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Methane Emissions from Process Equipment at Natural Gas Production Sites in the United States: Liquid Unloadings

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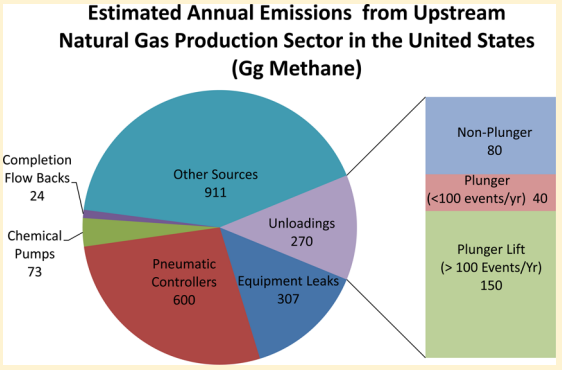
Supporting Information

ABSTRACT: Methane emissions from liquid unloadings were measured at 107 wells in natural gas production regions throughout the United States. Liquid unloadings clear wells of accumulated liquids to increase production, employing a variety of liquid lifting mechanisms. In this work, wells with and without plunger lifts were sampled. Most wells without plunger lifts unload less than 10 times per year with emissions averaging 21 000−35 000 scf methane (0.4−0.7 Mg) per event (95% confidence limits of 10 000−50 000 scf/event). For wells with plunger lifts, emissions averaged 1000−10 000 scf methane (0.02−0.2 Mg) per event (95% confidence limits of 500−12 000 scf/event). Some wells with plunger lifts are automatically triggered and unload thousands of times per year and these wells account for the majority of the emissions from all wells with liquid unloadings. If the data collected in this work are assumed to be representative of national populations, the data suggest that the central estimate of emissions from unloadings (270 Gg/yr, 95% confidence range of 190−400 Gg) are within a few percent of the emissions estimated in the EPA 2012 Greenhouse Gas National Emission Inventory (released in 2014), with emissions dominated by wells with high frequencies of unloadings.



INTRODUCTION

Natural gas production in the United States is increasing, driven by increased use of horizontal drilling and hydraulic fracturing.[1] As natural gas production has increased, interest has increased in the emissions of greenhouse gases along the natural gas supply chain.[2−10] Methane, the primary component of natural gas, is a potent greenhouse gas, and a variety of sources contribute to methane emissions along the natural gas supply chain. For some of these sources, emission measurements are sparse, including measurements of emissions from pneumatic controllers and liquid unloadings.[11] Measurements of emissions from pneumatic controllers have been described in a companion manuscript.[12] This work reports on emissions from gas well liquid unloadings.

A liquid unloading may be necessary when a gas well that also produces oil or water accumulates liquids in the well bore. The liquids accumulation may be due to a variety of causes, including decreases in gas velocity in the well, decreases in reservoir pressure, or changing gas to liquid ratios. As liquids accumulate, well production can decline and an operator may choose to unload the liquids from the well to restore production. Liquids can be unloaded in a variety of ways. For example, the well tubing can be modified to increase gas velocity or a pump may be installed to remove downhole

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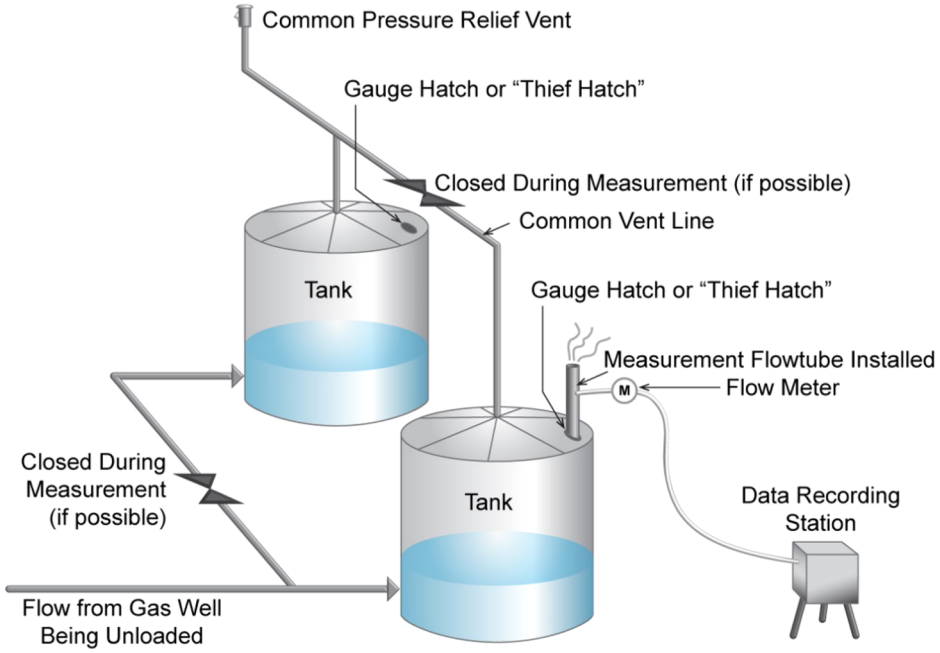

