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On the Long-Term Temporal Variations in Methane Emissions from an Unconventional Natural Gas Well Site

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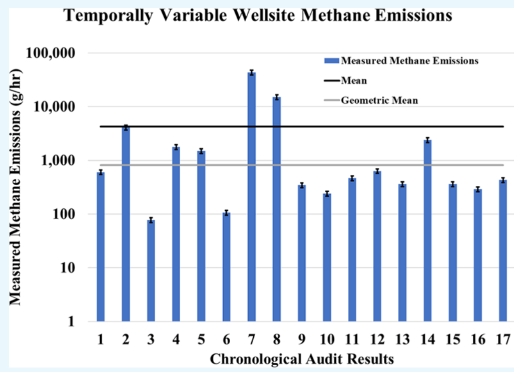
ABSTRACT: Understanding methane emissions from the natural gas supply chain continues to be of interest. Previous studies identified that measurements are skewed due to "super-emitters", and recently, researchers identified temporal variability as another contributor to discrepancies among studies. We focused on the latter by performing 17 methane audits at a single production site over 4 years, from 2016 to 2020. Source detection was similar to Method 21 but augmented with accurate methane mass rate quantification. Audit results varied from ∼78 g/h to over 43 kg/h with a mean emissions rate of 4.2 kg/h and a geometric mean of 821 g/h. Such high variability sheds light that even quarterly measurement programs will likely yield highly variable results. Total emissions were typically dominated by those from the produced water storage tank. Of 213 sources quantified, a single tank measurement represented 60% of the cumulative emission rate. Measurements were separated into four categories: wellheads (n = 78), tank (n = 17), enclosed gas process units (n = 31), and others (n = 97). Each subgroup of measurements was skewed and fat-tailed, with the skewness ranging from 2.4 to 5.7 and kurtosis values ranging from 6.5 to 33.7. Analyses found no significant correlations between methane emissions and temperature, whole gas production, or water production. Since measurement results were highly variable and daily production values were known, we completed a Monte Carlo analysis to estimate average throughput-normalized methane emissions which yielded an estimate of 0.093 ± 0.013%.



■ INTRODUCTION

Methane is the primary component of natural gas and is a potent greenhouse gas (GHG). In 2018, the Environmental Protection Agency (EPA) estimated that methane represented 10% of U.S. GHGs on a CO_2 equivalent mass basis.[1] Methane's global warming potential (GWP) is estimated to be 28−36 over 100 years.[2] Any methane lost in the production and distribution of natural gas represents a loss of energy and offsets the lower carbon intensity of natural gas.[3,4] With the successful development of the shale gas, numerous studies have focused on improving the understanding of methane emissions from across the entire natural gas supply chain. Many of these studies have highlighted extreme distributions of measurement values[5−8] and others have identified significant temporal variations in methane emissions.[3,4,9,10] Various studies have focused specifically on methane emissions from natural gas production sites (well sites) using both direct component-level measurements and indirect downwind methods.[11−16] Well sites are the first step of the supply chain and include the wells and some associated equipment necessary to introduce the produced gas to a local gathering pipeline. Improving the understanding of methane emissions from various sites or components can enable faster detection and repair to reduce losses and their associated environmental impacts. In addition, a better understanding of temporal variations highlights the need for frequent measurements to better assign emissions for inventory purposes. The following are more detailed reviews of literature as categorized by the focus of their analyses.

Well Site Emissions. Rella et al. reported on indirectly measured methane emissions from well sites in the Barnett shale, which encompasses 17 counties near Dallas, Texas.[11] They used a downwind ground-based mobile flux plane method to assess methane emissions from nearly 200 wells. Sites with detectable emissions had a mean emissions rate of 1.72 kg/h. Goetz et al. conducted similar indirect measurements using downwind tracer ratios and conducted measurements across the supply chain in the Marcellus shale, primarily located across Pennsylvania (PA) and West Virginia (WV).[12] The three unconventional well sites with multiple wells measured by Goetz et al. had estimated emissions rates of 0.61, 1.06, and 1.48 kg/h. Omara et al. focused specifically on conventional and unconventional well sites in the Marcellus

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shale by the tracer ratio method.[13] They estimated methane emissions from unconventional well sites at 18.8 kg/h with a 95% CI from 12 to 26.8 kg/h, but these data included four unconventional sites experiencing flowback conditions.

