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Methane Emissions from the Marcellus Shale in Southwestern Pennsylvania and Northern West Virginia Based on Airborne Measurements

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Key Points:
- A CH_4 emission rate of ~21 kg/s from a 4200 km^2 area of the southwestern Marcellus in 2015 with the bulk of the CH_4 coming from coalbeds
- We estimate a mean CH_4 emission rate of 1.1% of total natural gas production with a lower limit of 0% and an upper limit of 3.5%
- The mean emission rate indicates a climate impact of CH_4 combustion below that of coal, but the full range includes values above this point

Supporting Information:
- Supporting Information S1

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(continued)

Abstract Natural gas production in the United States has increased rapidly over the past decade, along with concerns about methane (CH_4) fugitive emissions and its climate impacts. Quantification of CH_4 emissions from oil and natural gas (O&NG) operations is important for establishing scientifically sound policies for mitigating greenhouse gases. We use the aircraft mass balance approach for three flight experiments in August and September 2015 to estimate CH_4 emissions from O&NG operations over the southwestern Marcellus Shale. We estimate a mean CH_4 emission rate as 21.2 kg/s with 28% coming from O&NG operations. The mean CH_4 emission rate from O&NG operations was estimated to be 1.1% of total NG production. The individual best-estimate emission rates from the three flight experiments ranged from 0.78 to 1.5%, with overall limits of 0% and 3.5%. These emission rates are at the low end of other top-down studies, but consistent with the few observational studies in the Marcellus Shale region as well as the U.S. Environmental Protection Agency CH_4 inventory. A substantial source of CH_4 (~70% of observed CH_4 emissions) was found to contain little ethane, possibly due to coalbed CH_4 emitted either directly from coal mines or from wells drilled through coalbed layers in O&NG operations. Recent regulations requiring capture of gas from the completion-venting step of hydraulic fracturing appear to have reduced the atmospheric release of CH_4. Our study suggests that for a 20-year time scale, energy derived from the combustion of natural gas extracted from this region likely exerts a net climate benefit compared to coal.

Plain Language Summary In this study methane (CH_4) emission rates were estimated for the southwest Marcellus Shale based on airborne observations. A mean emission rate of ~21 kg CH_4/s was observed from a 4,200-km^2 study area. A significant portion (~70%) of the emitted CH_4 was found to originate likely from coalbeds. Our mean estimated emission rate of 1.1% of total natural gas production indicates a climate benefit of natural gas combustion compared to coal, but the full range includes values above the 2.4% break-even point for the CH_4 global warming potential over a 20-year time horizon.

1. Introduction

Natural gas production in the United States (U.S.) has increased rapidly over the past decade and the majority of the increase has come from shale gas operations (US Energy Information Administration (EIA), 2018a; Figure 1). Technological developments of hydraulic fracturing and horizontal drilling, combined with policy and current economics, have rendered new geographic areas economically feasible for extraction (US EIA, 2011). In May 2018, shale gas production accounted for about 53% of the total U.S. natural gas production,

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with the Marcellus Shale accounting for 37% of total U.S. shale gas production or 20% of total U.S. natural gas production. The U.S. dry natural gas production was 7.61×10^{11} m^3/year in 2017. This is expected to rise to 1.22×10^{12} m^3/year by 2050 (US EIA, 2018b). In the Marcellus Shale region, natural gas production was 1.33×10^{10} m^3/year in 2010 and is expected to increase to 1.81×10^{11} m^3/year in 2020 (Considine et al., 2010); this growth is well underway as shown in Figure 1.

The increase in oil and natural gas (O&NG) operations provides direct economic benefits and can reposition the United States geopolitically by increasing its energy security (American Chemical Council, 2013; US EIA, 2018b). As a result of increased natural gas production, low cost, cleaner-burning natural gas has replaced substantial amounts of coal as fuel for power plants. This change results in power-plant emission reductions of nitrogen oxides [NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)], sulfur dioxide (SO_2), particulate matter, carbon monoxide (CO), and mercury. Downsides of O&NG operations include the potential for surface and groundwater contamination (Colborn et al., 2011; Finkel & Hays, 2013; Gordalla et al., 2013; Jackson et al., 2013; Osborn et al., 2011; Rozell & Reaven, 2012; Vidic et al., 2013) and air pollution (Field et al., 2014; McDermott-Levy et al., 2013). Significant emissions of methane (CH_4), volatile organic compounds (VOCs), and NO_x have been associated with O&NG operations, causing formation of secondary pollutants such as ozone and aerosols downwind of these areas (Bunch et al., 2014; Gilman et al., 2013; Rich et al., 2014; Roy et al., 2014; Swarthout et al., 2015; Yuan et al., 2015). In particular, the release of CH_4 to the atmosphere, which can arise from a number of steps in natural gas production, processing, storage, transport, and delivery to consumer, is a significant concern for climate. In absorbing infrared radiation, CH_4 is 86 times as potent as carbon dioxide (CO_2) over a 20-year time horizon and 34 times as potent as CO_2 over a 100-year time horizon (on a per mass basis with climate-carbon feedbacks) according to the Intergovernmental Panel on Climate Change (IPCC, 2013). Quantifying emissions of CH_4 from O&NG operations is thus essential to establish scientifically sound, cost-effective policies for mitigating greenhouse gases (GHGs).

There have been several observation-based (top-down) studies to quantify emissions of CH_4 from O&NG fields in the United States (Allen et al., 2013; Barkley et al., 2017; Caulton et al., 2014; Karion et al., 2013; Lamb et al., 2015; Marchese et al., 2015; Omara et al., 2016; Peischl et al., 2013, 2015, 2016, 2018; Pétron et al., 2012; Schneising et al., 2014; Zimmerle et al., 2015). The estimated emission rates of CH_4 obtained from these studies cover a wide range (Table 1) and have been the subject of some controversy (Allen et al., 2015; Alvarez et al., 2018; Guglielmi, 2018; Howard, 2015a, 2015b; Howard et al., 2015; Howarth, 2015). However, recent reports suggest emissions per unit of natural gas production may be trending downward (Schneising et al., 2014; Schwietzke et al., 2014, 2016; Vinciguerra et al., 2015), while the atmospheric column-averaged CH_4 mole fraction increased at a growth rate of 6.2 parts per billion by volume per year (ppbv/year) between 2007 and 2014 after its stagnation between 1999 and 2006 (Hausmann et al., 2016). Ethane (C_2H_6) and C_2H_6 to CH_4 ratios have been used to help identify and quantify the origin of plumes of CH_4, with sources such as coal mines showing low C_2H_6-to-CH_4 ratios. However, coal seams may be penetrated in the drilling for natural gas (Caulton et al., 2014) and C_2H_6-to-CH_4 ratios from well sites can vary widely (Goetz et al., 2015), complicating the use of this metric (National Academies of Sciences (NAS), Engineering, and Medicine, 2018).

