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Aircraft-Based Measurements of Point Source Methane Emissions in the Barnett Shale Basin

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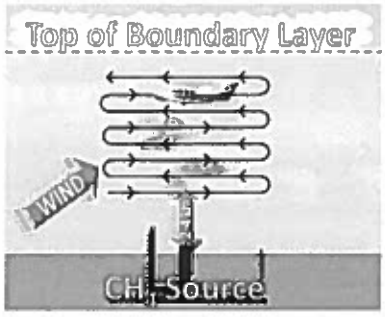
Supporting Information

ABSTRACT: We report measurements of methane (CH_4) emission rates observed at eight different high-emitting point sources in the Barnett Shale, Texas, using aircraft-based methods performed as part of the Barnett Coordinated Campaign. We quantified CH_4 emission rates from four gas processing plants, one compressor station, and three landfills during five flights conducted in October 2013. Results are compared to other aircraft- and surface-based measurements of the same facilities, and to estimates based on a national study of gathering and processing facilities emissions and 2013 annual average emissions reported to the U.S. EPA Greenhouse Gas Reporting Program (GHGRP). For the eight sources, CH_4 emission measurements from the aircraft-based mass balance approach were a factor of 3.2−5.8 greater than the GHGRP-based estimates. Summed emissions totaled 7022 ± 2000 kg hr^{-1}, roughly 9% of the entire basin-wide CH_4 emissions estimated from regional mass balance flights during the campaign. Emission measurements from five natural gas management facilities were 1.2−4.6 times larger than emissions based on the national study. Results from this study were used to represent "super-emitters" in a newly formulated Barnett Shale Inventory, demonstrating the importance of targeted sampling of "super-emitters" that may be missed by random sampling of a subset of the total.



INTRODUCTION

In 2012, natural gas production from the Barnett Shale in North Texas, the second-largest natural gas resource in the U.S., reached peak levels. The Barnett Shale is a 6458 square mile natural gas shale formation located in North Texas that is estimated to hold 43.4 trillion ft^3 of technically recoverable natural gas, whose primary component is methane (CH_4), a potent greenhouse gas (GHG).[1] In the region of this study, there are 29 900 wells, 276 compressor stations, 38 gas processing plants, and 733 landfills.[2] To facilitate informed GHG policy and mitigation efforts, a comprehensive understanding of the nature and magnitude of CH_4 emission rates for various anthropogenic and natural sources is required. Emission inventories can be constructed using bottom-up methods, which either measure component-level emissions directly or use activity and emission factors to calculate emissions from a subset of sources and subsequently scale up by the number of sources to a total emission estimate.[2−4] Alternatively, top-down methods can be used, which measure total atmospheric GHG enhancements downwind of a source or group of sources to capture the complete emission of the source area.[2−4] Both techniques have their weaknesses, however, with bottom-up methods potentially failing to include significant sources leading to emission underestimation, and top-down techniques not being able to easily attribute emissions that may then result in emission overestimation for individual sector-specific sources.[2−4] By bridging the gap between bottom-up and top-down methods, a more robust system for GHG monitoring and estimating can be developed.

To provide policymakers with national GHG emissions data, the Environmental Protection Agency (EPA) implemented two

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complementary programs, the Inventory of Greenhouse Gas Emissions and Sinks (GHGI, 1997) and the Greenhouse Gas Reporting Program (GHGRP, 2009). At present, these databases function as the primary sources of GHG emission data for policy development. The GHGI provides an overall national emission estimate by sector using emission and activity factors, whereas the GHGRP provides facility-specific, self-reported annual CH_4 emissions (http://www.epa.gov/ghgreporting/). The GHGRP involves mandatory reporting of GHGs from sources that emit greater than 25 000 t of CO_2 equivalent per year (equivalent to 114 kg CH_4 hr^{-1} using a CH_4 GWP of 25). Independent top-down ground,[4−7] aircraft,[8−11] and space based[12] investigations call into question the accuracy of commonly used inventories,[2] including the GHGRP, suggesting that GHGRP estimates may underestimate the actual emission rate by up to a factor of 3.8 due to underestimated facility emissions, temporal variability of emissions, and the exclusion of nonreporting facility emissions.[10,12,13]

To enable scientifically defensible policy development, methods for determining CH_4 emissions must be representative and accurate. This can be challenging because inventories typically use outdated activity and emission factors and may fail to account for contributions from super-emitters. This can result in overlooking fugitive CH_4 emissions from natural gas facilities resulting from malfunctions and maintenance issues that are not represented in the yearly reported emissions. Landfill emissions monitoring can also be challenging due to emission variations caused by fluctuations in atmospheric pressure, temperature, and precipitation. Choice of landfill cover material, the efficiency and consistency of gas collection systems, the presence of flares, and the percentages of active, intermediate, and final cover can also cause variations in emissions.[14]

