6.1). The coverage results further suggests that fitting a log-normal distribution gives an unrealistically narrow uncertainty range around the mean estimate.

Sixth, heavy-tailed distributions create challenges for required sample sizes. We investigate these impacts via simulation (S6). We illustrate this with a device-specific data set (data set 4 in Figure 1c). The first case (Figure 4a) samples repeatedly from the empirical distribution with increasing sample sizes to characterize how the CI around the mean shrinks with increasing sample size. We see that the CI stays wide up to and beyond sample sizes achieved in ground studies (n = 1000). Figure 4b shows that sampling from a fitted log-normal predicts mean emissions well (as expected) but has a CI that is overly narrow at any given sample size. The ratio of empirical to log-normal CI is plotted in Figure 4c, showing that the problem of an overly narrow CI from a log-normal fit only slowly improves with sample size. Figure 4d shows that increasing the sample sizes from a log-normal-derived population does not remedy the underestimation of the contribution of superemitters.

Seventh, there are statistical challenges to pooling results across studies. It might seem reasonable to address the challenge of small sample sizes by aggregating measurements of similar sources made across multiple studies. For example, measurements of emissions from “threaded connections” (i.e., nonwelded connections between devices and pipes) can be grouped across the 7 studies that report these kinds of leaks. However, after applying source category classifications to create cross-study data sets (S4.1), few of these groupings pass statistical muster: observations from similarly named sources but different studies rarely pass the two-sample KS test, indicating that studies’ samples of similarly named devices appear to be drawn from different underlying populations

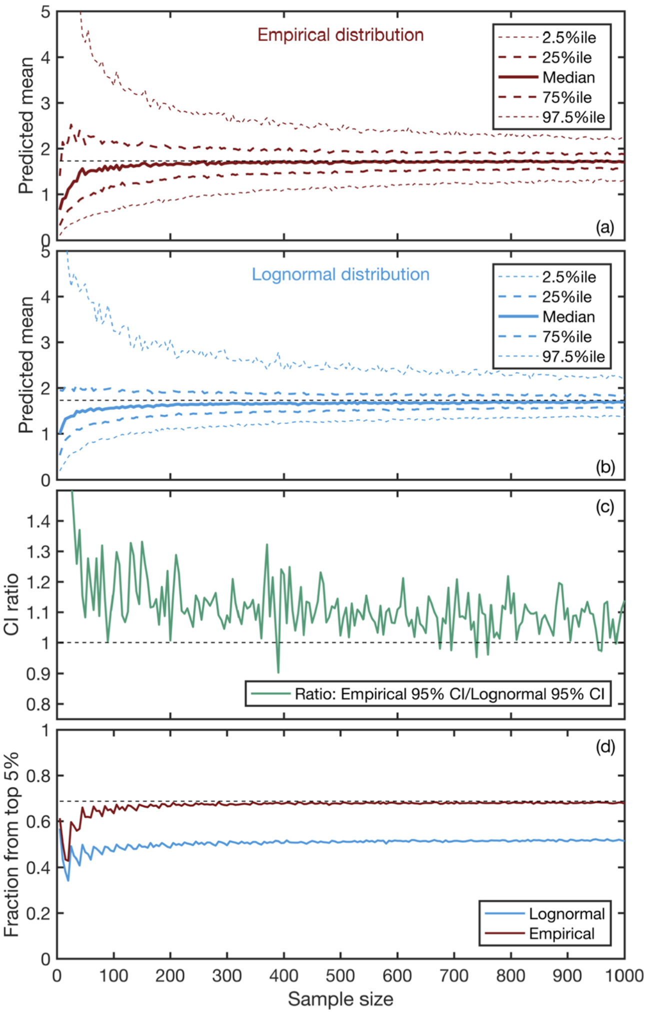

Figure 4. Effects of changing sample size on uncertainty in mean estimate, after drawing from (a) empirical distribution (data set 4 from Figure 1b) or (b) its best-fitting log-normal distribution. (c): The ratio of empirical 95% CI to log-normal-derived 95% CI is nearly always above 1, and only decreases slowly with sample size, suggesting that log-normal CIs are consistently too narrow. (d): Under-prediction of the importance of the top 5% of emitters is not remedied by increasing sample size.

(S4.2). For a cross-study category of “threaded connections” with observations from seven studies, 20 out of 21 unique pairwise study comparisons fail the two-sample KS test at the p = 0.01 level (S4). That is, in almost all cases, when we compare any two data sets of leaks from devices called “threaded connections”, they do not appear statistically to be derived from the same population. Similar results are seen widely for cross-study aggregation (see SI).