Distributions and Super-Emitters. With recent data sets collected across the supply chain, researchers have examined the distribution of measurements. Multiple studies have identified that distributions are not normal and often skewed with fat tails caused by "super-emitters". These findings have been identified as a possible contributor to discrepancies between various estimation methods. Brandt et al. first posited this in their seminal Science article.[17] Brandt et al. subsequently analyzed 15,000 measurements from 18 studies.[5] The unifying result was that 5% of "leaks" typically contributed to over 50% of the leak volume−known as the "5-50 rule". Zavala-Araiza et al. examined these super-emitter phenomena and found that they were caused by "abnormal process conditions".[6] In their analysis, they defined a super-emitter threshold of 26 kg/h as it corresponded to the highest 1% of sites, which contributed to 44% of site emissions. Caulton et al. conducted an extensive mobile measurement survey of Marcellus shale well sites (in PA) and reported on the importance of super-emitter well sites.[7] Their estimated geometric mean emissions rate of 673 well sites was only 2.0 kg/h; however, the presence of super-emitters produced a mean emissions rate of 5.5 kg/h. The top 10% of emitters represented 77% of the total emissions. They examined super-emitters based on both emissions rate and proportional losses. Their mass-based super-emitter threshold was defined as 9 kg/h. Numerous other studies have highlighted the skewed nature of emissions across various scales of analysis including national estimates,[14] well sites in the Barnett,[11] gas sites in California,[15] individual well sites in multiple basins,[16] abandoned oil and gas wells in California,[18] marginally producing wells,[19] and conventional and unconventional well sites in the Marcellus shale.[13] We note that most new studies have identified similar skewed distributions, and some have been used to improve datasets used for inventories. However, it is important to note that regulatory reporting still uses older emissions factors (EFs), or simple average values based on overall component categories.

Temporal Variations. Multiple studies have suggested that the previously discussed super-emitters and distributions contributed to discrepancies between various studies. Alternatively, Vaughn et al. studied spatial and temporal variability using multiscale emission measurements and activity data to explain the differences between top-down and bottom-up methods to estimate methane emissions from operations in the Fayetteville shale gas basin in Arkansas.[3] They found that high-resolution temporal activity data along with contemporaneous measurements were critical to improving the understanding of methane emissions from this dry gas-producing basin. However, they also noted the importance of accounting for high-emitting sources and abnormal process conditions. We previously reported on temporal variations from six direct quantification audits over 21 months at a single production site in the Marcellus shale.[9] These preliminary data showed that methane emissions varied temporally from 86 g/h to 4.1 kg/h varying by a factor of 54. Here, we have expanded the time scale to 4 years, and this extended analysis showed additional variability and now includes some super-emitter-type observations. Alden et al. identified that methane emissions from natural gas storage facilities varied temporally after conducting continuous long-term monitoring.[10] From a total of 11 months of data, they showed that the highest 10% of 3 h time periods represented 41% of the total observed emissions. Maximum emissions were 2.4 times the 95% fractile of the distribution, and overall, the data were lognormally distributed. In addition, and as discussed later, many studies attempt to utilize snapshots in time and normalize those values based on natural gas or produced liquids rates. The issue of temporal variability in methane emissions normalized by throughput is confounded over time as both gas and liquids production rates decrease over the life of the well. Cardoso-Saldana and Allen recently examined these temporal evolutions for oil and gas wells.[4]

Throughput-Normalized Methane Emissions. Cardoso-Saldana and Allen examined both wet and dry gas wells using recent emissions measurements, Monte Carlo (MC) simulations, and production decay terms to determine methane intensity, or methane emissions as a percentage of gas production at different times over the life of the well.[4] Their model showed that for dry gas sites, water production declined faster than the decay of gas production, which matched with production data available for our studies' focus site. Their middle scenario varied between 0.04 and 1.51% with an average lifecycle methane intensity of 0.21%. The 2016 Omara et al. study also examined the natural gas production from their sites and presented throughput-normalized methane emissions (TNME). We used the same metric here to define our data. Omara et al. determined that TNME for unconventional well sites had a median value of 0.13% with a range from 0.01 to 1.2%. They then used site-level methane emissions from 1000 well sites to synthesize and produce a national estimate.[14] Their new measurements included direct quantifications at the component level, downwind tracer ratio results, and downwind OTM 33A measurements. New data were added to recent data in the literature to model estimated average production site emissions. Regression modeling estimated per site emissions of 0.67 kg/h/site (TNME of 0.59%). Nonparametric modeling estimated per site emissions of 1.7 kg/h/site (TNME of 1.5%). Caulton et al. also used monthly production data with their measurements in the Marcellus and found a geometric mean TNME of 0.53% with a 95% confidence interval of 0.45−0.64%.[7]

Marcellus Shale Energy and Environmental Laboratory. The site analyzed here was the Marcellus Shale Enerrgy and Environmental Laboratory (MSEEL). The MSEEL was developed as a long-term field site to investigate and validate new knowledge and technology, which could improve recovery efficiency while minimizing environmental implications of unconventional resource development (additional information can be found at the project website).[20] The laboratory was developed through a collaboration with researchers at West Virginia University, the Ohio State University, Northeast Natural Energy, LLC, Schlumberger, the Department of Energy, and others. The production site includes four unconventional wells targeting the Marcellus shale. The site includes associated equipment for initial gas processing (enclosed gas processing units (EGPUs), sand filters, pneumatics, and thermoelectric generator), and a single produced water storage tank. The wells produce dry gas with methane representing over 97% of the composition, and no other liquid tanks are located at the site. Two of the wells have been in production since early 2012, while two newer wells began production in 2016. Direct methane quantification audits commenced after the initial flow back period

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(November 2016) and continued periodically until November 2020. Audits were conducted semi-randomly every 2−5 months. Researchers generally provided the operator with an estimated window of 1−2 weeks, and these were generally approved so long as no major site activity was scheduled. Semi-random audits may have led to biased results, but based on the variations in emissions and associated trends of the major sources, we feel that any bias was negligible regarding assessment of the site as normally encountered. We have no information regarding operator site visits or any record of leak detection and repairs made by the operator.