To date, no comprehensive, measurement-based study of CH_4 emissions from the entire Barnett region of Texas exists. Thus, in October 2013 the Environmental Defense Fund launched the Barnett Coordinated Campaign,[15] to combine top-down atmospheric measurements with bottom-up inventory data to improve CH_4 emissions estimates from oil and gas systems, landfills and other sources in the Barnett Shale. Here we report facility-scale top-down emission rates from the Barnett collaborative campaign in which we determined CH_4 emission rates for eight CH_4 emitters (>150 kg CH_4 hr^{-1}) in the Barnett shale region of Texas, including four natural gas processing plants, one compressor station, and three landfills. An aircraft-based mass balance approach was employed at all eight sites to measure CH_4 emission rates. To investigate the reliability of the measurements and the temporal variability of emissions, the emission rates at four of the sites were compared to emission estimates made during the Barnett Campaign using an alternative aircraft-based method (described in SI) and or two unique surface-based mobile measurement approaches (Lan et al.,[16] Yacovitch et al.[17]). Emission estimates were also compared to the 2013 annual average emissions reported to the GHGRP and throughput-based emission estimates based on a recent national study of emission measurements at 130 gathering and processing facilities reported in Mitchell et al.,[13] which we consider the most extensive and best available estimate in the absence of other measurements for comparison.

Sites were selected that were expected to be significant contributors to the basin-wide total and that had potential emission rates above our limit of quantification (~15 kg hr^{-1}). The three landfills (LF I-III) and one gas processing plant (GPP-I) were preselected based on high CH_4 emissions from the 2012 GHGRP. The other three GPPs and compressor station were selected quasi-randomly upon observation of CH_4 plumes during exploratory aerial surveying. Therefore, the results for these sites may be representative of large emitters that may have been experiencing anomalous conditions during the time of the experiment. While the targets were not randomly selected, our measurements represent in-field observations of high emission sites during a campaign that included aircraft mass balance estimates of the Barnett total emissions.[18]

Emission rates for oil and gas facilities tend to be positively skewed by "super-emitters", sites that emit much more CH_4 than that represented by, for example, the mode of the sampled distribution of their facility type.[2,3,13] Super-emitting facilities occur by definition with very low frequency, and therefore emissions are better captured by targeted sampling of high emission sites rather than unbiased sampling of the large number of sites in a basin such as the Barnett.[2] Therefore, the data from this study and others[16,17] were used in the Lyon et al.[2] inventory development to characterize fat-tail emission sources, or "super-emitters", that were above the maximum value of a national study of facility-level CH_4 emissions at 130 gathering and processing facilities conducted by Mitchell et al.[13] Accounting for these high emission sources, which may represent anomalous events that are often excluded from other studies, is important for accurately estimating regional emissions.

MATERIALS AND METHODS

CH_4 emission rate measurements were conducted for the 8 point sources in the Barnett shale region of Texas shown in Figure 1, with small gray dots representing active oil and gas infrastructure and cyan dots representing active landfills in the region. Five mass balance flights were conducted in 2013 on October 17, 19, 23, 24, and 26 in the convective boundary layer (CBL) in Purdue's Airborne Laboratory for Atmospheric Research (ALAR) (http://science.purdue.edu/shepson/research/bau/alar.html, see SI) at an average airspeed of 70 m s^{-1}.[19−22] ALAR is a modified Beechcraft Duchess fitted with a Picarro cavity ring-down spectroscopy (CRDS) system (model no. G2401-m) for real-time high frequency (0.5 Hz) measurements of CH_4, CO_2, CO, and H_2O with precision of 2.6 ppb (CH_4) and 0.1 ppm (CO_2).[19] The aircraft is also equipped with a nine-port Best Air Turbulence (BAT) pressure probe[23,24] for obtaining high frequency (50 Hz) 3-dimensional wind data when used with a high precision global positioning and inertial navigation system (GPS/INS) (Novatel Black Diamond System).[25,26] The horizontal wind measurement accuracy is ±0.4 m s^{-1}, as discussed by Garman 2009.[27] Ambient temperature measurements are made using a microbead thermistor located at the center of the probe hemisphere.

Two air inlets on the nose cone of the aircraft continuously direct sample air through a 5 cm diameter Teflon sample line to the Picarro through a tee connection at a flow rate of ~1800 L min^{-1} with a residence time of ~0.1 s using a DC blower installed at the rear of the aircraft. The delay time from the nose to the detection cell is ~11 s. In-flight and on-ground calibrations were performed daily with a computer controlled CH_4/CO_2/CO valve switching system using three NOAA certified CH_4, CO_2, and CO reference cylinders (see SI).