There are also discrepancies in CH_4 emission rates between observation-based (top-down) and inventory-based (bottom-up) methods (Table 1), suggesting that further observations are needed to better assess CH_4 budgets. In this work, we quantify CH_4 emissions from the Marcellus Shale gas operations in southwestern Pennsylvania and northern West Virginia using a mass balance approach based on observations obtained during three flight-based experiments conducted in August and September 2015. The data from this study increase substantially the database for such measurements. Emission rates as fractions of natural gas production are estimated based on the measured CH_4 emission rates, the total natural gas production, and the CH_4 emissions in sectors other than O&NG operations in our surveyed area.

2. Experimental and Methods

2.1. University of Maryland's Cessna 402B Research Aircraft

The University of Maryland (UMD) operates a Cessna 402B research aircraft equipped with an instrument package to measure gaseous and particulate air pollutants. The instrument package listed in Table 2 has

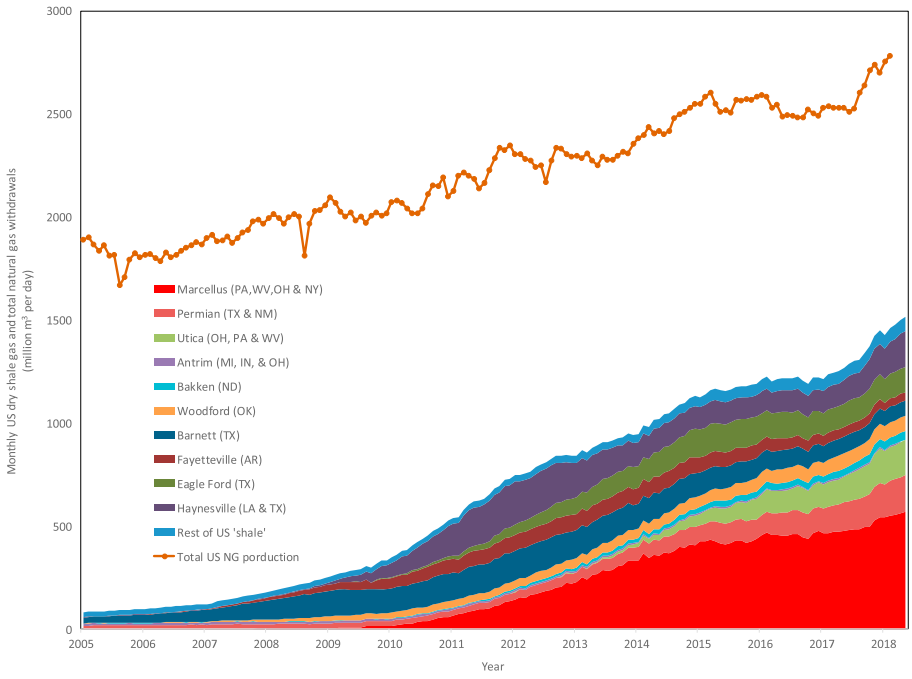

Figure 1. Monthly U.S. total natural gas (linked brown dots) and dry shale gas (shaded area) withdrawals from January 2005 to May 2018. Data are adapted from http://www.eia.gov (accessed June 2018).

been described in detail elsewhere (Ren, Salmon, et al., 2018). The original wind measurements reported by a Garmin G600 system equipped on the Cessna have been corrected due to an error in the aircraft true heading. This instrument error affected some, but not all of our wind measurements. Data reported here supersede those reported in a retracted paper (Ren, Hall, et al., 2018); see section S1 of the supporting information (SI) (Conley et al., 2014; Healey et al., 1998; Mueller & Wagner, 2006).

Mixing ratios of CH_4, CO_2, CO, and water vapor were measured with a Picarro analyzer (Model G2401-m, Picarro Inc., Santa Clara, CA) at a frequency of 0.5 Hz. Ambient air from the nose of the aircraft was pulled through a rear-facing PFA Teflon tube (O.D. = 0.95 cm and I.D. = 0.64 cm) at a total flow rate of 10 L/min (equivalent to a 0.7-s residence time in the sample line) using a diaphragm pump installed at the end of the sample line. The Picarro analyzer was connected to the sample line via a T-connector, pumping air continuously through the analyzer at a sampling flow rate of 0.40 standard L/min. During each flight experiment, 5–6 stainless steel canisters were used to acquire whole air samples analyzed at the Maryland Department of Environment's Air Toxics and Photochemical Assessment Monitoring Station (PAMS) Analytical Laboratory via gas chromatography with flame ionization detection (GC-FID). Other trace gas and particulate matter analyzers installed on the aircraft have been used in the past; additional details regarding current and previous measurement methodologies have been documented in previous publications (Brent et al., 2013; Hains et al., 2008; He et al., 2014, 2016; Ren, Salmon, et al., 2018; Taubman et al., 2006).

For the flights over the Marcellus Shale, the Picarro analyzer was calibrated for CH_4, CO_2, and CO both on the ground and during flight with analytical standards certified at the National Institute of Standards and Technology (NIST). The Picarro analyzer has measurement precisions of 0.02 parts per million by volume (ppmv) for CO_2, 0.2 ppbv for CH_4, and 4.2 ppbv for CO (standard deviations (1σ) of 0.5 Hz data over 5 min). The accuracies are estimated to be about 0.2 ppmv for CO_2, 2 ppbv for CH_4, and 10 ppbv for CO.

2.2. Flight Experiments

The UMD Cessna 402B aircraft was used to perform three mass balance flight experiments over the Marcellus Shale region in southwestern Pennsylvania and northern West Virginia on 25 and 29 August and 14 September 2015 (Figure 2). In each mass balance experiment, multiple vertical profiles and horizontal transects were flown upwind (generally to the west) and downwind (generally to the east) of natural gas

Table 1
A Survey of Estimates for Methane Emissions From Oil and Natural Gas Production Operations