We note that this well site is somewhat unique in that it primarily provides natural gas to the greater Morgantown metropolitan area and when demand is low, one or more wells may be shut in to adjust supply. Figure S1 shows that gas throughput correlated with daily average low temperatures, as the area experiences higher demand based on seasonal heating. Additional production details are available on the MSEEL website. Although it is part of the research program, the well site functions as a typical dry gas well pad for the production and sale of shale gas.

■ MATERIALS AND METHODS

Our audit approach generally aligned with those set forth in the Code of Federal Regulation (CFR) 40 CFR Subpart W - 40 CFR § 93.324 for Monitoring or Method 21 of 40 CFR Part 60.[21,22] This included on site leak detection with a handheld methane concentration instrument and quantification with our customized and highly accurate high-volume sampler device. We note that many operators have transitioned from scanning with handheld units to identifying leaks with optical gas imaging cameras. We separated potential methane sources into four categories—the wells themselves (plumbing, controls, wellhead, and casing cellar), two EGPUs, the produced water storage tank, and other sources. Other sources included any leaks and losses identified with all above ground components not directly connected to the EGPUs, wells, or tank. Wellheads themselves were tented and sampled as four separate components. These measurements included all fittings and other emissions sources such as well casings or fittings below grade, within the cellar. These measurements typically lasted between 20 and 30 min and were background-corrected with a baseline tent flux. The EGPUs were quantified using their own shelters where possible as aggregated components. The tank was sampled in the condition upon arrival and emissions typically came from an open thief hatch or the tank vent. The tank did not include any emissions control. Other sources were identified with a screening approach similar to Method 21.[22] Components were scanned with a handheld methane detector (Eagle 2, RKI Instruments) and marked for subsequent quantification when concentrations were 500 ppm or higher. All components were accessible during 16 of the 17 audits, so no components were not accessible. We note that early audits included gas analysis of the exhaust stacks of the EGPUs, but methane emissions were low in comparison to other sources and their operation tended to be intermittent and limited.

Quantification of mass-based emissions occurred using the patent-pending full flow sampling system (FFS). The primary system components were an explosion-proof blower, which enabled capture of entire leak plumes plus dilution air, a combination of laser spectrometers primarily focused on methane concentration measurement, and a calibrated flow meter. Concentrations were background-corrected using a site background that was collected at the well site in a region where no equipment was located. Note that this background correction applied to all measurements except the well values, which used a separate tented background. Operating procedures have been developed, and additional details have been presented in the literature.[9,23,24] Equation 1 shows the overall calculation to convert measured variables to a methane mass emissions rate (MMER), typically reported in grams per hour (g/h)

$$\mathrm{MMER} = Q \times \left(\frac{\mathrm{CH_4meas} - \mathrm{CH_4background}}{10^6}\right) \times \rho \times \eta \times M \times k_\mathrm{P} \times k_\mathrm{RH} \times k_\mathrm{T} \times k_{\mathrm{CH_4}} \quad (1)$$

where the MMER is in grams per hour (g/h), Q is the measured total sample flow rate in cubic feet per minute (CFM), CH_4meas and CH_4background are the concentrations of methane in parts per million by volume (ppm) of the measurement and background, respectively, ρ is the volume conversion constant of 28.3 L/SCF, η is the molar volume conversion of 24.042 L/mole in standard conditions, and M is the molar mass of methane of 16.04 g/mol. k values are correction factors based on pressure, relatively humidity, and methane concentration. These values are typically unity but can be corrected in post-processing if variations were significantly different from calibration conditions, and that would impact the standard accuracy. The accuracy of the system has been demonstrated to be ±5.5% for mass emissions from 1 g/h to 1 kg/h. This overall system accuracy was determined from a single-blind test of known methane mass emissions rates produced using a mass flow controller. These tests were known as full sample recovery tests, similar to propane injections used for verification of an automotive-style dilute sampling system as specified in 40 CFR Part 1065. However, multiple data points were below or above the target calibration ranges and we present a conservative measurement uncertainty as ±10% for all mass measurements. Additional information is provided in the Supporting Information for example system details for calibrations and verifications—see Figures S2−S4 and Table S1.