Possible reasons for KS test failure include (a) devices physically differ in design, size, etc. despite being similarly named; (b) operator practice or management strategies differ; (c) scientific instruments or measurement methods differ; (d) studies mistakenly aggregate unlike devices into a common category; or (e) the aggregation categories we tested are invalid. KS test failure may imply that source category definitions are not precise enough to identify populations with similar emissions distributions, or perhaps that determinants of emissions rates are poorly understood and incorrectly stratified in sampling design (e.g., component age and operating pressure

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may be more useful classification variables than component type, or may be important subcategory classifications). An additional implication is that KS-test failure raises concerns about extrapolating experimental results from sampled devices to their full populations.

Importantly, GHG inventories[3,44] are generally constructed by summing estimated emissions from many source categories within a given sector. This summation could reduce the uncertainty in sector-wide emissions through compensating errors: overestimates in one source category can counteract underestimates in others. However, because of the wide range in absolute magnitude of emissions across source categories, this compensation is of unknown effectiveness (e.g., an underestimate in a large source category may be difficult to fully offset with overestimates in smaller source categories). Further, if inventories are to be useful for prioritization of emissions reduction efforts, then large uncertainties in source-level emissions estimates can result in suboptimal allocation of mitigation resources.

The above results also have implications for regulatory design. Technological fixes alone will not solve problems arising from damage or out-of-specification conditions that might cause superemitter behavior. Each of millions of global natural gas infrastructure sites (e.g., gas wells or compressor stations) can contain hundreds (or possibly thousands) of potential points of leakage. In this context there is no substitute for diligence: to reduce frequency of superemitters, formal leak detection and repair (LDAR) programs have been demonstrated to be effective.[48] Given the stochastic nature of device failures and large consequences of small numbers of superemitters, this suggests that a regulatory approach mandating repeat checkups (as in recently proposed EPA regulation)[49] could effectively reduce superemitter emissions. Regulators can learn from other domains where superemitters are a major challenge (e.g., vehicle emissions).

Performance targets for novel detection technologies[50] can be informed by the emission distributions synthesized here. Figure 5 shows cumulative absolute emissions magnitudes for various sources. Across device-level leaks from all included studies, 90% of emissions result from devices with emissions greater than ≈60 kg CH_4/d. In contrast, a recent U.S. Federal funding effort[50] aimed to detect 90% of emissions with a sensitivity target of 2.7 kg CH_4/d. While we cannot claim that our aggregate data set is representative of the actual real-world mix of leaks, basing R&D targets on the largest data set possible could possibly allow more efficient solutions to the problem (i.e., avoid "over-engineering" of detector technologies).

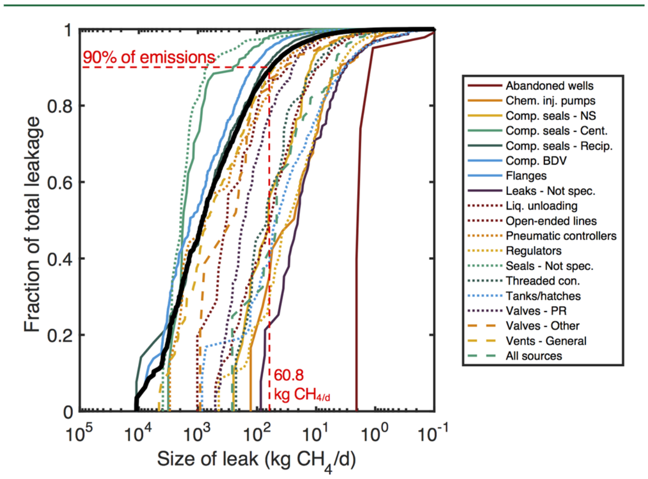

Figure 5. Cumulative fraction of leakage as a function of leak size for multistudy device-specific data sets. Cumulatively, 90% of all emissions from device-level measurements come from leaks larger than 60 kg CH_4/d.

Superemitters are attractive as a mitigation target for achieving substantial emissions reductions at low marginal cost. However, as seen in Figure 5, certain source categories have much larger emissions than others. This suggests that a two-tiered policy approach could be efficient. Such an approach could include LDAR programs to find and repair superemitting devices, coupled with empirically based emission limits or more rigorous and pro-active preventative maintenance schedules for devices that are known to be large emitters. The growing body of work we synthesize here can inform improvements to the technical design of both approaches.