Figure 1. Conceptual diagram of a tank layout on a well site and the positioning of the temporary stack used to measure volume of gas vented during a liquid unloading.

liquids. Neither of these methods lead to venting emissions. Other unloading methods, such as temporarily diverting the flow from the well to an atmospheric vent, do lead to emissions. This work focuses on unloadings that result in emissions.

In the most recent national inventory of greenhouse gas emissions (for calendar year 2012, released in 2014, referred to here as the EPA 2012 GHG NEI),[13] the EPA estimates that 60 810 natural gas wells, out of an estimated 470 913 natural gas wells in the United States (not including oil wells with associated gas production), have liquid unloadings that result in methane emissions. This represents 13% of gas wells in the EPA 2012 GHG NEI. Collectively, liquid unloadings from these wells are estimated to emit 273.6 Gg of methane per year (14.2 billion standard cubic feet, bcf), or approximately 14% of the estimated 1992 Gg of methane emissions from the natural gas production portion of the natural gas supply chain.

The estimates of methane emissions from liquid unloadings in EPA 2012 GHG NEI are generally consistent with more recent information collected through the EPA's Greenhouse Gas Reporting Program (for calendar year 2012, released in 2013, referred to here as the EPA 2012 GHGRP).[14] The GHGRP reports approximately 276 Gg of methane emissions from liquid unloadings at facilities that meet threshold reporting requirements. Information for 58 663 wells that have unloading emissions was reported in 2012. In October 2014, GHGRP data were released for reporting year 2013 as well as revised data for reporting year 2012. In the 2014 data release, the number of wells with methane emissions from unloadings was reported as 55 491 for 2013, a 5.4% decrease from the number of wells originally reported for 2012. The number of wells with methane emissions from unloadings in 2012 was revised from 58 663 (released in October 2013) to 59 162 (released in October 2014). In this work, the 2012 data are used in order to allow comparisons with the 2012 GHG NEI. The originally released data are used since changes in reporting for 2012, as reflected in the well count, were relatively minor. Some changes were more significant, however, so a sensitivity analysis, using revised 2012 and 2013 GHGRP data, is reported in Supporting Information (SI). The liquid unloading emission estimates from the EPA GHGRP are shown, by production region, in SI (Section S1).

Emissions from liquid unloadings of natural gas wells are not uniformly distributed in time or space. Estimated emissions from liquid unloadings are spatially concentrated in Rocky Mountain production regions. Wells in the Rocky Mountain region account for more than half of estimated emissions from liquid unloadings in the 2012 GHGRP. Temporal distributions also vary. Some wells release unloading emissions several times per day while others may release unloading emissions only once per year or once during the well's production life cycle. Wells may only release unloading emissions for a portion of their production lifetime, leading to a dependence of unloading emissions on well age. In addition to spatial and temporal variability in emissions of wells that vent, both estimates and measurements indicate that a small fraction of wells that vent account for a majority of emissions. For example, for one type of well with unloading emissions (wells without plunger lifts, see definition later in text), emission estimates reported by the American Petroleum Institute/America's Natural Gas Alliance (API/ANGA), indicate that three percent of wells accounted for half of emissions from this type of well and half of the wells accounted for more than 90% of emissions.[15] In a limited number of measurements of methane emissions from a single type of well with unloading emissions (wells without plunger lifts—see definition later in text), Allen et al.[11] found that 95% of the emissions came from less than half of the wells.

Emission estimates, and a limited number of measurements of methane emissions from liquid unloadings, both suggest that a small fraction of wells, in particular geographical regions, and at particular times in the well's life cycle, account for a large fraction of liquid unloading emissions. These characterizations of unloadings emissions are primarily based on emission estimates, however, and there are few data in the scientific literature to test the reliability of emission estimates. This leads

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to potentially large uncertainties in the emissions from this source category. More measurement data are needed, along with a better understanding of the relationships between well characteristics and unloading emissions.

This work reports measurements of methane emissions from 107 natural gas wells with emissions associated with liquid unloading. These data represent the most extensive set of measurements of emissions from liquid unloadings in the scientific literature. The relationships between emissions magnitude, unloading event frequency and other well characteristics are explored.