Emission rate as % of NG production	Region	Method	Reference
17%	Los Angeles Basin, California	Aircraft measurements and emissions inventory	Peischl et al. (2013)
~12%	Eagle Ford, Texas	Remote sensing	Schneising et al. (2014), Howarth (2015)
10.1 ± 7.3%[a]	Bakken, North Dakota	Remote sensing	Schneising et al. (2014), Peischl et al. (2016)
2.8 – 17.3%	*Southwestern Pennsylvania*	*Aircraft mass balance*	Caulton et al. (2014)
6.2 – 11.7%	Uintah, Utah	Aircraft mass balance	Karion et al. (2013)
4.2 – 8.4%	Bakken, North Dakota	Aircraft mass balance	Peischl et al. (2016)
3.6% – 7.9%	US National	Estimates based on emission estimates from EPA and GAO reports	Howarth et al. (2011)
5.4 ± 2.0%	Bakken, North Dakota	Aircraft mass balance	Peischl et al. (2018)
2.3 – 7.7%	Northeastern Colorado	Ground level ambient tall tower and mobile sampling	Pétron et al. (2012)
3.2 ± 1.1%	Eagle Ford East, Texas	Aircraft mass balance	Peischl et al. (2018)
2.3%[b]	US National	Ground-based facility-scale measurements	Alvarez et al. (2018)
2.1 ± 0.9%	Denver Basin, Colorado	Aircraft mass balance	Peischl et al. (2018)
2.0 ± 0.6%	Eagle Ford West, Texas	Aircraft mass balance	Peischl et al. (2018)
1.3 –1.9%	Barnett, Texas	Aircraft mass balance	Karion et al. (2015)
1.5 ± 1.0%	Barnett, Texas	Aircraft mass balance	Peischl et al. (2018)
1.42%	U.S. national	Source sampling	Kirchgessner et al. (1997)
1.35%	*Pennsylvania and West Virginia*	*Ground facility-level source sampling*	Omara et al. (2016)
1.2%[c]	U.S. National	U.S. EPA GHGI 2015 and U.S. EIA U.S. total natural gas production in 2015	U.S. EPA (2018) U.S. EIA (2018a)
1.1% (0 – 3.5%)	*Southwestern Pennsylvania and northern West Virginia*	*Aircraft mass balance*	*This work*
1.0 ± 0.5%	Haynesville, Louisiana	Aircraft mass balance	Peischl et al. (2018)
0.47%	U.S. National	Ground source sampling at gathering and processing facilities	Marchese et al. (2015)
0.42%	U.S. National	Source sampling and national emission inventory estimates	Allen et al. (2013)
0.08 – 0.72%	*Northeastern Pennsylvania*	*Aircraft mass balance*	Barkley et al. (2017)
0.18 – 0.41%	*Northeastern Pennsylvania*	*Aircraft mass balance*	Peischl et al. (2015)

Note. Studies are listed in approximate order from high to low emission rates. Studies in italic are those conducted in the Marcellus Shale region. Satellite-based measurements using SCIAMACHY (Schneising et al., 2014) were more reliable for the Bakken and Eagle Ford plays, where the emission rate was estimated to be about 10% (3–17%) of total energy content, than for the Marcellus. EPA= Environmental Protection Agency; EIA = Energy Information Administration.
[a]The Bakken value estimated by Peischl et al. (2016) by converting back from percent total energy content losses is 39%. [b]The percentage is 1.9% if only production, gathering, and processing are included (Alvarez et al., 2018). [c]This emission rate is calculated from the total CH_4 emissions (6.65 million tons) from the natural gas system in the U.S. GHG inventory for 2015 (U.S. EPA, 2018) divided by the U.S. total natural gas production (932 billion m^3) in 2015 (U.S. Energy Information Administration (EIA), 2018a; U.S. Energy Information Administration (EIA), 2018b). This percentage is 0.87% if only production, gathering, and processing are included (U.S. EPA, 2018).

operations, roughly perpendicular to the wind direction. The enhancement in CH_4 concentration relative to background was captured. Flights over the Marcellus Shale region usually started at approximately noon to minimize planetary boundary layer (PBL) growth throughout the duration of the experiments. Typically, one upwind transect and three downwind transects were conducted, during times when the PBL height was approximately constant. Each of three mass balance experiments consisted of two flights as refueling was necessary. Usually, the upwind transect was accomplished at the beginning of the first flight and the downwind transects were completed at the end of the first flight and in the second flight after the airplane had been refueled.

We defined a 77-km × 55-km rectangle as our surveyed area with coordinates for the four corners of (39°36′N, 80°36′W), (39°36′N, 79°48′W), (40°06′N, 80°42′W), and (40°06′N, 79°48′W). This area covers most of our flight tracks near the Marcellus Shale and represents the majority of natural gas production in the region where Pennsylvania, West Virginia, and Ohio come together (Figure 2). The natural gas production from this surveyed area was 2.48×10^9 m^3 in September 2015, representing 19% of total Marcellus Shale natural gas production and 3.2% of total U.S. natural gas production in September 2015.

Table 2
UMD Cessna 402B Research Aircraft Instrumentation

Variable	Method	Sample frequency
Position	GPS	1 s
Meteorology (T, RH, P, 2-D Wind)	Thermistor, hygristor, capacitance manometer, Garmin G600 system	1 s
Greenhouse gases CO_2/CH_4/CO/H_2O	Cavity ring down spectroscopy Picarro Model G2401-m	2 s
Ozone (O_3)	UV absorption	5 s
Sulfur dioxide (SO_2)	Pulsed fluorescence	5 s
Nitrogen dioxide (NO_2)	Cavity enhanced absorption spectroscopy, Los Gatos	10 s
VOCs	Grab canisters/GC-FID	5–6 per flight
Aerosol scattering, b_{scat} (450, 550, 700 nm)	Nephelometer	1 s
Aerosol absorption, b_{abs} (565 nm)	Particle soot absorption photometer (PSAP)	1 min
Black carbon (370, 470, 520, 590, 660, 880, 950 nm)	Aethalometer, 7 wavelengths	2 min

Note. GPS = Global Positioning System; UV = ultraviolet; VOCs = volatile organic compounds; GC-FID = gas chromatography with flame ionization detection.

2.3. Mass Balance Approach

A mass balance approach was used to quantify the CH_4 emissions from the surveyed area. This method relies on the assumptions of consistent emission rates and stationary PBL depth during a given experiment period and is robust for the estimate of total emissions from a given area (Cambaliza et al., 2014; White et al., 1976). Wind carrying background concentrations of CH_4 blows over the Marcellus Shale area, where it picks up CH_4 emissions (Figure 3). Horizontal transects are flown perpendicular to the prevailing wind direction downwind of the natural gas extraction area, and enhancements in CH_4 above background are intercepted and quantified. The CH_4 emission rate from the area can be calculated using equation (1) (Ren, Salmon, et al., 2018; White et al., 1976):

$$\text{Emission Rate} = \int_0^z \int_{-x}^{+x} \left([\mathrm{C}]_{ij} - \overline{[\mathrm{C}]}_b \right) \times U_{\perp ij} \, \mathrm{d}x \mathrm{d}z \tag{1}$$