■ RESULTS AND DISCUSSION

Audit Results and Distributions. Over the 4 year period, we completed 17 direct quantification audits, which are presented in Table S2 along with daily production and weather details for the site. Each well was measured at each audit resulting in 78 measurements, the tank was quantified at each audit resulting in 17 measurements, the EGPUs were quantified at all but one audit representing 31 measurements, and other sources varied from audit to audit (n = 0 to 10) resulting in 97 measurements. Audits were conducted over the course of several hours, during which measurements were made one after another. The total measurements over all audits were 213. Figure 1 presents the total site results for all audits in g/h. We note that total site methane emissions varied temporally by a factor of ∼560 ranging from a minimum of 77.8 g/h to over 43.4 kg/h. The arithmetic mean was 4.24 kg/h, while the geometric mean was 821 g/h. Our arithmetic mean was lower than that reported by Omara et al.[13] for Marcellus wells, and our geometric mean was similar to other reported values on the order of ∼1 kg/h. Our geometric mean

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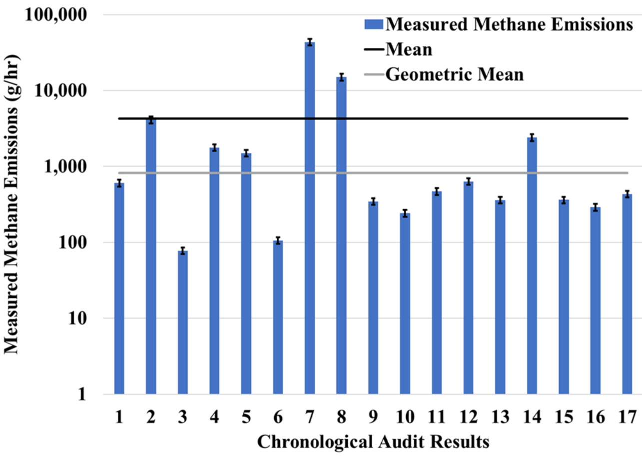

Figure 1. Total site emissions from all 17 audits between 2016 and 2020. Note the log scale of the ordinate axis.

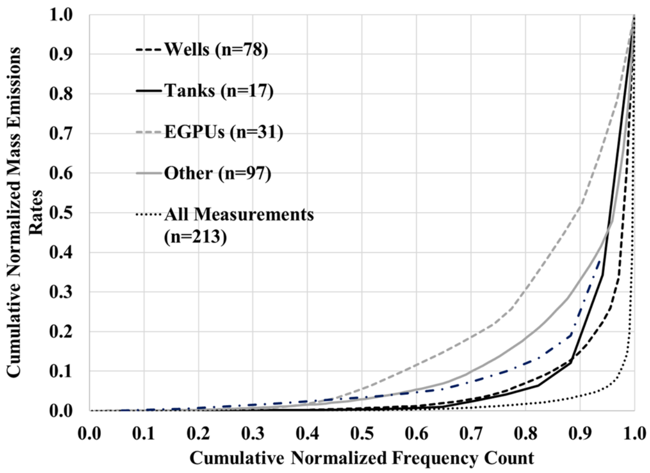

Figure 2. Cumulative normalized mass emissions by normalized count frequency for each subcategory, for all measurements, and for all audits.

was less than half of the geometric mean (2.0 kg/h) reported by Caulton et al.,[7] and our arithmetic mean was about 77% of their arithmetic mean of 5.5 kg/h. Audit data were highly skewed due to excessive tank emissions quantified during Audits 7 and 8, where tank-only methane emissions were 43.3 and 14.7 kg/h, respectively. Tank emissions represented the majority of emissions for eight audits (54.7−99.7% by mass) and overall represented 91% of all measured methane emissions. These data highlight that single snapshots in time from direct methane quantification audits could significantly overpredict or underpredict methane emissions on an annual basis. Some proposed legislation may seek to require quarterly audits at natural gas sites, and such measures may help to capture the temporal range of emissions attributed to a single site, noting that quarterly results varied by orders of magnitude.

Zavala-Araiza et al. used 26 kg/h as a super-emitter threshold,[6] and we saw that tank emissions during Audit 7 would have represented a super-emitter condition. Caulton et al. identified mass-based super-emitters in their study as sites above 9 kg/h in the Marcellus.[7] Both Audits 7 and 8 would be classified as super-emitters with this metric. Audits 7 and 8 occurred after the replacement of an EGPU and could represent abnormal process conditions. The operator was notified but could not confirm a stuck or malfunctioning dump valve or any liquids unloading. We note that having more site operational data may lead to better interpretation of results. Figure 2 shows the plots of the cumulative normalized mass emissions rates by category, by audits, and for all measurements. We see that by any method, each data set was skewed with a fat tail attributed to a few high emitting cases. Others have used the 5-50 rule or demonstrated that the top 1% accounted for 44% of total emissions. For these data, the top 1% of all measurements (n = 2, tank measurements) represented nearly 80% of mass emissions measured. Both of these were from the uncontrolled produced water tank. The summary statistics of each series and their skewness are presented in Table S3.