MATERIALS AND METHODS

Emission Measurements. The liquid unloadings reported in this work are grouped as plunger-lift unloadings and unloadings of wells without plunger lifts.

In a manually triggered unloading of a well without a plunger lift, an operator manually diverts the well's flow from a production separator, which typically operates at pressures of multiple atmospheres, to an atmospheric pressure tank. This allows the well to temporarily flow to a lower pressure destination (the atmospheric pressure tank or vent, rather than the pressurized separator). The resulting higher pressure gradient allows more gas to flow, increasing velocity in the production tubing and entraining and lifting liquids out of the well. Gas is discharged through the tank vent to the atmosphere until liquids are cleared. In a small number of wells (~0.1% of wells reported by companies participating in this work), this process is automated, resulting in two subcategories of unloadings for wells without plunger lifts, manual and automatic. All of the measurements reported in this work for wells without plunger lifts are for wells that had unloadings that were manually triggered; no wells without plunger lifts were observed in the sampling that had automated unloadings.

Emissions from unloadings of wells without plunger lifts were measured in this work by directing flow through a temporary stack installed on top of the vent. Figure 1 shows a conceptual diagram of a tank layout on a well site and the positioning of the temporary stack. Grounded metal or metal lined tubing was used to construct the temporary stack, to prevent static discharge. Flow rate through the temporary stack was measured continuously, near the centerline of the temporary stack, using a thermal gas mass flow meter. The thermal meter was extended into the middle of the temporary stack, which was between two and eight inches in diameter, with the diameter depending on the anticipated flow rate. Since the width of the meter's probe was approximately 3.5 cm (1.4 in.), the thermal meter recorded a centerline velocity. Total volumetric flow was calculated by multiplying the product of the measured gas velocity and the cross-sectional area of each stack by a correction factor to convert the centerline velocity in the stack to an estimated average velocity in the stack, accounting for the change in velocity profile from friction near the stack walls and accounting for the cross sectional area of the stack obstructed by the flow meter (see SI Section S2). In some well configurations (31 of the 107 wells on which measurements were made), measurement through a temporary stack on the atmospheric tank was not technically feasible. In these cases, measurements were made by inserting a segment of pipe (with the thermal gas mass flow meter in the pipe) into the process line between the separator and the atmospheric tank in order to measure the flow into the tank.

The methane fraction of the vented gas was assumed to be equal to the methane fraction in the normally produced gas. This was presumed to be a more accurate indicator of total methane emissions than measurements of the gas composition made through the temporary stack. The gas exiting through the temporary stack during the unloading period is a combination of the unloaded gas from the well and the gas initially in the vapor space of the tank (typically much lower in methane than the site's produced gas). At the end of the unloading, the tank will contain more methane, from the unloading, than was in the tank at the start of the unloading. This methane, which is associated with the unloading event, will eventually be released as part of normal tank operations. Multiplying the measured vented gas volume by the methane fraction of the produced gas captures these emissions that occur because of the unloading but that are not released during the period when the tank is actively venting.

Uncertainty in these measurement methods is estimated at 10−20% of the measured emissions and this estimate is dominated by the assumed uncertainty in the flow, which includes both uncertainties in the stack gas volumetric flow measurement, and determining when flows return to zero. Variability in the gas composition from the well is expected to be much less than 10%. As described in the Results section, these measurement uncertainties are small compared to the combined measurement uncertainty and uncertainty introduced by selecting only a subpopulation of wells for measurement (sampling uncertainty), which are 50% or more of measured emissions.

Liquids can also be unloaded from a well using a plunger lift system. This liquid removal operation holds a plunger at the top of the well, and either manually or by automation occasionally closes (shuts-in) the well and releases the plunger, allowing it to fall down the well bore below the accumulated liquids. The well is then reopened, allowing the gas to push the plunger and the liquid back up the well bore as a slug of liquid. If the plunger returns to the top and the liquid and gas flow to the separator, there is no venting and all gas from the separator is routed to sales. In some cases, if the plunger does not return to the surface as expected, the plunger controller may bypass the separator and direct the flow to an atmospheric pressure vent, such as a vented tank. Directing flow to the lower pressure vent causes the plunger to return to the surface but also allows gas to vent. Plunger cycles may be initiated manually, on a timed interval, or based on certain well parameters such a reduced gas flow. In this work, measurements were made on both wells in which the unloading was automated through use of a controller (automatically triggered), and wells in which the plunger lift cycle was manually initiated by an operator (manually triggered).