Lastly, these results have implications for meeting country's intended nationally determined contributions (INDCs) of reducing GHG emissions made in the recent 2015 Paris climate agreements.[51] If a particular country plans to rely on natural gas for their INDCs, compliance and achievement of these targets cannot simply rely on estimates of GHG emissions at the point of combustion, but must also conduct comprehensive sampling "upstream" of the power stations and other points of use to ensure no degradation of performance due to methane leaks.

Gaps remain in our understanding of superemitters, and much work remains. Researchers and funders can use the results presented here to improve sampling design to enhance the robustness of results from methane measurement studies, optimize sample sizes, and address critical gaps in knowledge.

The above analysis illustrates the deficiency of assuming a log-normal distribution, but any parametric distribution, when fitted to the entire data set, is likely to poorly represent the upper tail due to the small number of tail observations that will be outweighed by the body of the observations. Consequently, CIs generated using parametric methods will likely underrepresent the uncertainty associated with the mean estimates. Alternatively, using a nonparametric approach such as resampling does not assume any underlying distribution, and instead directly employs the values observed in tail. However, resampling comes with its own challenges: it requires adequate sample sizes, and the extremely heavy tails exhibited by methane leakage data sets imply that standard CI methods may not be suitable (S4).

Standardizing source category classification schemes would increase robustness of results, including extrapolations to national populations, while allowing for future meta-analysis. Lastly, inventory uncertainty quantification could be improved by leveraging available data to develop more accurate confidence intervals and statistical models; available evidence suggests that uncertainty is greater than currently estimated.

Other nonstatistical challenges remain that are not well addressed by the above analysis. One challenge in many experimental designs (including some reviewed here) is the fact that on-site measurements require participation of operating companies. This subjects all such studies to difficult-to-quantify sampling bias (i.e., volunteering companies may not represent all companies). In addition, there is currently little understanding of superemitter persistence and intermittency. Nor is there much understanding of the root causes of superemitter failures.

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Environ. Sci. Technol. 2016, 50, 12512−12520

Addressing the methane leakage challenge is a necessary condition for natural gas to contribute to a clean energy future. And solutions to this methane challenge will be more effectively mandated, more efficiently designed, and more economically deployed if we improve our understanding of superemitting sources.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04303.

Additional information as noted in the text (PDF) (XLSX)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) White House. Climate change and President Obama's action plan: The Clean Power Plan. 2015. https://www.whitehouse.gov/climate-change.

(2) Intergovernmental Panel on Climate Change, Climate Change. In *The Physical Science Basis*Stocker, T., et al., Eds.; Cambridge University Press: Cambridge, 2013.

(3) EPA. *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2013*; EPA, 2015.

(4) 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.; Brown, N. J.; Bradley, R.; Stucky, G. D.; Eardley, D.; Harriss, R. Methane Leaks from North American Natural Gas Systems. *Science* **2014**, *343*, 733–735.

(5) Harriss, R.; Alvarez, R. A.; Lyon, D.; Zavala-Araiza, D.; Nelson, D.; Hamburg, S. P. Using Multi-Scale Measurements to Improve Methane Emission Estimates from Oil and Gas Operations in the Barnett Shale Region, Texas. *Environ. Sci. Technol.* **2015**49, 7524.10.1021/acs.est.5b02305

(6) Intergovernmental Panel on Climate Change. Climate Change In *Mitigation of Climate Change*; Edenhofer, O., et al., Eds.; Cambridge University Press: Cambridge, U.K., 2014.

(7) Nisbet, E. G., Dlugokencky, E. J., Bousquet, P. Methane on the Rise – Again. *Science*. **2014***343*(6170) 493–495.10.1126/science.1247828

(8) Kort, E. A.; Frankenberg, C.; Costigan, K. R.; Lindenmaier, R.; Dubey, M. K.; Wunch, D. Four corners: The largest US methane anomaly viewed from space. *Geophys. Res. Lett.*, **2014***41*, 6898–6903.10.1002/2014GL061503

(9) Rice, A. L.; Butenhoff, C. L.; Teama, D. G.; Roger, F. H.; Khalil, M. A.; Rasmussen, R. A.; Atmospheric methane isotopic record favors fossil sources flat in 1980s and 1990s with recent increase. *Proc. Natl. Acad. Sci. U. S. A.* **2016***113*(39). 10791–10796.10.1073/pnas.1522923113

(10) IEA. Electric power transmission and distribution losses (% of output). Dataset EG.ELC.LOSS.ZS, http://www.iea.org/stats/index.asp (accessed October 4, 2016).