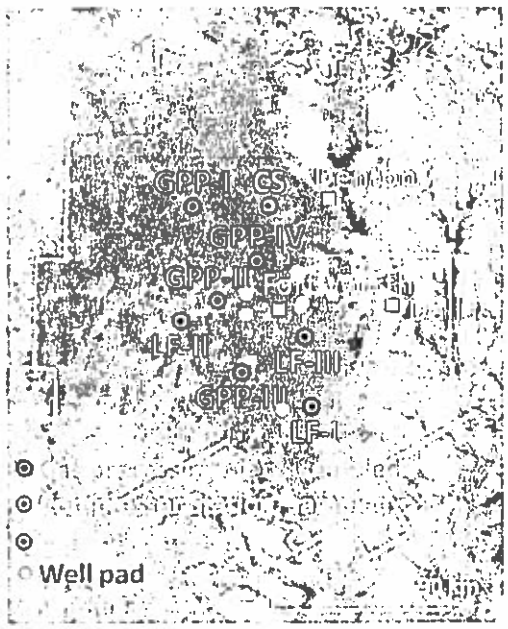

Figure 1. Map of the Barnett Shale. Outlined in white are the 15 counties that compose the Barnett shale, according to the TCEQ's Web site, updated on 12−5−2013 (http://www.tceq.texas.gov/airquality/barnettshale/bshale.maps). The location of each sampling site is marked with a red (gas processing plant), yellow (compressor station), or green (landfill) circle and each is labeled according to its pseudonym (GPP-I, LF-III, etc.). Small gray dots represent active oil and gas infrastructure and cyan dots represent active landfills in the region.

Mass balance experiments spanned ~1−2 h, between 1200 and 1800 h local time (LT), to ensure full development of the CBL and minimal temporal variation in winds. The mass-balance technique permits the calculation of a net mass flow through a vertical plane downwind of the source, according to the conservation of mass.[19,21,22,28] Eight CH_4-emitting point sources were investigated, including four gas processing plants (GPP−I-IV), one compressor station (CS), and three landfills (LF-I-III). Sampling site coordinates, counties, and dates of analysis are reported in SI Table S1. Meteorological parameters and details for each flight, including average wind speed and direction, distance downwind of the source, total number of transects, and flight durations, can be found in Table S4 (see SI). The SI provides full details regarding flight descriptions, instrumentation, CH_4 quantification determination, and uncertainty estimation.

During the campaign, emission rates for GPP-I, GPP-IV, LF-I, and LF-III were also determined from concentration data collected via different methods, including an alternative Aircraft-based Survey Approach (ASA) and two surface-based measurement approaches (Yacovitch et al.;[1] Lan et al.[16]). ASA used an aircraft-based chemical transport model using an off-axis integrated cavity output spectrometer (RMT-200, Los Gatos Research, Inc.) to measure CH_4 concentrations within a 2.5 km-spaced line pattern over the Barnett at an altitude of 1000 ft above ground level[29] (see SI). Yacovitch et al.[1] and Lan et al.[16] employed a surface-based measurement approach and plume dispersion model for quantifying CH_4 emissions, using vehicles equipped with an aerodyne tunable infrared laser direct absorption spectrometer (TILDAS)[1,30] or a Picarro cavity ring down laser spectrometer.[16] Method details can be found in the provided references. All four methods reported in this study conducted emission measurements under suitable meteorological conditions with relatively high, consistent winds and no rain.

RESULTS AND DISCUSSION

Point Source CH_4 Emission Measurements. Locations of the CH_4-emitting sources sampled are shown in Figure 1 and site descriptions are provided in SI Tables S1 (site coordinates and counties), SI Table S2 (plant capacities, use of best available monitoring methods (BAMM) option in 2013 GHGRP, and reported malfunctions at natural gas facilities) and S3 (landfill properties). Figure 2 shows a sample flight path

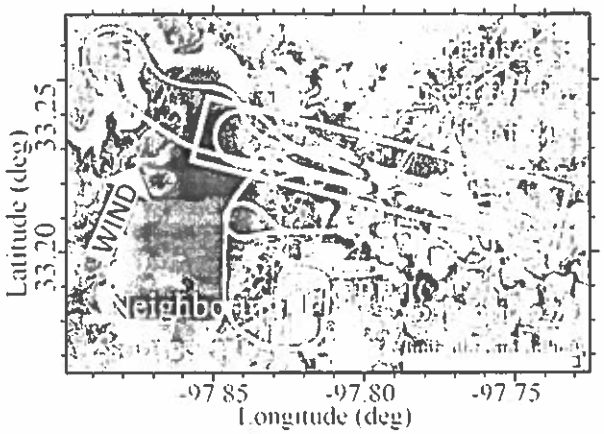

Figure 2. Experimental mass balance flight at GPP-I on 17 October 2013. Flight path is shown with CH_4 concentration overlay (ppm) represented by a changing color gradient (see key on right side of map) and a change in diameter of plotted flight path points for added clarity (larger size corresponds to higher CH_4 concentration). The gas processing plant (GPP-I) is denoted by a purple triangle and a neighboring source is marked with a blue square. Average wind direction and speed were 200° SSW at 3.6 m s^{-1}, respectively.