In both the manually triggered plunger lift unloadings and the automatically triggered plunger lift unloadings, the volume of vented gas was measured using the same procedures as used for the wells without plunger lifts. For the automatically triggered unloadings, the measurement equipment was typically left in place for one to several days, making measurements continuously. This allowed automated plunger unloading venting events to be measured only when and if they occurred in routine operation, without artificially triggering the events. For all the plunger lift unloading events, the composition of the vented gas was assumed to be the same as the composition of the gas produced by that well. Produced gas composition was provided by site operators.

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Table 1. Unloading events measured in this work. Wells with manual unloadings typically had one event per well, while automated Plunger Lift Unloadings Had Multiple Events Per Well; A Mapping of Region Boundaries is Provided in Supporting Information

		wells with unloadings sampled				
type of well	initiation system	U.S. total	Appalachian	Rocky Mountain	Gulf Coast	Mid-Continent
plunger	auto	25	0	20	1	4
	manual	50	7	29	1	13
non- plunger	manual	32	4	2	14	12
total		107	11	51	16	29

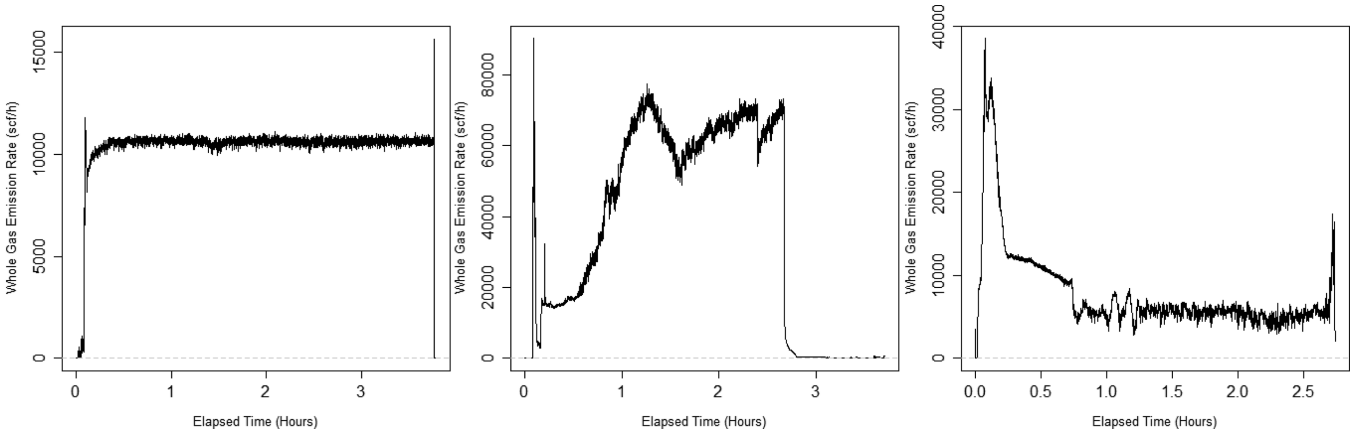

Figure 2. Representative time series of methane flow rates during manually triggered liquid unloadings from wells without plunger lifts (USH-47-0201 left; USH-47-0701 middle; UCG-03-0301 right); Note differences in horizontal and vertical scales.

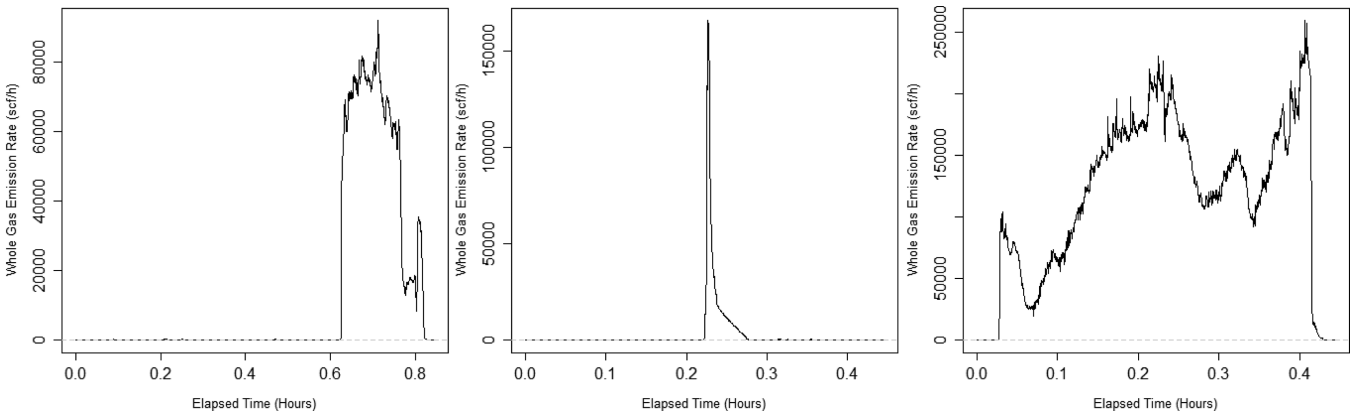

Figure 3. Representative time series of methane flow rates during manually triggered liquid unloadings from wells with plunger lifts (UBB-45-0101 left; UJR-46-0601 middle; USH-45-0202 right); Note differences in horizontal and vertical scales.