Facilities that exceed 25,000 metric tons of CO_{2eq} of GHG emission annually are required to report to the EPA's Greenhouse Gas Reporting Program (GHGRP). Note that this metric does not necessarily apply to single production sites, but when a set of various production sites within a basin exceeds this threshold, the operator must report the aggregated GHG emissions by county and for different source categories annually. The operator reported to the EPA GHGRP for years 2017, 2018, and 2019, and these data were analyzed.[25] The two newer wells did not report any liquids unloading for any of these years, while both older wells reported unloading annually. GHGRP summary data for each site presented if liquids unloading occurred (i.e., yes or now) and the type of unloading. Site-specific unloading emission estimates were not available but estimated total unloading emissions for the county were reported. For Monongalia county: 5 wells were unloaded for 7 total events in 2017, venting an estimated mass of methane of 35.53 metric tons (5.08 mt/event on average), 8 wells were unloaded for 35 total events in 2018, venting an estimated mass of methane of 165.5 metric tons (4.73 mt/event on average), and 3 wells were unloaded for 19 events in 2019, venting an estimated mass of methane of 73.51 metric tons (3.87 mt/event on average). Note that plunger lifts were not used at the MSEEL. Assuming average values, the produced water tank emissions of 43 kg/h would have correlated to liquid unloading events lasting in duration from 3.75 to nearly 5 days. Allen et al. reported that unloading events they characterized were as short as 10−15 min with some lasting 2 or more hours.[26] Further, manual unloading event durations for wells without plungers ranged from 0.17 to 4.5 h.[27] With this thought exercise and the required durations based on our measurements, it was unlikely that the super-emitter tank conditions represented liquid unloadings, especially since the lower value of 14.7 kg/h would have required even longer durations. Alternatively, Zavala-Araiza et al. and Lyon highlighted that stuck separator dump valves can represent abnormal process conditions leading to super-emitter emissions.[6,8] Based on throughput data presented below, these super-emitter tank conditions represented around 0.23 to 2.3% of production and therefore it is our supposition that these emissions were attributed to dump valve-related abnormal process conditions and not liquid unloading events.

Comparisons with Emissions Factors (EFs). Often, industry reverts to the use of EFs to estimate annual emissions. These values can be combined with counts and activity factors to complete inventory analyses in lieu of direct measurements. We note that in the case of the excessive tank emissions (Audit 7), if emissions were continuous, this single site would

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represent over 10,600 metric tons of CO_{2eq} based on a 100 year GWP of 28 for methane. In examining the GHGRP data,[25] we note that no GHG data were included for tanks within this county for any reporting year. Some industry has moved to deploy controls for condensate or even condensate and produced water tanks. However, it is common that in dry gas regions such as the Marcellus shale, where sites only deploy produced water tanks, they are often vented directly to the atmosphere unless state regulations require control. If tanks are often excluded from GHG reporting in dry gas regions, this could represent another contributor to discrepancies between top-down and inventory emission results.

We compared the tank and well emissions with EFs obtained for unconventional wells for 2018 as presented in the 2020 Greenhouse Gas Inventory (GHGI-national level).[28] Tank EFs were used for both small tanks (STs) and large tanks (LTs) since the daily water production averaged 10 bbl/day, which was exactly the threshold used for tank size classifications in the GHGI. The 2020 GHGI uncontrolled EFs for small and large tanks were 0.6 and 0.2 kg/bbl, respectively. The 2020 GHGI EF for unconventional gas wells was 137.7 kg/well/year or 15.72 g/well/h. Figure 3 presents the measured emissions for the produced water tank and wells as compared to 2018 EFs. Note that both ordinates are on the log scale. Regarding tank emissions, measured values were less than the EF estimates for LTs in seven cases but increased to nine when compared to the EF estimates for STs. Measured values exceeded both emissions factors in eight cases. The geometric mean for all tank measurements was 4.23 kg/h, and the geometric mean of estimates for ST was 4.27 kg/h. Regarding well emissions, 94% of the time, measured values were below the GHGI EFs for 2018. As shown in Figure 3b, emissions from the two older wells tended to be higher than those of the two newer wells.

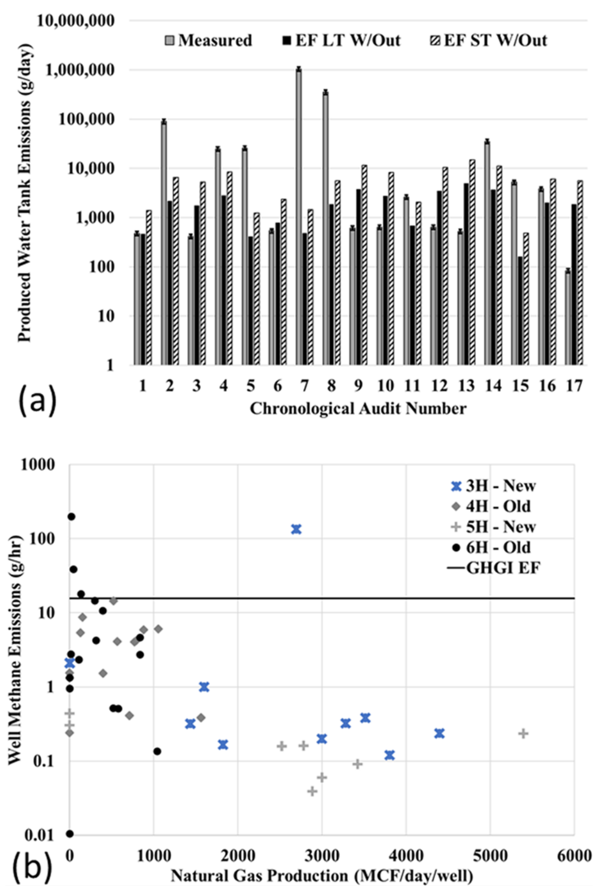

Figure 3. (a) Comparison of measured tank emissions from all audits compared to estimates using GHGI 2018 uncontrolled EFs for LTs and STs. (b) Measured well emissions by well for all audits compared to the GHGI 2018 EF for unconventional wells.