from the 17 October 2013 flight experiment conducted at Gas Processing Plant I (GPP-I) in which nine horizontal transects were flown ~3.0 km downwind of the source, perpendicular to the wind direction (mean wind direction and speed was 200° SSW at 3.6 m s^{-1}) and at multiple altitudes. One transect was omitted due to a temporary shift in wind direction and the location of the transect. The boundary layer height for GPP-I was approximated by visual inspection of the cloud deck altitude. For other flights, CBL height was determined either by flying a vertical profile or by use of high resolution doppler lidar (HRDL) data (see SI). However, for all cases the plume did not extend to the top of the CBL, and therefore this uncertainty in the CBL top is not important to the calculation, as shown in Figure 3. Horizontal transects were long enough to extend past both sides of the plume to achieve sampling of local background air and the complete vertical and horizontal distances of the plume were captured within the transects. In cases where potential CH_4 emitters were nearby, sites were circled to attribute the CH_4 emission to a specific source. SI Figure S6 shows the flight path for each site with raw CH_4 concentration overlay in ppm. The flight experiment conducted at GPP-II was unique in that it was performed twice: four transects were flown at 2 km downwind of the site and four

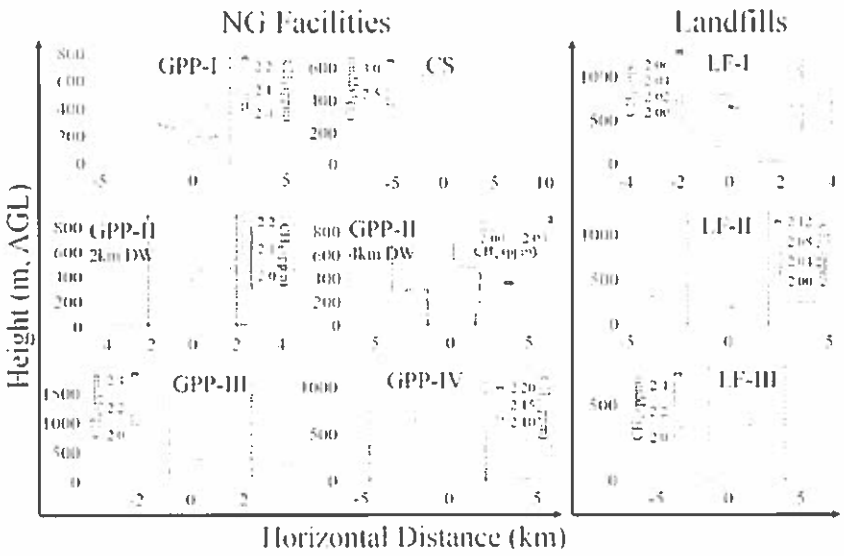

Figure 3. Interpolated plots of CH_4 concentration as a function of height above ground level (m) and horizontal distance (km) are shown for natural gas facilities (GPP−I IV and CS) (left) and landfills (LF I III) (right). Area in between black dashed lines represents the horizontal distance for which the plume is defined and the flux is calculated

Table 1. Comparison of Multi-Transect Kriging Approach (ALAR) CH_4 Emission Measurements to Gas Processing Plant and Compressor Station Emission Estimates Derived from Ref 13. and EPA's 2013 GHGRP (Reported Emissions for the Specified Facility)

site	ALAR[a] (kg hr^{-1})	Mitchell et al.[13b] (kg hr^{-1})	ALAR/Mitchell et al.[13]	GHGRP[c] (kg hr^{-1})	ALAR/GHGRP
GPP I	322 ± 190	200	0.7−2.6	115	1.1−4.5
GPP II (avg)[d]	195 ± 120	104	0.7−3.0	20	3.8−15.8
GPP II (2 km)	181 ± 110	104	0.7−2.8	20	3.6−14.6
GPP II (4 km)	209 ± 120	104	0.9−3.2	20	4.5−16.5
GPP III	491 ± 290	187	1.1−4.2	76	2.6−10.3
GPP IV	386 ± 230	166	0.9−3.7	47	3.3−13.1
CS	2038 ± 1200	530	1.6−6.1	0.2	4190−16 190
LF I	829 ± 500			308	1.1−4.3
LF II	316 ± 190			320	0.4−1.6
LF III	2415 ± 1500			658	1.1−6.0
total[d]	7022 ± 2000			1544	4.5±1.3

[a]Emission rate uncertainties shown represent ±95% confidence limits. [b]Calculated using best fit trend line of emissions vs plant capacity (GPPs) or emissions vs horsepower (CS), as reported[13] [c]2013 GHGRP self reported CH_4 emissions estimates for the specified facility [d]Total calculated using GPP I, II (avg), III, IV, CS, LF I III. ("GPP II (avg)" is average of "GPP II (2 km)" and "GPP II (4 km)")

transects were flown immediately following at 4 km downwind of the site, enabling assessment of repeatability (9% difference, in this case).

The average emission rate for each site was determined using the multitransect kriging method described previously[19,21,22] and in the SI. For each site, 3−4 backgrounds, 3 CBL depths, 3 perpendicular wind scenarios across the uncertainties cited in Gariman 2009 (±0.4 m s^{-1}),[27] and the most probable mixing scenario based on a large eddy simulation plume dispersion model[31] were used to provide 27−72 total emission rate estimates (see SI). Raw CH_4 concentration horizontal distribution plots before (SI Figure S7) and after interpolation (Figure 3) are provided. The average of the iterations was used to determine the final emission rate measurement for each site and results are reported as an average ± the 95% confidence level (CL) uncertainties, the latter as determined for point sources in Cambaliza et al.[19] The results are presented in Table 1, and compared to emission rate estimates based on the Mitchell et al.[13] data (facility type estimate) and reported 2013 GHGRP estimates (specific to facility).