Sampling Strategies. Emission estimates reported through the EPA 2012 GHGRP[14] indicate that a small fraction of wells, in particular geographical regions, account for a large fraction of emissions from liquid unloadings. The sampling strategy employed in this work was to sample most extensively in regions that were likely to dominate emissions (SI, Section S1). Details of the sampling approach are provided in SI. Briefly, the sampling team would visit a region for one or multiple weeks and sample a randomly selected subset of those wells that were unloading during that period. Consequently, more samples were collected on wells that unloaded more frequently. The features of these sample collection methods (preferential sampling in regions with high estimated emissions from unloadings and sampling of wells that tended to have high unloading frequencies) are important to consider when the data presented in this work are used to establish national emission estimates.

RESULTS AND DISCUSSION

Methane emissions from liquid unloadings were measured at 107 natural gas wells. A summary of the geographical locations of the wells sampled is provided in Table 1.

For the 32 wells without plunger lifts (manually unloaded) sampled in this work, one event was typically sampled for each well; a few wells had more than one event sampled and for these wells, average values are reported. The unloadings of wells without plunger lifts sampled in this work had durations that lasted between 0.17 and 4.5 h, and vented methane volumes that ranged between 550 and 135 000 standard cubic feet (scf) of methane per event (0.011−2.6 Mg). Representative time series for the methane emissions from wells without

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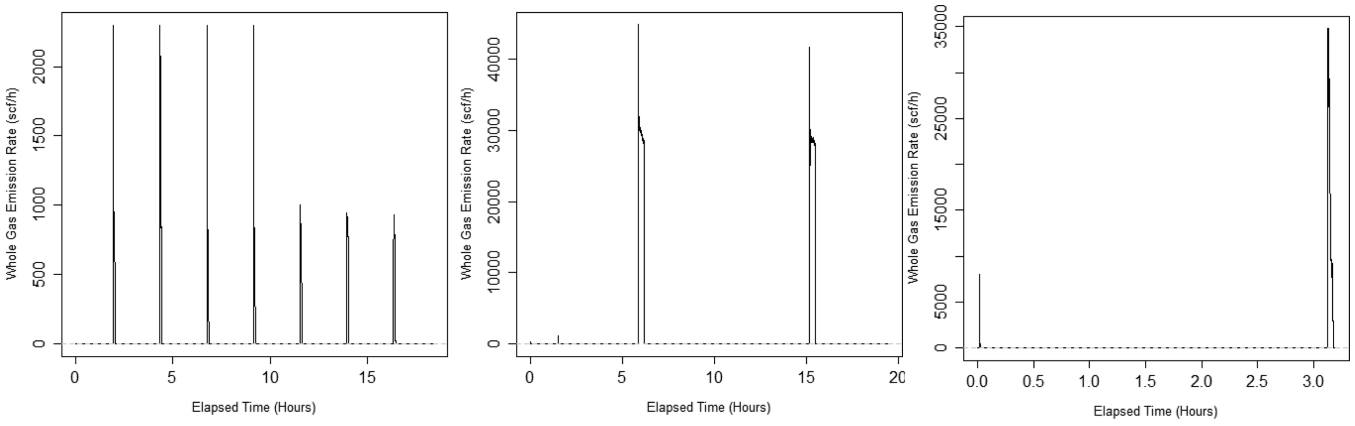
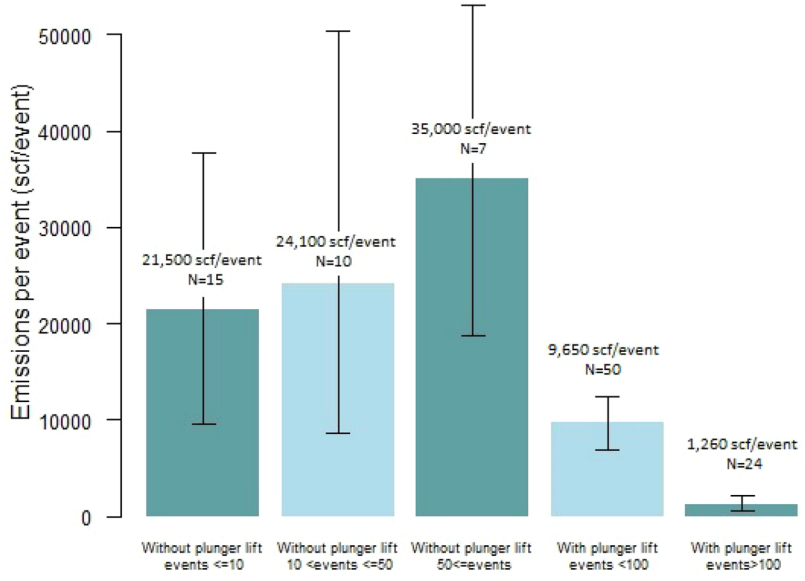