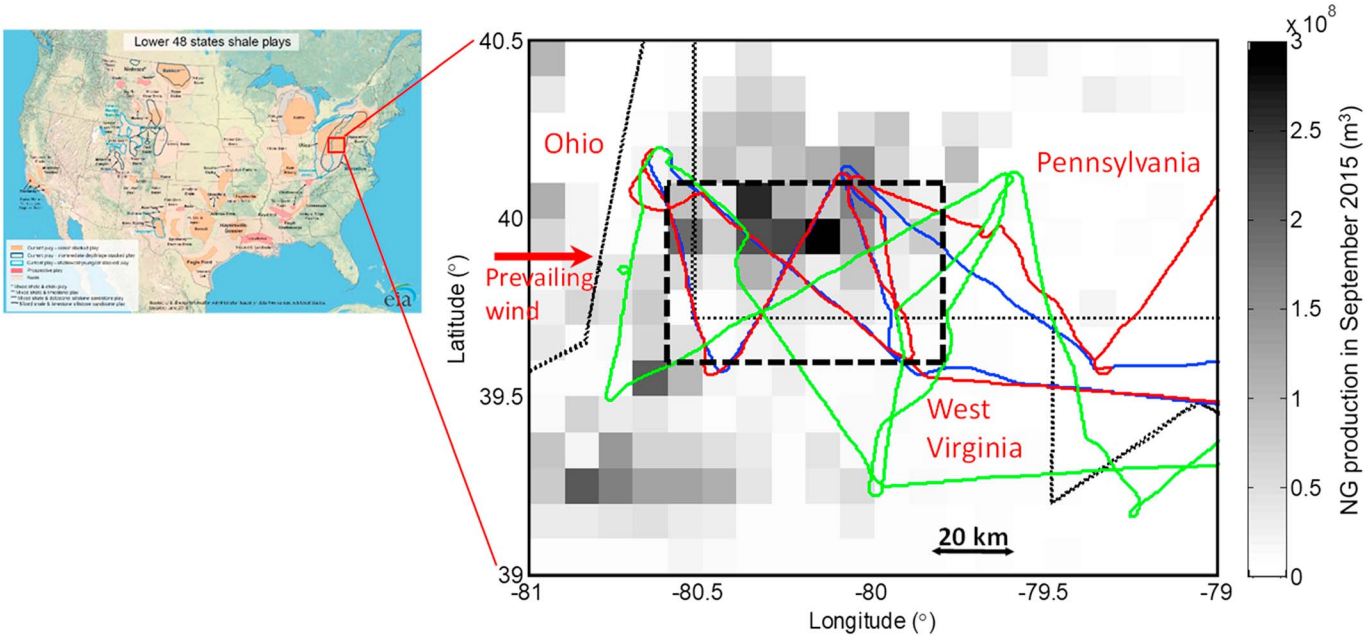

Figure 2. Location of the surveyed area and flight paths (blue, red, and green) for three mass balance experiments conducted on 25 and 29 August and 14 September 2015, respectively. The black dashed rectangle represents a 77-km × 55-km area that covers the surveyed O&NG operation region. Monthly Marcellus Shale natural gas production is summed into 0.1° × 0.1° grids in Pennsylvania (data obtained from www.paoilandgasreporting.state.pa.us), West Virginia (data obtained from http://www.dep.wv.gov/oil-and-gas/databaseinfo/Pages/default.aspx), and Ohio (data obtained from http://oilandgas.ohiodnr.gov/production) for September 2015.

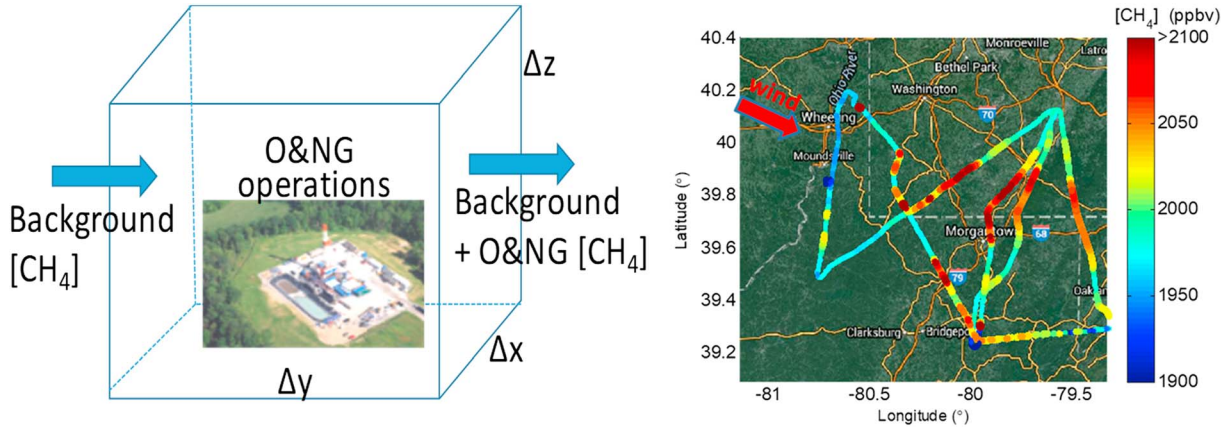

Figure 3. (left) The conceptual model of a mass balance approach to quantify methane emissions from an O&NG operation area. (right) Methane mixing ratios measured along the flight track on 14 September 2015. An enhancement of CH_4 was clearly observed along the downwind transects.

where, $[C]_{ij}$ is the concentration of CH_4 at a downwind location (x_i, z_j); i and j are the indexes for horizontal and vertical distances, respectively; $[C]_b$ is the background concentration detected upwind; $U_{\perp ij}$ is the perpendicular wind speed at a downwind location of (x_i, z_j); $[-x, +x]$ defines the horizontal width of the plume from the surveyed area; and $[0, z]$ defines the height of the PBL. Emission rates for individual downwind transects were calculated and then averaged to come up with an emission rate for a given flight experiment.

Several sources of uncertainty associated with parameters affect the mass balance approach (equation (1)). We estimate the uncertainties (2σ) in the measurements used in equation (1) to be: ±18% for the enhancement of the CH_4 mixing ratio ($[C] - [C]_b$) measured downwind, ±20% for perpendicular wind speed ($U_\perp$), ±15% for the PBL height (Δz), ±6% for the plume width (Δx), and ±10% for the variation in the fluxes at different altitudes. The combined uncertainty in CH_4 emission rate estimation using equation (1) is about ±33%. A detailed uncertainty analysis for the estimation of CH_4 emission rate can be found in Ren, Salmon, et al. (2018). This uncertainty is slightly larger than the averaged uncertainty (±31%, 2σ) estimated for the mass balance approach during the INFLUX study (Cambaliza et al., 2014), likely because of greater uncertainties in the wind fields and PBL height due to orographic effects (rolling hills) in our study area. Uncertainties in emissions of CH_4 from coalmining and other non-O&NG sources contribute additional uncertainties to the range of possible CH_4 emission rates inferred from active O&NG operations (see Table 4).

2.4. Weather Research and Forecasting Model

To compare measured and modeled winds (section S1 of the SI), the Weather Research and Forecasting (WRF) model was used in this study to calculate modeled winds. The model was composed of a 9-km grid with a one-way nested 3-km grid, each composed of 202 grid points and centered at the location of the flights used in this study. North American Regional Reanalysis (NARR) data were used to initialize the model for each flight day, and four-dimensional data assimilation were applied to allow for meteorological observations to nudge the model solutions in the final analysis. Additional details on the model setup and parameter selection can be found in Barkley et al. (2017). In the comparison of the WRF simulation with the aircraft data, model output was selected from the 3-km domain closest in space to each observation at the nearest hour interval. The results of this comparison are provided in section S1.3 of the SI.