Gas Processing Plant CH_4 Emission Rates. For the mass balance aircraft based (ALAR) CH_4 emission rate measurements, GPP−II IV were selected for study after identification of a large emission during flyby. Measured ALAR CH_4 emissions rates (95% confidence) for the gas processing plants are shown in Table 1. During the campaign, emission rates were also estimated using alternative methods for GPP I (ASA; Yacovitch et al.;[17] Lan et al.[16]), and −GPP IV (Yacovitch et al.[17]). Emissions at GPP I were sampled on five separate days by ALAR and the other three techniques, providing a total of 10 measurements and allowing evaluation of the temporal variability of GPP I emissions (Table 2). Average measurements for GPP I are essentially identical for aircraft (ALAR and ASA; 395 ± 150 kg hr^{-1}) and surface (453^{+656}_{-135} kg hr^{-1}) methods. However, significant temporal variability exists for CH_4 emission rates at GPP I, ranging from 126 to 1723 kg hr^{-1}, indicating that emissions at this site are highly variable.

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Table 2. Variability of CH_4 Emission Measurements Across Different Methods and Times[a]

	GPP-I			GPP-IV		LF-I		LF-III	
method	date MMDDYY	time, LT HH:MM	CH_4 emission rate kg hr^{-1}	date MMDDYY time, LT HH:MM	CH_4 emission rate kg hr^{-1}	date MMDDYY time, LT HH:MM	CH_4 emission rate kg hr^{-1}	date MMDDYY time, LT HH:MM	CH_4 emission rate kg hr^{-1}
ALAR	101713	16:38–17:21	322 ± 190	102413 14:05–14:20	386 ± 230	101913 17:08–17:42	829 ± 500	102613 13:30–14:10	2445 ± 1500
ASA	102013	~15:00	467^{+}_{-}			102513–12:00	585^{+}_{-}		
Vaouvach[i] et al.[a]	032813	20:18–20:20	313^{+}_{-}	032813 12:12–13:30	163^{+}_{-}				
	032813	20:22–20:29	169^{+}_{-}						
	032813	20:40–20:45	205^{+}_{-}						
	032813	20:45–20:52	126^{+}_{-}						
	032813	20:56–21:08	180^{+}_{-}						
	102413	~06:21	162^{+}_{-}						
Lan et al.[b]	102413	14:01–14:24	746^{+}_{-}					101913 13:33–13:44	562^{+}_{-}
	102913	11:09–11:42	1723^{+}_{-}						
aircraft and surface-based average			441^{+}_{-}		275^{+}_{-}				1504 ± 1100
aircraft average			395 ± 150				707 ± 350		
surface-based average			453^{+}_{-}						

[a] All measurements are reported to 95% confidence.

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Similarly, variability in CH_4 emission rates over time was apparent at GPP-IV, which was measured on two separate days by ALAR (10/24/13, 386 kg hr^{-1}) and Yacovitch et al.[17] (03/28/13, 163 kg hr^{-1}). We note that there could be a time of day dependence of natural gas facility emission rates, due to work schedule operations variability. Measurements at GPP-I conducted by ALAR, ASA, and Lan et al.[16] occurred between 1100 and 1800 LT and exhibited larger average emissions than the measurements conducted outside of normal work hours reported by Yacovitch et al.,[17] but not statistically significantly so. All measurements conducted by ALAR, ASA, and Lan et al.,[16] and measurements at GPP-IV by Yacovitch et al.,[17] occurred during standard work hours.

The top-down CH_4 emission rate measurements for the natural gas point sources (GPP−I IV, CS) were then compared to CH_4 emission rate estimates based on facility level data reported in Mitchell et al.,[13] who reported methane emission rates at 114 natural gas gathering and 16 processing facilities from top gas producing basins, measured via a downwind tracer flux method.[32−34] For gas processing facilities, fugitive CH_4 emissions increase with CH_4 throughput. To find throughput based emission rate estimates for comparison to our measurements, raw data from Mitchell et al.[13] were plotted as the weighted average facility-level emission rate (WAFLER) vs plant capacity (gas processing plants, R^2 = 0.24) and as the WAFLER vs combined horsepower ("C" type compressor stations, R^2 = 0.70) (SI Figure S1). The best-fit line was used to estimate emissions for facilities in this study based on their plant capacity (GPP−I IV) or horsepower (CS) (SI Table S2). The resulting CH_4 emission rate estimates based on Mitchell et al.[13] data were lower than ALAR's measurements for gas processing plants by a factor of 2.1, on average (Table 1). For sites with repeat measurements, the average measured emission rate was larger than the Mitchell et al.[13] estimate by a factor of 2.2 (GPP I, 4 measurement techniques (ALAR, ASA, Yacovitch et al.,[17] Lan et al.[16])) and 1.7 (GPP-IV, 2 measurement techniques (ALAR, Yacovitch et al.[17])).