Figure 4. Representative time series of methane flow rates during automatically triggered liquid unloadings from wells with plunger lifts (UBB-42-0401 left; UBB-42-0201 middle; UEF-49-0501 right); Note differences in horizontal and vertical scales.



*95% confidence bounds are:	mean (scf methane/event)	95% confidence bounds
Wells without plunger lifts ≤10 events per year:	21,500	9600-37,800
Wells without plunger lifts 10<events≤50 per year:	24,100	8700-50,400
Wells without plunger lifts 50<events:	35,000	18,700-53,000
Wells with plunger lifts ≤100 events per year:	9,650	6900-12,400
Wells with plunger lifts >100 events per year:	1260	500-2100

Figure 5. Average emissions per event for wells with and without plunger lifts, sorted by frequency of events (events per year per well).

plunger lifts are shown in Figure 2. These three events shown had durations that ranged from 2.72 to 3.75 h. Vented volumes for these three events shown ranged between 21 000 and 135 000 scf methane (0.40−2.6 Mg). As illustrated by these representative time series, some manual unloadings without plunger lift rapidly rose to a high flow rate, then maintained a steady flow throughout the event; others rose more slowly to a peak flow, then had variable flow during the event; still others rapidly rose to a peak flow, then had declining flows throughout the event. This complex flow behavior makes it difficult to generalize about the flow characteristics for manually triggered unloadings of wells without plunger lifts.

For the 50 plunger lift wells with manually triggered unloadings, one event was typically sampled for each well. The manual unloadings of wells with plunger lifts sampled in this work had durations that lasted between 0.03 h and more than 3 h, and had vented methane volumes that ranged between approximately 200 and 49 000 scf methane per event (0.004−0.94 Mg). Representative time series for the methane emissions from a manual unloading are shown in Figure 3. These three events shown had durations that ranged from 1.2 to 20 min. Vented volumes ranged between 1220 and 27 000 scf methane for the three events shown (0.02−0.52 Mg). As illustrated by these representative time series, some manually triggered unloadings with plunger lift rapidly rose to a high flow rate, then almost immediately fell rapidly, leading to a relatively short duration event; others rose rapidly to a peak flow that was maintained for 5−10 min or more; still others had complex flow patterns over an event lasting 10 min or more. As was the case for manually triggered unloadings without plunger lifts, this complex flow behavior makes it difficult to generalize about the flow characteristics.

For automated plunger lift wells, the sampling equipment was left in place for one to several days at each well, and

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typically more than one event was sampled for each well. The automatically triggered unloadings (with plunger lift) sampled in this work had durations that lasted between <1 min and more than 20 min, and vented methane volumes that ranged from 50 scf methane to more than 8000 scf methane per event) (0.001−0.15 Mg). The numbers of events sampled per well ranged from 2 to more than 70; average values of emissions per event were used when multiple events were recorded. Representative time series for the methane emissions from automated plunger lift unloadings are shown in Figure 4. Individual unloading events for these three wells had durations that ranged from 2 to 20 min. Vented volumes per event ranged between 60 and 8600 scf methane for the three wells shown (0.001−0.15 Mg). As illustrated by these representative time series, some plunger lift wells with automated unloadings had emissions per event that were quite similar, and that occurred with a regular frequency. In contrast, however, some automated plunger lift wells had events that had qualitatively different emissions and/or variable event frequencies.