Correlations and Throughput-Normalized Methane Emissions (TNME). Studies often attempt to correlate site emissions with natural gas, produced water, or gas condensate production statistics. The MSEEL site is a dry gas site with no condensate production and a single-produced water tank. Figure S1 displays that natural gas production tended to decrease with increasing temperatures. Figure S5 shows the general tendency for water production to increase with natural gas production. We previously suggested that sitewide emissions and tank emissions were weakly correlated with historical 3 day water production (highest $R^2 = 0.8903$) during the initial 2 year period.[9] However, for the extended measurements over 4 years, we found no significant correlations ($R^2 > 0.5$) between any emissions categories as compared to daily, 3 day, and even weekly natural gas or water production.

Table S4 provides the TNME for the total measured methane emissions and the corresponding daily whole natural gas production. Due to the stochastic nature of the emissions combined with variable production volumes, TNME varied from a low value of 0.002% to a high value of 2.36%. The geometric mean was 0.018% with an arithmetic mean of 0.169% for the 17 audit results. To better estimate the overall TNME, we created five distributions (using cubic spline fits) based on measurement results that included distributions of leak counts and leak, EGPU, tank, and other emissions rates. Similar to the approach of others in the field,[6,14,29,30] we used an MC simulation to estimate an overall TNME value over a 4 year period from November 2016 through December 2020 (1517 days). Distributions were randomly sampled 10^4 times to create a new distribution or pool of total daily emissions. Then, an emissions rate from the population ensemble was randomly selected and assigned to each of the daily throughput values to create daily TNME data. Figure 4a shows an example of total site emissions randomly assigned to days over the entire period. Figure 4b shows an example of the TNME for the given period based on historical production data. Note that audit results were also assigned to the dates when they occurred for all iterations. To determine an average and confidence interval, the 4 year period was then bootstrapped 10^4 times with replacement. The resulting distribution of TNME is presented in Figure S7. The average TNME was 0.093% with a 95% confidence interval of 0.081 to 0.106%.

Alternatively, we also examined the case of single audits applied to the entire multi-year data set for all days with corresponding production values. Table S5 provides the statistics of this analysis of 25,772 different daily estimates of TNME. Due to the highly skewed audit results and relatively small variance in production values, the fat-tailed nature of super-emitting events propagated through the analysis, see Figures S8 and S9. In this case, the mean TNME value was 0.117% and 70% of projections were less than 0.05%.

Both method results align well with the median value (0.13%) reported by Omara et al. for Marcellus shale well sites.[13] Our results, both modeled and measured, were lower than those reported by Caulton et al. for the Marcellus shale

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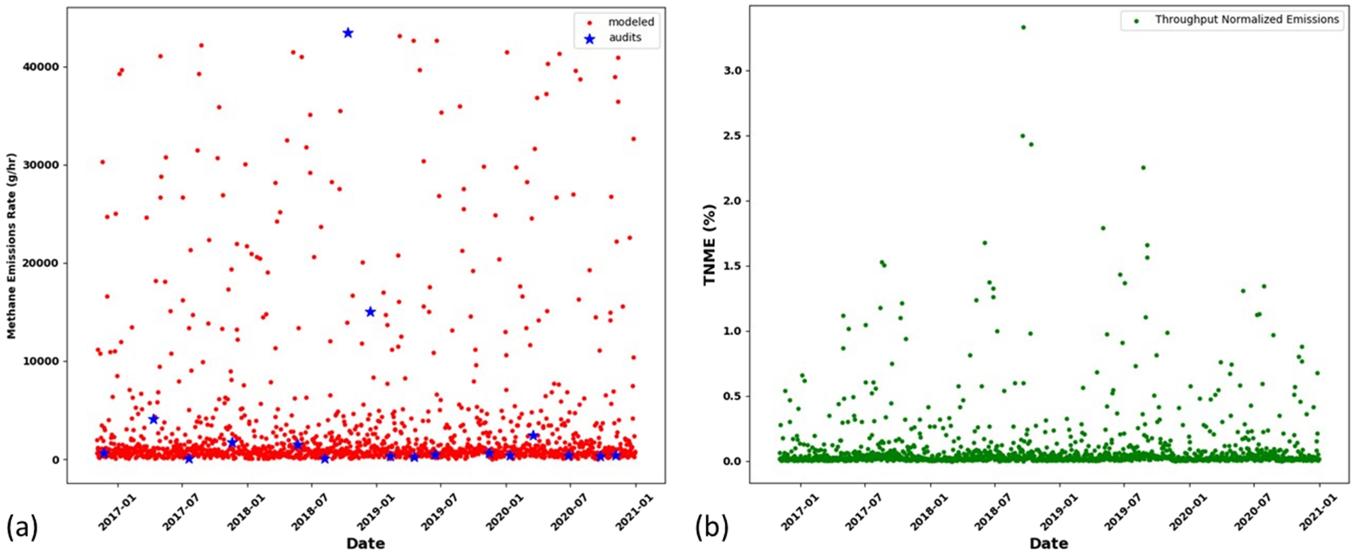

Figure 4. (a) Example of 4 year period of randomly assigned total emissions. (b) Example of TNME by dividing randomly assigned total emissions by historical whole gas production values.