Next, we compare measured emission rates to the facility specific 2013 GHGRP data (Table 1). Total measured CH_4 emission rates from the gas processing plants were a factor of 5.4 higher than the GHGRP reported rates. For sites with repeat measurements, the average measured rate was larger than the GHGRP estimate by a factor of 3.8 (GPP I, 4 measurement techniques (ALAR, ASA, Yacovitch et al.,[17] Lan et al.[16])) and 5.9 (GPP-IV, 2 measurement techniques (ALAR, Yacovitch et al.[17])). Unlike the GHGRP and Mitchell et al.[13] estimates, we targeted sites that are known to have or were observed to have abnormally high emissions, given that such sites are arguably important to accurately represent in inventories. Nonetheless, gas processing plant emission rate estimates from Mitchell et al.[13] were closer to the emission rates measured by ALAR than for the 2013 GHGRP reported data. Therefore, independent top-down studies of emissions, reported here and from Mitchell et al.,[13] support the observation of higher emission rates compared to the GHGRP self-reported data, suggesting that the GHGRP could improve the accuracy of emissions reporting by updating calculation methods.

A significant level of day to day (GPP I, IV) and possibly hour to hour (GPP I) variability in emissions exists at the gas processing plants. However, measurements made by the Aerodyne mobile laboratory on 3/28/13 were not statistically significantly different,[17] and so the fluctuations may reflect variability in the measurement method. In principle, surface based measurements can underestimate emissions because convective mixing above the sampling point results in under-sampled data, preventing proper simulation of the plume by dispersion models. The model adjusts for this using a vertical dispersion parameter. However, emission rates are only biased slightly (<30% for 79% of facilities in the study) by partial recovery of emissions.[13] The ALAR method is capable of capturing the complete plume by flying at multiple altitudes, resulting in lower uncertainties. The aircraft based and surface based average measurements for GPP I, however, exceed the Mitchell et al.[13] estimate by a factor of 2.0 and 2.3, respectively, and the GHGRP estimate by a factor of 3.4 and 3.9, respectively. The two aircraft based measurements for GPP-I, conducted 3 days apart, differ by 37%. Potential contributors to variable plant emissions include scheduled venting of natural gas to the atmosphere to depressurize the equipment, or "blowdown" events, which cause a temporary and significant increase in emissions. Blowdown emissions may have been captured during our measurements, yielding higher than typical emission rates, however, the dates of blowdowns are unknown to us. For reference, the total reported blowdown events in 2013 for GPP I-IV with total and average CH_4 emissions per event are shown in SI Table S2. The 2013 average CH_4 emissions per event were 430, 6941, 45, and 316 kg (GPP−I IV, respectively) and were released over the course of 15 min to 3 h.[35] In 2013, the average number of blowdown events per week at each plant was 0.08, 0.06, 6.04, and 2.12 (GPP I IV, respectively), suggesting that measurements at GPP-III and -IV are more likely to have captured blowdown emissions than measurements at GPP I and -II. In 2013, blowdowns for these four gas processing plants alone totaled ~71 500 kg of CH_4 emissions, as reported to the GHGRP. This indicates that blowdowns are a significant temporary source of increased GHG emissions which can contribute significantly to annual emission totals.[2]

Our measurements could differ from the GHGRP as it does not require inclusion of tank emissions in gas processing plant emission calculations and some engine venting emissions are omitted depending on operating mode.[36] Reciprocating compressor rod packing emissions and centrifugal compressor wet seal emissions are only required to be reported when in "operating" mode. However, studies have shown that emissions can be significant from rod packing and seals while in "not-operating, pressurized" mode, which compressors are in 34% of the time,[37] and from compressors in "not operating depressurized" modes.[13] Compressor emissions are only required to be measured in "not operating, depressurized" mode once every three years.[36] Therefore, some of the temporal variability and underestimated emissions relate to reporting requirements that discount emissions from different operating conditions. After natural gas is extracted, the raw product is transported to GPPs where the gas is separated from water and other hydrocarbons (i.e., ethane, butane, propane, etc.) by compression and cooling and is then transported through the transmission system.[38−40] During this process, fugitive CH_4 leaks can occur with valves being the largest source (30% of total emissions), followed by connectors (21%) and compressor seals (23%).[41] Equipment that is subject to high use, temperature cycling, and or vibration is more likely to experience wear that leads to leaking.[41] Since equipment leak surveys are only required annually, new, unreported leaks may exist during our measurements.