SI (Section S3) provides details of the unloading emissions and well characteristics for each of the 107 wells sampled in this work. A summary is provided in Figure 5. A relatively small number of wells have high emissions and most wells have much lower emissions. For example, 20% (6 of 32) of the wells account for 83% of the annual emissions for wells without plunger lifts, where annual emissions are estimated by multiplying the emission for an unloading event, measured in this work, by the number of times that well unloaded during calendar year 2012 or 2013 (whichever was the most recent report available), as reported by the well operator. The six wells that account for 83% of the annual emissions of wells without plunger lifts vent 6% of their collective annual production. For manually and automatically triggered plunger lift wells, 20% of the wells account for 65% and 72% of the annual emissions, respectively. These wells vent 2% and 20% of their collective annual production, for manually and automatically triggered wells, respectively.

Because the distributions of event emissions are not normally distributed about a mean, uncertainties in the average values of emissions per event are reported based on the results of a bootstrapping method, rather than as a simple standard deviation of the data set. In the bootstrapping procedure, the original data set of each type of well was recreated by making random event selections, with replacement, from the data set. A total of 1000 of these resampled data sets were created and the mean value of the emissions for each resampled data set was determined. The 95% confidence intervals for the emission estimates represent the 2.5% and 97.5% percentiles of the means in the 1000 resampled data sets. So, for example, for the 25 automatically triggered plunger lift wells, a mean value for emissions per event, for each well, was calculated by selecting 25 emission measurements, at random and with replacement. This mean was tabulated and the process was repeated 1000 times to generate 1000 mean values. The 2.5% and 97.5% percentiles were determined to be 538 and 2085 scf methane per event, and these values are the 95% confidence bounds for the mean value of the measurements (in this case 1260 scf methane/event). The bootstrapping procedure leads to a combined sampling and measurement uncertainty. This uncertainty has a much larger range (typically 50% or more of the mean value, see Figure 5) than would be estimated from the uncertainty associated with the measurement alone (approximately 10−20% of the measured value) and is a reflection of the heterogeneity of well characteristics in the data sets and the underlying population of wells with unloading emissions.

Statistical analyses were conducted to identify well and unloading event characteristics that could explain the variability in the measured emission data. Variables that were considered included well pressures, well bore volumes, well ages, unloading event durations and unloading frequencies. The variable that explained the largest amount of variability in the observed annual well emissions was unloading frequency, although there was also a positive correlation of event frequencies with well age (older wells had more unloading events per year than younger wells) and a negative correlation of annual emissions with well depth (deeper wells, which were generally newer, had lower annual emissions than shallower, generally older, wells). Correlations with emissions per event were generally weaker than for annual emissions. Additional details are provided in SI (Section S4). As shown in Figure 5, for wells without plunger lifts, average emissions for individual unloading events range between 21 000 and 35 000 scf methane per event, if the events are binned into wells that have less than 10 events per year, between 11 and 50 events per year, and 51 or more events per year. The differences in annual emissions from manually unloaded wells without plunger lifts are largely due to the frequency of events, rather than the volume of gas emitted per event. For wells with plunger lifts, Figure 5 reports average emissions in two frequency bins. Manually triggered plunger lift wells were binned as a single group; all had less than 100 events per year (maximum observed value of 52 events per year). Automatically triggered plunger lift wells were also considered as a single category since all of these wells had more than 180 unloadings per year (average of 1870 unloadings per year in the sampled population). Plunger lift wells that were manually triggered had average emissions per event of 9650 scf methane. Plunger lift wells with automated triggering of the unloading had average emissions of 1260 scf methane per event.

The measured emissions per event were compared to predictions made using emission estimation methods commonly used in EPA GHGRP reporting. For wells with plunger lifts, the emission estimates averaged 4500 scf/event as compared to an average of 8000 scf/event for the study measurements (difference is statistically different, $p = 0.004$). Despite the differences in mean predicted and observed emission rates, the paired measurements and estimates were weakly, but statistically significantly correlated. For wells without plunger lifts, the emission estimates averaged 31 000 scf/event as compared to an average of 27 000 scf/event for the measurements (difference is not statistically significant), however, while the averages are similar, the estimates were not well correlated with the observations. See SI (Section S4) for more details.

Implications for National Emission Estimates. National emissions, based on the measurements made in this work, are estimated by multiplying an emission factor, based on the measurements, by an activity factor. Emission event counts, stratified into categories based on emission events per year per well, were chosen for the activity factor because of the process used for selecting wells to be sampled and because annual emission estimates for wells with unloadings depended most strongly on event frequency.