2.5. HYSPLIT Back Trajectory Model

Six-hour back trajectory simulations were conducted with the starting locations and times initialized along the flight tracks. The back trajectories are used to illustrate the transport history associated with the sampled air parcels. The back trajectories were simulated using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT; Stein et al., 2015) and meteorological data from the North American Mesoscale (NAM) Forecast System model (Janjic, 2003; Janjic et al., 2001), with a horizontal resolution of 12 km, 26 vertical levels up to 20,000 m (including nine levels under 2,000 m), and a temporal resolution of 3 hr. In addition, the HYSPLIT model was also run with two other sources of meteorological data,

including the High-Resolution Rapid Refresh (3-km resolution) forecast model and the NARR (32-km resolution) to derive model wind speed and wind direction (section S1.3 of the SI).

2.6. Other Data Sets Used in This Study

Well locations and natural gas production data for Pennsylvania were obtained from the Pennsylvania Department of Environmental Protection, PDEP (2018), for West Virginia from the West Virginia Department of Environmental Protection, WVDEP (2018), and for Ohio from the Ohio Department of Natural Resources, OHDNR (2018). Locations of known point sources of CH_4, including coal mines and landfills in the surveyed area, were obtained from the 2015 U.S. Environmental Protection Agency (EPA) Greenhouse Gas Reporting Program (GHGRP) website (http://ghgdata.epa.gov/ghgp/main.do, accessed July 2018). As shown in Figure 1, total shale gas and natural gas production data were obtained from the EIA Website. The average natural gas chemical composition from the surveyed area was determined from a 2014 U.S. Geological Survey (USGS) database (https://pubs.usgs.gov/of/2014/1207, accessed July 2016) for wells located within the study region. An average CH_4 molar fraction of 0.877 $\pm$ 0.084 in natural gas was derived from this study with 80 samples collected in the survey area (Román-Colón & Ruppert, 2014).

3. Results

3.1. Aircraft Observations

Observations from a typical mass balance experiment shown in Figure 4 include one upwind transect followed by three downwind transects, all flown at an airspeed of about 70 m/s. The mean mixing ratio observed in the upwind transects was used as CH_4 background for the air parcels entering the surveyed area. Note that the background is consistent with the CH_4 levels at the edges of the downwind transect. CH_4 enhancements in the downwind transects were calculated from the downwind CH_4 mixing ratios after subtracting the CH_4 background. For the flight experiment on 29 August 2018, CH_4 in the PBL during the first flight was not well mixed, so only two downwind transects in the second flight were used to calculate the CH_4 emission rate. For this flight the CH_4 background was determined as the mean CH_4 level observed during the upwind transect in the residual layer (section S7 of the SI).

En route profiles were conducted along both upwind and downwind transects to characterize the vertical variation of CH_4 mixing ratio. The PBL height was generally the same in the upwind and downwind transects. Figure 5 shows a typical vertical profile of CH_4 and CO_2, potential temperature, and water vapor within the PBL. Air within the PBL was generally well mixed. On ascent, the PBL height (i.e., the dashed line in Figure 5) is determined to be the altitude where the CH_4 mixing ratio reaches its free-tropospheric background level (~1,890 ppbv), the water vapor mixing ratio drops significantly, and the potential temperature begins to increase rapidly.

The HYSPLIT back trajectories shown in Figure 6 demonstrate an example of a plume from the surveyed Marcellus Shale area captured on 14 September 2015. Three downwind transects were performed in each mass balance flight experiment and they illustrate the repeatability and relatively uniformity of CH_4 mixing ratios observed within the PBL, at different times and locations.

3.2. Methane Emission Rate Estimate

Highly spatially resolved observations of CH_4 and wind during the flight experiments allow us to calculate mass emission rates of CH_4 from the surveyed area. Using the measurements in the three mass balance experiments, the mean and standard deviation of the CH_4 emission rate (Table 3) were determined to be 21.2 $\pm$ 2.0 kg CH_4/s (or 0.668 $\pm$ 0.063 Tg CH_4/year) from the surveyed area using equation (1). This emission rate in the surveyed area in 2015 is about 2.3 times the CH_4 emission rate (9.3 kg CH_4/s) in the Maasakkers annual CH_4 inventory for 2012 (Maasakkers et al., 2016). For each mass balance experiment, we analyzed every transect separately assuming CH_4 was well mixed within the PBL, and then averaged the emission rates derived from three downwind transects. We conducted two additional mass balance flight experiments in summer 2016. The mean CH_4 emission rate was 29.0 $\pm$ 17.0 kg CH_4/s in 2016, higher than that found in 2015 by a factor of 1.37, even though the drilled and completed wells in 2016 were half of their 2015 values (http://www.eia.gov/petroleum/drilling/#tabs-summary-3). The details of these additional flights are

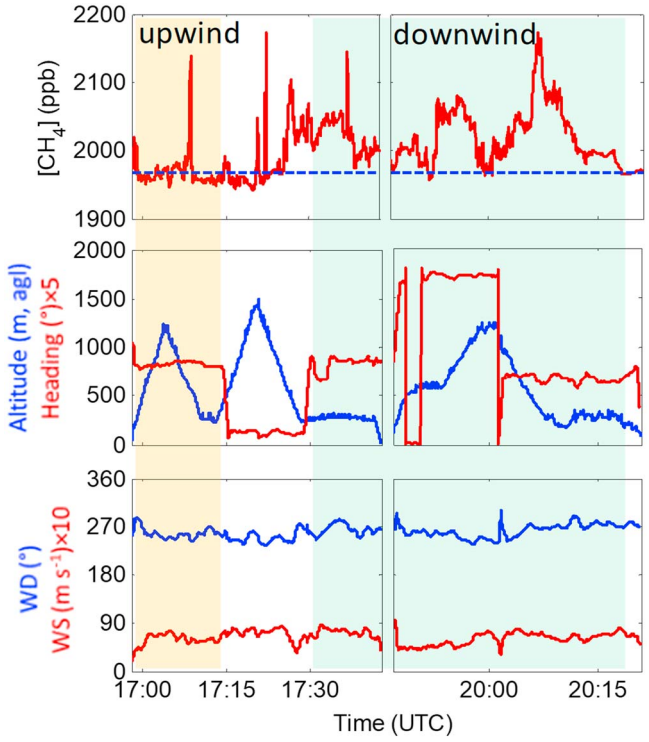

Figure 4. Time series of CH_4 mixing ratio (top), altitude above ground level (agl) and aircraft heading (middle), and wind direction (WD) and wind speed (WS) (bottom) measured in the upwind transect (yellow shaded) and downwind plumes (green shaded) during a mass balance flight experiment on 25 August 2015. The blue dashed line in the top two panels indicates the average mixing ratio of CH_4 in the upwind transect. UTC is Universal Time Coordinated.

provided in section S5 of the SI. These results obtained with the new flights provide reinforcement of the CH_4 emission estimate for this area.