(0.53%).[7] They identified TNME for super-emitters to be above 7% for unconventional well sites, while our peak measured values at our study site were only 2.3%. It is important to note that their data included wet gas sites, which could have higher emissions from tanks if not controlled. However, their study also relied on monthly throughput equally divided over days. Such variations obfuscated by using monthly reported data could also contribute to higher-than-expected TNME depending on the overall behavior of the site when the "snapshot" in time measurements occurred. We used daily production values for TNME analyses, which were available through the MSEEL program. Figure S10 presents the monthly and daily variability that could contribute to variances in TNME using daily emissions values (snapshots) but using average production values for an entire month.

Our supposition is that our two super-emitter tank events (Audits 7 and 8) were likely associated with abnormal dump valve operation as opposed to liquids unloading based on our earlier analysis compared to literature and GHGRP data. Therefore, our MC analysis includes typical operation and values representing abnormal super-emitting events. It does not however include the additional emissions attributed to liquids unloading; therefore, the MC estimates are likely conservative. We know that two of the wells reported at least one unloading in each reporting year (2017−2019). Based on the number of reported wells that were unloaded, total number of unloadings each year, and reported unloading emissions for the county, we developed estimated emissions for the wells at this site. The minimum and maximum mass emissions as reported were 3869 to 24,503 kg annually per well. Therefore, we estimated that annual emissions for two wells that experienced at least one unloading could range from 7378 to 49,007 kg annually or 30,952 to 196,027 kg for the 4 year period. Total production over the 4 year period from all four wells represented 8692 million cubic feet (MMCF). Assuming pure methane (>97%), the total throughput would be 175.7 Gg. As such, conservative TNME due to well unloading would increase the overall MC TNME by 0.018 to 0.112%. The combined TNME from sources captured by our audits and MC analysis and from estimated emissions from liquid unloading for two of the four wells ranges from 0.111 to 0.218%. The lower estimate still aligns well with data presented by Omara et al. for Marcellus shale well sites (0.13%)[13] and would still be below the Marcellus estimates by Caulton et al. (0.53%).[7]

CONCLUSIONS

We completed 17 methane emission audits at an unconventional natural gas well site in the Marcellus shale over the course of just over 4 years (2016−2020). An analysis of the first six audits showed significant variability in site-level emissions between audits, and this pattern continued through 11 additional audits with two audits that likely represented super-emitter conditions. When site emissions were high, they were typically dominated by emissions from the produced water storage tank, which was uncontrolled (i.e., vented to atmosphere). While other studies have focused on increasing sample size by conducting measurements at multiple sites, we sought to characterize the temporal variability in emissions from a single natural gas production site through a series of repeated site audits. Although our data were from a single site, they too followed similar patterns of skewed distributions in both total emissions and component-level emissions. Most companies conduct leak detection campaigns at sites on an annual basis, but some regulations have suggested increased quarterly audits. Even if quarterly audits were required, quarterly and year-to-year results may still vary substantially based on our findings (noting that minimum and maximum results varied by a factor of ∼560). Our multi-year study likely captured both normal operation and some upset conditions that led to excessive tank emissions; however, our results likely did not capture additional emissions caused by periodic liquid unloading, which would further obfuscate the true TNME. Natural gas and water production at the site all varied in time, but methane emissions from 17 audits over 4 years appear stochastic in nature and showed no significant correlation to weather or site production status.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00874.

Additional measurements and system details and images, additional site and audit details including gas and liquid production, statistics for audits, categories, and all measurements, comparison of liquid production to gas production, tabular data and figures for Monte Carlo and throughput normalized emissions analyses (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) U.S. Environmental Protection Agency*Overview of Greenhouse Gases*; https://www.epa.gov/ghgemissions/overview-greenhouse-gases (accessed on April 1, 2021).

(2) U.S. Environmental Protection Agency*Understanding Global Warming Potentials*; https://www.epa.gov/ghgemissions/understanding-global-warming-potentials (accessed on April 1, 2021).

(3) Vaughn, T. L.; Bell, C. S.; Pickering, C. K.; Schwietzke, S.; Heath, G. A.; Pétron, G.; Zimmerle, D. J.; Schnell, R. C.; Nummedal, D. Temporal Variability Largely Explains Top-Down/Bottom-Up Difference in Methane Emission Estimates from a Natural Gas Production Region. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 11712−11717.

(4) Cardoso-Saldaña, F. J.; Allen, D. T. Projecting the Temporal Evolution of Methane Emissions from Oil and Gas Production Sites. *Environ. Sci. Technol.* **2020**, *54*, 14172−14181.

(5) Brandt, A. R.; Heath, G. A.; Cooley, D. Methane Leaks from Natural Gas Systems Follow Extreme Distributions. *Environ. Sci. Technol.* **2016**, *50*, 12512−12520.