As documented in SI (Section S1), the measurement team typically visited production Basins for approximately a week, and sampled randomly selected wells that had scheduled (for

manually triggered wells) or anticipated (for automatically triggered wells) unloading events for that week of sampling. This meant that the study team was far more likely to sample wells that unloaded weekly or more frequently, rather than wells that unloaded just a few times per year. This sampling approach resulted in a representative distribution of events, but not a representative distribution of wells. For example, 85% of the wells, without plunger lift, that have unloading emissions and that are operated by the companies that provided sampling sites in this work, had fewer than 10 emission events per year (See SI, Section S5). In the measurements performed for this work, 15 of the 32 wells without plunger lift (47%) had 10 or less events per year. These wells are therefore under-represented in the measurement data, relative to their presence in the participating companies' overall well population. Because of differences in the distributions of event frequency between the sampled wells and the national population of wells, it would not be appropriate to choose an emission factor of emissions per well per year and an activity factor of number of wells, without adjusting for this difference in event frequency distribution.

An additional reason for stratifying wells by frequency of events in the activity factor is the data shown in Figure 5, which indicate a reasonable degree of consistency in per event emissions. Wells without plunger lifts had measured mean values of 21 000−35 000 scf methane/event. Wells with plunger lifts had measured mean values of 1000−10 000 scf methane/event, but much larger ranges of event frequencies. For the calculations reported in this work, national, rather than regional averages of emissions per event will be used, due to the limited number of observations in individual regions.

In this work, national estimates of numbers of unloading events were based on a survey of the participating companies (see SI, Section S5). Data on event counts from the EPA GHGRP were not used since event counts for plunger and nonplunger wells are either partially reported or of uncertain quality. The national event counts were assumed to have the same distributions as reported in the participant survey. Based on this survey, it was estimated that the 32 225 wells with plunger lifts (based on data from the 2012 GHGRP) have a total of 6.8 million events per year. Only 206 500 of these 6.8 million events are associated with wells that vent less than 100 times per year. Total annual emissions from plunger lift wells are estimated at 10 billion cubic feet of methane per year (bcf/yr) (190 Gg/yr), with 80% of those emissions associated with wells that vent more than 100 times per year (additional details in SI, Section S5). For wells that vent more than 100 times per year, the average emissions per well per year are 1 400 000 scf per well per year (27 Mg/yr) with 95% confidence bounds of 600 000−2 500 000 scf (10−50 Mg, based on the confidence bounds in the emissions per event).

For wells without plunger lifts, it was estimated that 26 438 wells (based on data from the 2012 GHGRP) vent a total of 177 000 times per year, with total emissions of 4.4 bcf/yr (84 Gg/yr). Again, the wells that vent with highest frequency have the highest emissions per well. The 1.1% of wells that vent more than 50 times per year have average emissions of 3.2 million scf methane/yr. For wells without plunger lifts, however, these wells account for only 1.1% of the wells with unloading emissions, so the emissions from these wells venting at high frequency account for only 25% of emissions from wells without plunger lifts. Additional details are provided in SIn, Section S5).

The overall emission estimate for liquid unloadings (plunger and nonplunger wells), based on the measurements made in this work, is 270 Gg (14 bcf/y), which is within a few percent of the national emissions estimated in either the 2012 GHG NEI (273 Gg/yr) or the 2012 GHGRP (276 Gg/yr). The 95% confidence range for this estimate is 190−400 Gg/yr, based on the reported confidence ranges in the per event emission factors, but not accounting for uncertainties in event counts. SI (Section S5) reports sensitivity analyses that suggest uncertainties in event count estimates may be large, up to a factor of 2 or more, which could have a significant impact on national emission estimates. Regardless of the exact national total of emissions, however, wells with high frequencies of unloadings have annual emissions that are a factor of 10 or more greater than the annual emissions of wells with low frequencies of unloadings.

■ ASSOCIATED CONTENT

Supporting Information

Additional material as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interest(s): Lead author David Allen serves as chair of the Environmental Protection Agencys Science Advisory Board, and in this role is a paid Special Governmental Employee. He is also a journal editor for the American Chemical Society and has served as a consultant for multiple companies, including Eastern Research Group, ExxonMobil, and Research Triangle Institute. He has worked on other research projects funded by a variety of governmental, nonprofit and private sector sources including the National Science Foundation, the Environmental Protection Agency, the Texas Commission on Environmental Quality, the American Petroleum Institute and an air monitoring and surveillance project that was ordered by the U.S. District Court for the Southern District of Texas. Adam Pacsi and Daniel Zavala-Araiza, who were graduate students at the University of Texas at the time the work in this paper was done, have accepted positions at Chevron Energy Technology Company and Environmental Defense Fund, respectively. John Seinfeld served as a consultant for Shell in 2012. A. Daniel Hill owns ExxonMobil, BP, and ConocoPhillips stock, serves on the Advisory Board for Sanchez Oil and Gas, for which he is compensated, and has been a consultant for Schlumberger and numerous oil and gas operating companies..

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