3.3. Estimate of Methane Emission Rate From Oil and Natural Gas Operations

Here we relate the CH_4 emission rate found from the three mass balance experiments (Table 3) to an emission rate as percentage of natural gas production. As described in section 2, we must account for emissions of atmospheric CH_4 from other sources in the survey region, for example, coal mining, natural gas distribution pipes, cattle (enteric fermentation), and landfills. Table 4 relates the observed emission rates on the three flight days to these other sources. Data from the U.S. EPA GHGRP (http://ghgdata.epa.gov/ghgp/main.do, 2015) were used to derive the CH_4 emissions from coal mines and landfills in the area. The GHGRP only reports underground coal mines and does not report emissions from surface or abandoned coal mines. We estimated CH_4 emissions from surface and abandoned coal mines in the surveyed area to be approximately 0.05 and 0.35 kg CH_4/s, respectively, based on a gridded national inventory for US CH_4 emissions (Maasakkers et al., 2016). We have included CH_4 emissions from surface and abandoned coal mines in the total CH_4 emissions from coal mining in Table 4. Losses from natural gas distribution and delivery can also be substantial (Jackson et al., 2014; Phillips et al., 2013; PHMSA, 2015, 2016) and must be considered when evaluating the net climate impact of the natural gas system. The estimates of CH_4 emissions from natural gas distribution pipes and cattle (enteric fermentation) are described in the SI. Note that CH_4 emissions from several other sources, such as animal manure, power plants, refineries, and metal/paper production, are not included in Table 4, because they are either negligible or do not exist in the surveyed area.

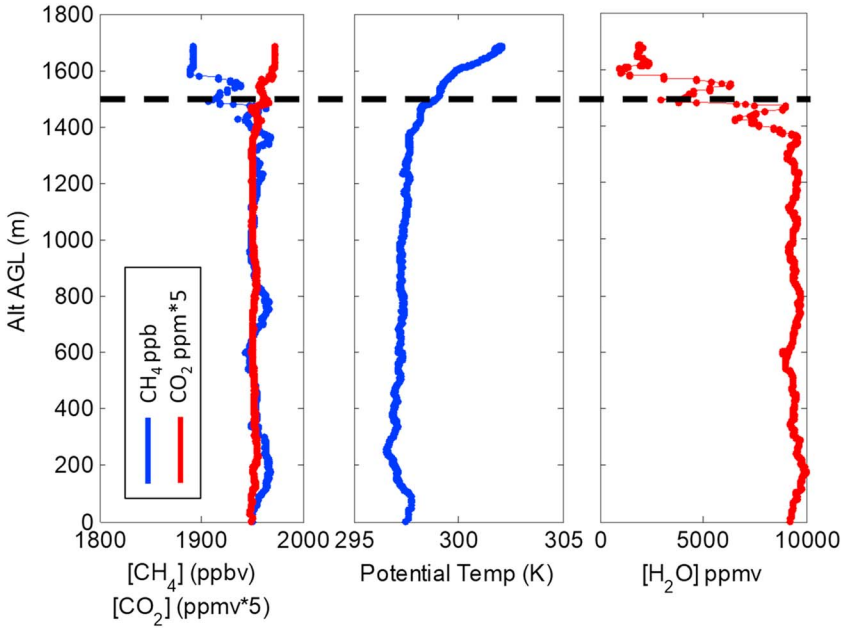

Figure 5. $[CH_4]$, $[CO_2]$, potential temperature, and H_2O mixing ratio during a vertical profile in a flight experiment conducted on 14 September 2015. The dashed line indicates the top of the planetary boundary layer (PBL).

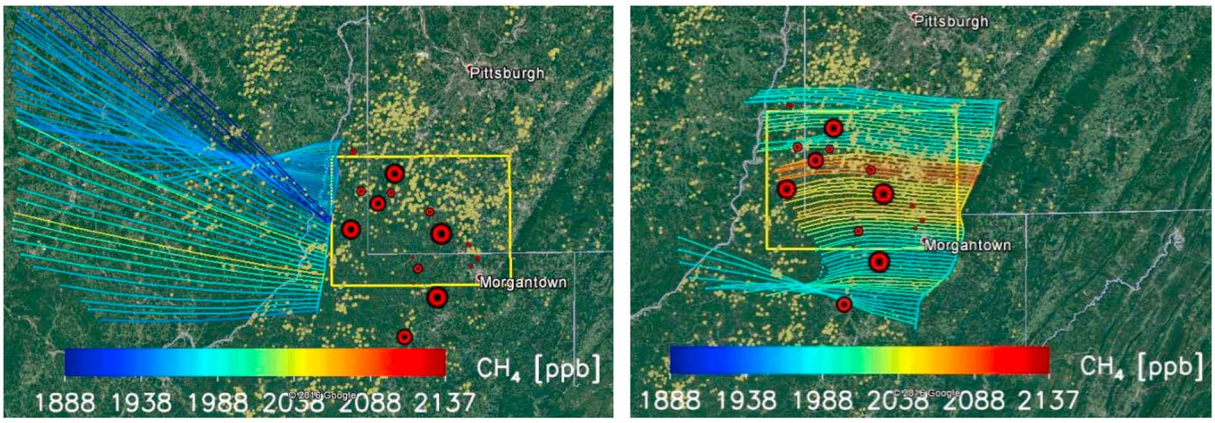

Figure 6. Upwind (left) and downwind (right) transects and HYSPLIT 6-hr back trajectories initiated from the flight transects, at 20-s intervals. The transects are colored with in situ measured CH_4 mixing ratios and each back trajectory has the same color as its starting point on the transect. The colored lines where back trajectories start represent upwind (west) and downwind (east) transects of the aircraft. The yellow rectangle represents the designated survey area. The yellow dots are the locations of shale gas wells. The red dots show the locations of major coal mines in the region with the diameter of each dot approximately proportional to the CH_4 emission from each coal mine in Environmental Protection Agency's Greenhouse Gas Reporting Program data set.

The column labeled O&NG CH_4 emission rate in Table 4 is the difference between the observed total CH_4 emission rate and the four other CH_4 emission sources. Note that the higher upper end uncertainties are the final positive uncertainties in the CH_4 emissions from the oil and natural gas operations when all other emission sources are expressed with their most negative uncertainties so that the upper limit CH_4 emissions from O&NG operations reach a maximum. The lower end uncertainties are determined assuming all other emission sources have their most positive uncertainties, which results in a physically unreasonable result that O&NG operations are a CH_4 sink. As a result, the lowest CH_4 emission rate is set to zero (rather than negative). Our estimate for mean CH_4 emissions of 4.4–8.2 kg/s from the O&NG operations in the surveyed area is similar to the 2015 EPA GHG Inventory estimate of 4.8 kg CH_4/s from natural gas systems in the surveyed area (Tables 3–54 of the EPA GHG inventory for 2015; U.S. Environmental Protection Agency, EPA, 2018), assuming an emission rate of 0.87% for natural gas production, gathering, and processing (Table 1). The mean observed CH_4 emission rate (5.98 ± 2.0 kg CH_4/s) from the O&NG operations in the surveyed in 2015 is a factor of 1.7 greater than that (3.44 kg CH_4/s) in the US CH_4 inventory for 2012 (Maasakkers et al., 2016), but total natural gas production from the Marcellus Shale has increased by a factor of 2.3 from 2012 to 2015, which likely explains the higher CH_4 emission rate found in 2015.