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Compressor Station CH_4 Emission Rates. The natural gas compressor station (CS) was chosen for study after identification of a large CH_4 plume (4.6 ppm) while in flight. During the campaign, only ALAR conducted measurements at this site. The measured ALAR CH_4 emission rate for the CS was a factor of 1.6−6.1 larger than the Mitchell et al.[13] estimate, and 4 orders of magnitude larger than the 2013 GHGRP estimate (Table 1). This indicates that the CS is a "super emitter" for the time period of our measurements. In the Mitchell et al.[13] study, 108 compressor stations were investigated and observable emissions were reported at 71 facilities via infrared camera, which included venting from liquid storage tanks (68%), leaking or venting from compressor equipment (59%), and gas pneumatics (39%).[13] All sites had emissions observed by CH_4 enhancement.[13] They reported storage tank-related emissions ranging between 10−630 kg hr^{-1} and showed that these facilities had roughly 4 times the CH_4 emissions of similar facilities without tank emissions, which contributed to a skewed distribution where less than 30% of compressor stations contributed ~80% of total CH_4 emissions.[13] It is, however, noteworthy that the CS we studied had an emission rate more than three times greater than the highest emitting station sampled by Mitchell et al.,[13] however, they observed short term emissions up to 1826 kg hr^{-1} during a compressor blowdown, indicating that our measured emission rate is reasonable for short term events.

The significant discrepancy between ALAR's measurement and the GHGRP estimate is likely due to the nature of GHGRP reporting requirements and the temporal variability of emission. The CS is classified as a "gathering facility" and therefore is only required to report combustion emissions and not vented or fugitive GHG emissions, as opposed to gas processing plants which report all three.[30] The GHGRP uses a default emission factor for natural gas consumption that represents fuel slips from a highly efficient turbine, not the much higher fuel slip of reciprocating engines used in most gathering stations. Use of improved emission factors that are specific to individual units improve the accuracy of reported results, such as those from the compilation of air pollution emission factors (AP-42) or from manufacturer data sheets.[42,43] To understand the effect that these underestimated combustion emission factors had on CH_4 emissions, we recalculated combustion-based CH_4 emissions for GPP I, II, -IV, and CS using AP-42 emission factors (EFs), installed horsepower, and usage hours data collected from the Texas Commission on Environmental Quality (TCEQ), for a Clean Air Task Force project (SI Table S8). The AP-42 EF for a natural gas-fired 4 stroke lean-burn reciprocating engine, which were in use at the compressor station, is 5.7×10^{-1} kg/MMBTU fuel input, compared to the GHGRP's 1.0×10^{-4} kg/MMBTU EF. Therefore, actual average combustion emissions are estimated to be ~570 times higher than the GHGRP estimate. Furthermore, TCEQ requires facilities to report excess emission events above 5000 pounds (2270 kg) of natural gas (threshold weight includes only hydrocarbons with 3 or more carbons, C_3^+), excluding methane and ethane. If we assume the CS gas is 64% CH_4 and 20% C_3+ by weight based on the Wise County average, then a facility could emit over 7200 kg methane without exceeding the state reporting threshold. We note that during the time we were at the CS site, it was emitting at ~2038 kg CH_4 hr^{-1}, and so for the 65 min measurement period, the total natural gas C_3+ emissions is likely lower than the reporting threshold. Variability in CS emissions may also result from changes in engine operating conditions, including ignition timing, torque, speed, air to fuel ratio, ambient temperature, humidity, and other factors.[44]

Landfill CH_4 Emission Rates. All 3 landfills sampled were preselected based on large reported CH_4 emissions to the 2012 GHGRP. Details concerning each landfill's capacity, cover type material, waste received in 2012, presence of flares, and details of gas collection systems are shown in SI Table S3. Measured ALAR CH_4 emission rates for the landfills are shown in Table 1. During the campaign, emission rate measurements were also conducted (Table 2) at LF I by ASA and LF III by Lan et al.[16] Aircraft based measurements for LF I were conducted 6 days apart, on 10/19/13 (ALAR) and 10/25/13 (ASA) and differed by 35% but were not statistically distinguishable. For LF III, aircraft based and surface based measurements were conducted 7 days apart, on 10/26/13 (ALAR) and 10/19/13 (Lan et al.[16]) and differed by a factor of 4.4 and were statistically significantly different (95% confidence).

The top-down measured CH_4 emission rates were then compared to landfill-specific GHGRP data (Table 1). Total measured ALAR CH_4 emission rates from all three landfills were a factor of 2.8 larger than the GHGRP reported estimates. Sites with measurements made by multiple methods were a factor of 2.3 (LF-I, 2 measurement techniques (ALAR, ASA)) and 2.3 (LF III, 2 measurement techniques (ALAR, Lan et al.[16])) greater than GHGRP estimates. Landfill CH_4 emissions are known to be inversely dependent on atmospheric pressure, and small increases in pressure (+0.17 kPa in 10 min) have been shown to rapidly decrease CH_4 concentrations by a factor of 25.[45] The strong negative dependence of landfill CH_4 emission rate on atmospheric pressure changes[32] can cause up to a 6 fold variation in daily emissions.[45] ALAR measured LF-I after a 7 h period of continuously declining barometric pressure and at the time of measurement the pressure had dropped from100.12 to 99.72 kPa, while ASA collected data after only 2 h of declining pressure and at a higher pressure of 100.03 kPa (dropped from 100.73 kPa) (SI Figure S8). At LF-III, ALAR conducted measurements after a 28 h period of declining pressure, from 100.73 to 99.72 kPa at time-of flight, whereas Lan et al.[16] measured LF-III after a 1 h. period of negligible pressure decrease, from 100.12 to 100.02 kPa.In both cases, therefore, the pressure change would tend to lead to a relatively greater emission rate for the ALAR measurement periods. Larger sample sets over an extended period of time and changing barometric pressure are needed to properly describe the temporal variability of emissions, and whether this difference is systematic.