(11) 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.

(12) Chambers, A. *Optical Measurement Technology for Fugitive Emissions from Upstream Oil and Gas Facilities*; Alberta Research Council: Edmonton, AB, 2004.

(13) Clearstone Engineering. *Identification and Evaluation of Opportunities to Reduce methane Losses at Four Gas Processing Plants*; Gas Technology Institute: Des Plaines, IL, 2002.

(14) Cormack, J. *Energy Management Workshop for Upstream and Midstream Operations: Increasing Revenue through Process Optimization & Methane Emissions Reduction*; Global Methane Initiative: Calgary, Alberta, Canada, 2007.

(15) Harrison, M. R.; Galloway, K. E.; Hendler, A.; Shires, T. M.; Allen, D.; Foss, M.; Thomas, J.; Spinhirne, J. *Natural Gas Industry Methane Emissions Factor Improvement Study*; EPA, 2011.

(16) National Gas Machinery Laboratory, Clearstone Engineering, Innovative Environmental Solutions. *Cost-Effective Directed Inspection and Maintenance Control Opportunities at Five Gas Processing Plants and Upstream Gathering Compressor Stations and Well Sites*; EPA, 2006.

(17) Picard, D. *Modern Technologies of Detection and Elimination of Methane Leakages from Natural Gas Systems*; Akademgorodok, Russia, 2005.

(18) Shorter, J. H.; McManus, J. B.; Kolb, C. E.; Allwine, E. J.; Lamb, B. K.; Mosher, B. W.; Harriss, R. C.; Howard, T.; Lott, R. A. Collection of Leakage Statistics in the Natural Gas System by Tracer Methods. *Environ. Sci. Technol.* **1997**, *31*, 2012–2019.

(19) Trefiak, T. *Pilot Study: Optical Leak Detection and Measurement*; ConocoPhillips, 2006.

(20) Lyon, D.; Zavala-Araiza, D.; Alvarez, R. A.; Harriss, 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, 8147–8157.10.1021/es506359c

(21) 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, 8139.10.1021/es5063055

(22) 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, 3252.10.1021/es5060258

(23) Allen, D. T.; Pacsi, A. P.; Sullivan, D. W.; Zavala-Araiza, D.; Harrison, M.; Keen, K.; Fraser, M. P.; Hill, A. D.; 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, 633.10.1021/es5040156

(24) 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: Liquid Unloadings. *Environ. Sci. Technol.* **2015**49, 641–648.10.1021/es504016r

(25) Yakovitch, 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, 7889.10.1021/es506352j

(26) Lamb, B. K.; Edburg, S. L.; Ferrara, T. W.; Howard, T.; Harrison, M. R.; Kolb, C. E.; Townsend-Small, A.; Dyck, W.; Possolo, A.; Whetstone, J. R. Direct Measurements Show Decreasing Methane

DOI: 10.1021/acs.est.6b04303
Environ. Sci. Technol. 2016, 50, 12512–12520

Emissions from Natural Gas Local Distribution Systems in the United States. *Environ. Sci. Technol.* **2015***49*, 5161.10.1021/es505116p

(27) Zimmerle, D. J.; Williams, L. L.; Vaughn, T. L.; Quinn, C.; Subramanian, R.; Duggan, G. P.; Willson, 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*, 9374.10.1021/acs.est.5b01669

(28) Rella, C. W.; Tsai, T. R.; Botkin, C. G.; Crosson, R. R.; Steele, D.; Measuring Emissions from Oil and Natural Gas Well Pads Using the Mobile Flux Plane Technique. *Environ. Sci. Technol.* **2015***49*, 4742−4748.10.1021/acs.est.5b00099

(29) 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*, 3219−3237.10.1021/es5052809

(30) Marchese, A. L.; 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*, 10718−10727.10.1021/acs.est.5b02275

(31) Kang, M.; Kanno, C. M.; Reid, M. C.; Zhang, X.; Mauzerall, D. L.; Celia, M. A.; Chen, Y.; Onstott, T. C.;. Direct measurements of methane emissions from abandoned oil and gas wells in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* **2014***111*, 18173−18177.10.1073/pnas.1408315111

(32) Kuo, Jeff. *Estimation of Methane Emission from the California Natural Gas System*; California State University: Fullerton, 2013; California Energy Commission. Publication number: CEC-500−2014-072.