With the derived CH_4 emissions from the surveyed area, the CH_4 emission rate from O&NG operations is estimated to be 0.78% to 1.50% of production, based on the total natural gas production and CH_4 emissions from sectors excluding O&NG operations in this area (Table 4). This emission rate spans the estimated range on the three flight experiments conducted in 2015. As stated in section 2.3, besides the 2σ uncertainty of 33% in the mass balance approach, additional errors, including the one associated with CH_4 emissions from coal mining, arise from uncertainties in other sources shown in Table 4. Using these uncertainties, a propagated error of 9.34 kg/s or 44% is estimated for the total CH_4 emission rate, so we estimate the mean CH_4 emission rate to be 1.1% of production, with a lower limit of 0% and an upper limit of 3.5% estimated from the individual flight experiments (Table 4). For the two flight experiments in August 2016, we estimated CH_4 emission

Table 3
Mean Measurements and Their Standard Deviations (2σ) Along the Transects Used in Equation (1) to Derive CH_4 Emission Rates (E.R.) for Three Mass Balance Experiments Over the Marcellus Shale in Southwestern Pennsylvania and Northern West Virginia

Flight date	$[CH_4]_{upwind}$ (ppbv)	$[CH_4]_{downwind}$ (ppbv)	WS (m/s)	WD (deg)	PBL height (m AGL)	CH_4 E.R. (kg/s)
8/25/2015	1,967 ± 44	2,023 ± 78	6.4 ± 2.2	263 ± 22	2,200 ± 330	23.43 ± 7.74
8/29/2015	2,016 ± 32	2,119 ± 100	3.2 ± 1.4	214 ± 26	1,950 ± 290	20.52 ± 6.77
9/14/2015	1,960 ± 56	2,032 ± 74	5.7 ± 2.0	281 ± 16	1,500 ± 220	19.65 ± 6.48

Note. Error bars are the standard deviations of measured parameters in the downwind transects, except for the last column where a 33% uncertainty is used for the observed total CH_4 emission rate. Dates are formatted as month/day/year.

Table 4
Methane Emission Rates From Different Sources and Derived Emission Rate as Fraction of Total Natural Gas Production in the Surveyed Marcellus Shale Area in Southwestern Pennsylvania and Northern West Virginia

Flight date	Obs. CH_4 E.R.[a] (kg/s)	Coal mining CH_4 E.R.[a] (kg/s)	NG distrib. CH_4 E.R.[a] (kg/s)	Enteric ferment. CH_4 E.R.[a] (kg/s)	Landfills CH_4 E.R.[a] (kg/s)	O&NG CH_4 E.R. (kg/s)	NG prod[b] (m^3/s)	CH_4 emission rate (% of NG prod.)
8/25/2015	23.44 ± 7.74	15.04 ± 2.26	0.09 ± 0.03	0.06 ± 0.01	0.03 ± 0.02	$8.21^{+10.76}_{-8.21}$	918.1	$1.50^{+1.97}_{-1.50}$%
8/29/2015	20.52 ± 6.77	15.04 ± 2.26	0.09 ± 0.03	0.06 ± 0.01	0.03 ± 0.02	$5.30^{+9.71}_{-5.30}$	918.1	$0.97^{+1.78}_{-0.97}$%
9/14/2015	19.66 ± 6.48	15.04 ± 2.26	0.09 ± 0.03	0.06 ± 0.01	0.03 ± 0.02	$4.43^{+9.40}_{-4.43}$	956.5	$0.78^{+1.65}_{-0.78}$%

Note. Dates are formatted as month/day/year.
[a]E.R. = emission rate. A 33% uncertainty is used for the observed total CH_4 emission rate (Ren, Salmon, et al., 2018). As the uncertainties in Table 1 of Maasakkers et al. (2016), the following uncertainties (2σ) are estimated in the CH_4 emission rates: ±15% for coal mining, ±30% for NG distribution, ±18% for enteric fermentation, and ±64% for landfills. The actual uncertainties for the CH_4 emissions from these sectors may vary from the uncertainties used here.
[b]The mean natural gas production within the surveyed area in August and September 2015 at 1 atm and 288.7 K. A CH_4 molar fraction of 0.877 ± 0.084 in natural gas (Román-Colón & Ruppert, 2014) in this area is used to derive total amount of CH_4 in natural gas.

rates from O&NG operations to be 0.44% and 4.18% of production, which is a broader range relative to the CH_4 emission rates obtained in three flight experiments in 2015 (Table S3).

3.4. Correlation Between Methane and Ethane/Propane

A strong correlation between CH_4 and C_2H_6 and a moderate correlation between CH_4 and propane (C_3H_8) were observed in the 16 VOC samples collected during the three flight experiments (Figure 7). These correlations strongly support that at least some of the CH_4 enhancements observed during the flights are the result of emissions from O&NG operations. Similar good correlations with these compounds have been found in previous studies in other O&NG operation areas (e.g., Karion et al., 2013; Peischl et al., 2015, 2016; Pétron et al., 2012; Smith et al., 2015). In a survey done by USGS in 2014, 80 samples were collected from different wells located within our study region (Román-Colón & Ruppert, 2014). The mean molar composition of natural gas was found to be 87.7% CH_4, 5.88% C_2H_6, 2.02% C_3H_8, 2.40% nitrogen, and 2.0% other compounds, implying an average ethane-to-methane molar ratio of 6.7% for these well samples in the surveyed area. This ratio is greater than the slope (2.3%) of the C_2H_6 versus CH_4 correlation plot in Figure 7 derived from our VOC canister samples (hereafter, C_2H_6-to-CH_4 ratio), implying that the O&NG CH_4 is diluted by other sources of CH_4 that do not contain C_2H_6.