Landfill CH_4 emissions exhibit seasonal variability due to the dependence of CH_4 oxidation rates on changing soil temperature and moisture. Therefore, use of average daily temperature and moisture data for calculating annual CH_4 emissions is problematic.[11] Notably, all three landfills were sampled during the warmest hours of the day (1300−1800 LT), therefore, the time of measurement did not likely contribute to the large emissions observed since high temperatures are associated with decreased CH_4 emissions.[16] Additionally, all three LFs had a gas collection system in place at the time of measurements (SI Table S3). However, if the gas collection system was not operating during our measurements the LFs could have emitted an additional 2898 (LF I), 569 (LF II), and 1281 (LF III) kg CH_4 hr^{-1}, as determined from their GHGRP data sheets (http://ghgdata.epa.gov ghgp main.do). We have confirmed with the landfill operators that during the time of ALAR's measurement at LF III, the gas collection system was operating

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normally (data unavailable for other landfill measurements). Therefore, it is likely that differences in landfill emissions could be attributed to the combined effects of varying barometric pressure and changes in soil temperature and moisture, variables which are not comprehensively considered by GHGRP emission calculations.

Considerations Regarding Super-Emitters for Inventory Accuracy. The need for improved GHG emission reporting is evident. Current inventories and the GHGRP data used by U.S. policy makers have clear limitations, only requiring emissions reporting from the largest emitters, omitting some emission sources, mandating potentially inaccurate methods for some sources, and incompletely accounting for the contribution of super-emitters. The 2013 GHGRP estimates basin-wide oil and gas-related CH_4 emissions in the Barnett to be 17 000 kg hr^{-1}, however, this study and other independent studies[2,13,16−18] suggest that the GHGRP may be significantly underestimating emissions from the region. Basin wide Barnett CH_4 emission estimates from oil and gas sources from an aircraft based mass balance study ($59 \pm 15 \times 10^3$ kg hr^{-1})[18] and a super emitter modified (in part from this study) emission inventory ($46^{+9} \times 10^3$ kg hr^{-1})[2] are statistically identical and roughly a factor of 2.2−3.7 larger than the 2013 GHGRP estimate. Facility-level top-down emission estimates from Mitchell et al.[13] and this study also support that bottom-up measurement and calculation methods used by the GHGRP underestimate emissions. Findings from top-down studies are therefore useful in understanding nonrepresented emissions to improve the robustness of bottom-up techniques.

Several factors may influence inconsistencies between our results and the GHGRP estimates, including the use of outdated emission factors and potential to miss some emissions from super-emitters. Changes in operational mode and equipment functions, including scheduled maintenance, malfunctions, and aging equipment, may result in gas leakage, contributing to components of the "heavy-tail".[3] At the time of our studies no excess emission events were reported that may have influenced results, but malfunctions resulting in the release of CH_4 may be exempt from TCEQ reporting (SI Table S2). Additionally, for some emission sources, facilities reporting to the GHGRP can choose from multiple methods for identifying, quantifying, and calculating yearly emissions estimates. Methods are not consistent across sectors, sources, or facilities and can change each year. Emissions comparison over time can therefore be difficult, limiting the long term value of such data and the ability to evaluate the effectiveness of new control measures. More consistent monitoring approaches for similar source-types and acknowledgment of anomalous emitters would facilitate comparison of temporal trends in emissions across facilities and sectors. Using our data to represent super-emitters, Lyon et al.[2] constructed a bottom-up inventory using improved emission calculation methods which effectively bridged the gap between top-down emission measurements[18] and bottom up emission inventory estimates.[2] The accuracy of such an approach depends on knowledge of the emission rates integrated across all operating states of all emitters in a system over appropriate time scales. This is a substantial challenge that emphasizes the complementary role of top down methods, which are capable of "seeing" the atmospheric integration of all states for a full system of thousands of emitters. Due to the highly skewed distribution of emission rates, targeted measurements of high emission sites, such as those made in this study, are critical for a bottom up understanding of regional CH_4 emissions.

ASSOCIATED CONTENT

Supporting Information

Supporting Information includes seven text sections, eight tables, and nine figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00410.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

GHG	green house gas
GHGRP	Green House Gas Reporting Project
EPA	Environmental Protection Agency
CFR	Code of Federal Regulations
bcf	billion cubic feet
BAT	best air turbulence
ALAR	Airborne Laboratory for Atmospheric Research
CRDS	cavity ring-down spectrometer
AGL	above ground level
CBL	convective boundary layer
LT	local time
GPP	gas processing plant
CS	compressor station
LF	landfill
NOAA	National Oceanic and Atmospheric Administration
ESRL	Earth System Research Laboratory
HRDL	High Resolution Doppler Lidar
ASA	Aircraft based Survey Approach
EF	emission factor
SI	supporting information
(WAFLER)	weighted average facility level emission rate

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