(33) Hendrick, M. F.; Ackley, R.; Sanaie-Movahed, B.; Tang, X.; Phillips, N. G. Fugitive methane emissions from leak-prone natural gas distribution infrastructure in urban environments. *Environ. Pollut.*, **2016***213*, 710−716.10.1016/j.envpol.2016.01.094

(34) Omara, M.; Sullivan, M. R.; Subramanian, R.; Robinson, A. L.; Presto, A. A.; Methane emissions from conventional and unconventional natural gas production sites in the Marcellus shale basin. *Environ. Sci. Technol.* **2016***50*, 2099−2107.10.1021/acs.est.5b05503

(35) Eastern Research Group, Sage Environmental Consulting. *City of Fort Worth Natural Gas Air Quality Study*, City of Fort Worth, TX, 2011).

(36) Harrison, M. R.; Galloway, K. E.; Hendler, A.; Shires, T. M.; Allen, D.; Foss, M.; Thomas, J.; Spinhirne, J. *Natural Gas Industry Methane Emissions Factor Improvement Study*, EPA, 2011.

(37) Harvey, S.; Gowrishankar, V.; Singer, T.; *Leaking Profits: The U.S. Oil and Gas Industry Can. Reduce Pollution, Conserve Resources, and Make Money by Preventing Methane Waste*. Natural Resources Defense Council.

(38) ICF. Economic Analysis of Methane Emission Reduction Opportunities in the U.S. Onshore Oil and Natural Gas Industries. Prepared for Environmental Defense Fund. March 2014.

(39) Zavala-Araiza, D.; Lyon, D.; Alvarez, R. A.; Palacios, V.; Harriss, 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*, 8167.10.1021/acs.est.5b00133

(40) Howard, T.; Ferrara, T. W.; Townsend-Small, A. Sensor transition failure in the high flow sampler: Implications for methane emission inventories of natural gas infrastructure. *J. Air Waste Manage. Assoc.* **2015***65*, 7, 856−862.10.1080/10962247.2015.1025925

(41) Howard, T. University of Texas study underestimates national methane emissions at natural gas production sites due to instrument sensor failure. *Energy Sci. Eng.* **2015**, *3*, 443−455.

(42) NOAA. Daily Summaries Station Details: Boulder CO, US, Network ID GHCND:USC00050848. National Centers for Environmental Information, National Oceanic and Atmospheric Administration.http://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USC00050848/detail.

(43) RFF. Data − Climate Change and Extreme Events: National Flood Insurance Claims by County and Crop Insurance Indemnities Paid. Resources for the Future. http://www.rff.org/events/event/data-climate-change-and-extreme-events (accessed October 2015).

(44) Yahoo Finance. S&P 500 historical prices. http://finance.yahoo.com/q/hp?s=%5EGSPC+Historical+Prices (ccessed October 1, 2015).

(45) IRS 2015. Number of Individual Income Tax Returns, Income, Exemptions and Deductions, Tax, and Average Tax, by Size of Adjusted Gross Income. http://www.irs.gov/uac/SOI-Tax-Stats-Statistics-of-Income (accessed October 8, 2015).

(46) Zavala-Araiza, D.; Lyon, D. R.; Alvarez, R. A.; Davis, K. I.; Harriss, R.; Herndon, S. C.; Karion, A.; Kort, E. A.; Lamb, B. K.; Lan, C.; 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. PNAS, Dec 22. 2015.

(47) UNFCC. Greenhouse Gas Inventory Data. United Nations Framework Convention on Climate Change. http://unfccc.int/ghg_data/items/3800.php (accessed January 2015).

(48) Heath, G. A.; Warner, E.; Steinberg, D.; Brandt, A. R. (2015) Estimating U.S. Methane Emissions from the Natural Gas Supply Chain: Approaches, Uncertainties, *Current Estimates, and Future Studies*. National Renewable Energy Laboratory http://www.nrel.gov/docs/fy16osti/62820.pdf.

(49) U.S. Federal Register. Final Rule: Oil and Natural Gas Sector: Emission Standards for New, Reconstructed, and Modified Sources. Document citation: 81 FR 35823.

(50) ARPA-E. MONITOR: Methane observation networks with innovative technology to obtain reductions. Advanced Research Projects − Energy. http://arpa-e.energy.gov/?q=arpa-e-programs/monitor.

(51) UNFCC. Synthesis report on the aggregate effect of the intended nationally determined contributions. October 2015,.

DOI: 10.1021/acs.est.6b04303
Environ. Sci. Technol. 2016, 50, 12512−12520