(6) 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.

(7) Caulton, D. R.; Lu, J. M.; Lane, H. M.; Buchholz, B.; Fitts, J. P.; Golston, L. M.; Guo, X.; Li, Q.; McSpiritt, J.; Pan, D.; Wendt, L.; Bou-Zeid, E.; Zondlo, M. A. Importance of superemitter natural gas well pads in the Marcellus shale. *Environ. Sci. Technol.* **2019**, *53*, 4747−4754.

(8) Lyon, D.R.Quantifying, Assessing, and Mitigating Methane Emissions from Super-emitters in the Oil and Gas Supply Chain. *Theses and Dissertations*. 2016, http://scholarworks.uark.edu/etd/1492.

(9) Johnson, D.; Heltzel, R.; Oliver, D. Temporal variations in methane emissions from an unconventional well site. *ACS Omega* **2019**, *4*, 3708−3715.

(10) Alden, C. B.; Wright, R. J.; Coburn, S. C.; Caputi, D.; Wendland, G.; Rybchuk, A.; Conley, S.; Faloona, I.; Rieker, G. B. Temporal Variability of Emissions Revealed by Continuous, Long-Term Monitoring of an Underground Natural Gas Storage Facility. *Environ. Sci. Technol.* **2020**, *54*, 14589−14597.

(11) 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.

(12) 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.

(13) Omara, M.; Sullivan, M. R.; Li, X.; 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.

(14) Omara, M.; Zimmerman, N.; Sullivan, M. R.; Li, X.; Ellis, A.; Cesa, R.; Subramanian, R.; Presto, A. A.; Robinson, A. L. Methane emissions from natural gas production sites in the United States: data synthesis and national estimate. *Environ. Sci. Technol.* **2018**, *52*, 12915−12925.

(15) Zhou, X.; Yoon, S.; Mara, S.; Falk, M.; Kuwayama, T.; Tran, T.; Cheadle, T.; Nyarady, J.; Croes, B.; Scheehle, E.; Herner, J. D.; Vijayan, A. Mobile Sampling of Methane Emissions from Natural Gas Well Pads in California. *Atmos. Environ.* **2021**, *244*, 117930.

(16) 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 compositions. *Environ. Sci. Technol.* **2017**, *51*, 8832−8840.

(17) Brandt, A. R.; Heath, G. A.; Kort, E. A.; O'Sullivan, F.; Pétron, 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.; Harriss, R. Methane leaks from North American natural gas systems. *Science* **2014**, *343*, 733−735.

(18) Lebel, E. D.; Lu, H. S.; Vielstädte, L.; Kang, M.; Banner, P.; Fischer, M. L.; Jackson, R. B. Methane Emissions from Abandoned Oil and Gas Wells in California. *Environ. Sci. Technol.* **2020**, *54*, 14617−14626.

(19) Deighton, J. A.; Townsend-Small, A.; Sturmer, S. J.; Hoschouer, J.; Heldman, L. Measurements Show that Marginal Wells are a Disproportionate Source of Methane Relative to Production. *J. Air Waste Manage. Assoc.* **2020**, *70*, 1030−1042.

(20) *Marcellus Shale Energy and Environmental Laboratory*; http://mseel.org/ (accessedon April 1, 2021).

(21) *Electronic Code of Federal Regulations*; https://www.ecfr.gov/cgi-bin/text-idx?SID=457c8f4a0a7d738d2c3b1ef275e75e2c&node=sp40.21.98.w&rgn=div6 (accessed on April 1, 2021).

(22) U.S. Environmental Protection Agency*Air Emission Measurement Center (EMC)*; https://www.epa.gov/emc/method-21-volatile-organic-compound-leaks (accessed on April 1, 2021).

(23) Johnson, D. R.; Covington, A. N.; Clark, N. N. Methane emissions from leak and loss audits of natural gas compressor stations and storage facilities. *Environ. Sci. Technol.* **2015**, *49*, 8132−8138.

(24) Johnson, D. R.; Covington, A. N.; Clark, N. N. Design and use of a Full Flow Sampling System (FFS) for the quantification of methane emissions. *J. Visualized Exp.* **2016**, *112*, 54179.

(25) U.S. Environmental Protection Agency*GHG Data*; https://ghgdata.epa.gov/ghgp/service/facilityDetail/2017?id=1012537&ds;=E&et;=&popup;=true (accessed on April 1, 2021).

(26) 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.

(27) Allen, D. T.; Sullivan, D. W.; Zavala-Araiza, D.; Pasci, 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.

(28) U.S. Environmental Protection Agency*Greenhouse Gas Emissions, Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990−2018*; https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2018 (accessed on April 1, 2021).

(29) 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*, 10718−10727.

(30) Englander, J. G.; Brandt, A. R.; Conley, S.; Lyon, D. R.; Jackson, R. B. Aerial Interyear Comparison and Quantification of Methane Emissions Persistence in the Bakken Formation of North Dakota, USA. *Environ. Sci. Technol.* **2018**, *52*, 8947−8953.

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