Previous studies have found that coal mines do not emit significant C_2H_6. As a result, the C_2H_6-to-CH_4 ratio in emissions from coal mines is much lower than found for emissions from natural gas operations (Kim, 1973). The numerical estimates in Table 4 suggest that coal mining and O&NG operations are the two

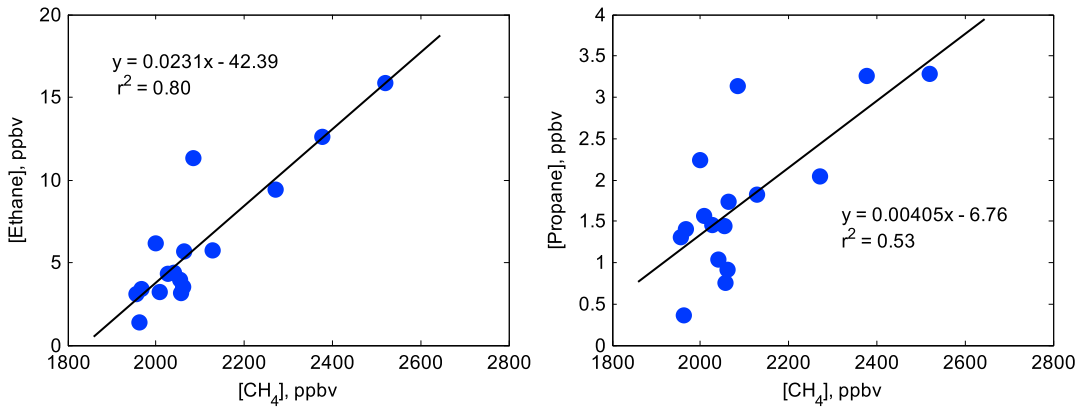

Figure 7. Ethane (C_2H_6) versus CH_4 (left) and propane (C_3H_8) versus CH_4 (right) over the surveyed Marcellus Shale area in southwestern Pennsylvania and northern West Virginia in August and September 2015. The solid lines show the least squares linear regression.

dominant CH_4 emission sources in the surveyed region. We are able to use the C_2H_6-to-CH_4 ratio observed in ambient air and the ratio in the natural gas (6.7%) and coal (0%) to infer the relative contributions to methane emissions from these two sources.

The C_2H_6-to-CH_4 ratio of 2.3% for ambient air implies that coal mining accounts for 66% of the total CH_4 emissions and O&NG operations account for the remaining 34%, resulting in a CH_4 emission rate of 1.3%. This emission rate falls within the range between the lower and upper limits of the emission rate (0–3.5%) that we had estimated based on the aircraft-based mass balance experiments and bottom-up CH_4 emissions from coal mining. For an extreme assumption of zero emissions of CH_4 from coal mining, the inferred CH_4 emission rate from natural gas production would be 3.8%, which is slightly greater than the upper limit of 3.5% based on mass balance (Table 4). However, there is considerable variability in the observed C_2H_6-to-CH_4 ratio on particular flight days, and thus there is uncertainty in the average ratio due to the limited number of canisters collected for VOC measurements in each flight experiment as shown in Figure S6. The variability may occur because emissions from coal mining and from O&NG operations are not always well mixed at the locations where the VOC samples were collected. In addition, variability of background ethane and methane concentrations can result in different slopes for individual flight days. The quantitative use of the C_2H_6-to-CH_4 ratio would benefit from a larger density of measurements.

In support of the idea that O&NG CH_4 emissions are diluted by coal-bed CH_4, it is known that there are significant emissions of natural gas from coal mines in the surveyed area. According to U.S. EPA's GHGRP, the U.S. CH_4 national inventory for 2012 (Maasakkers et al., 2016), and observed total CH_4 emission rate, CH_4 emissions from the coal mines account for about 71% of the total CH_4 emissions from our surveyed area (Table 4). A ground-based survey in the southwestern Marcellus indicated substantially more CH_4 from O&NG operations than from coalbed methane wells (Johnson & Heltzel, 2016). Caulton et al. (2014) also identified several shale well pads in our surveyed area with high CH_4 emissions. These pads were identified as in the drilling phase, a preproduction stage previously assumed to have little or no CH_4 emissions. These wells accounted for only 1% of the wells in their study area, but had 6–9% of the CH_4 emissions from all sources (Caulton et al., 2014). Drilling through coalbed layers would be associated with little emissions of C_2H_6, but high emissions of CH_4. Townsend-Small et al. (2016) measured CH_4 stable isotopes from abandoned oil and gas wells in Ohio, Colorado and Utah, and found that those wells emit both natural gas and coalbed CH_4. The O&NG wells in our surveyed area underlie coalbeds and have the potential for release of coalbed CH_4 (Lyon et al., 2015).

4. Discussion

The average CH_4 emission rate from the surveyed area (4,200 km^2) of the southwest Marcellus Shale was 21.2 ± 2.0 kg CH_4/s or 5.0 ± 0.5 g CH_4 km^{-2}/s. This emission rate is broadly consistent with the value of 2.0–14 g CH_4 km^{-2}/s reported by Caulton et al. (2014) for the same region, and larger than the values of 1.2 ± 0.6 g CH_4 km^{-2}/s reported by Swarthout et al. (2015) for the southwest Marcellus. Caulton et al. (2014) conducted nine flights in June 2012 and Swarthout et al. (2015) collected whole air samples throughout an 8,050-km^2 area surrounding Pittsburgh, PA, in June 2012. The CH_4 emission rate from our study is an order of magnitude larger than the emission rates we calculate to be 0.54 g CH_4 km^{-2}/s of Barkley et al. (2017) and 0.43 g CH_4 km^{-2}/s of Peischl et al. (2015), both obtained from the Marcellus Shale region in northeastern Pennsylvania. Observational aircraft studies are generally based upon a limited number of transects, two in the case of Peischl et al. (2015) and eight in our study.

Our mean CH_4 emission rate as a percentage of natural gas production was estimated to be 1.1%. This emission percentage is greater than the emission rate of 0.18–0.41% by Peischl et al. (2015) and 0.08–0.72% by Barkley et al. (2017) estimated for the Marcellus Shale region in northeastern Pennsylvania, but is similar in magnitude to the loss rates estimated by a number of other studies (Table 1), including a study that measured facility-level CH_4 emissions in southwestern Pennsylvania and northern West Virginia with a mean emission rate of 1.35% (a median emission rate of 11% for conventional wells and 0.13% for unconventional wells; Omara et al., 2016). One possible reason for the different emission rates between southwestern and northeastern Pennsylvania is that most wells in northeastern Pennsylvania are newer and unconventional (i.e., hydraulic fractured and horizontally drilled), while there are many older and conventional wells in

southwestern Pennsylvania and northern West Virginia. These old conventional wells tend to have higher emission rates according to a recent study conducted in the same area (Omara et al., 2016). In addition, compared to northern Pennsylvania the O&NG extracted from southwestern Pennsylvania is wetter, that is, containing more nonmethane hydrocarbons, which requires more separation and gas processing and can lead to more CH_4 losses, for example, from tank venting.

An emission rate of 2.4% for a 20-year time horizon based on the global warming potential of CH_4 is the climate benefit limit, beyond which natural gas becomes worse with respect to climate forcing than coal. The calculation of this break-even point, described in section S4 of the SI, also includes the emission of CH_4 from coal mining. Because the methane lifetime in the atmosphere is about 10 years (Voulgarakis et al., 2013), a 20-year (or a few decades) time horizon should be preferred to consider in terms of the global warming potential of CH_4. Given our measured emission rate of 1.1% for the Marcellus Shale in southwestern Pennsylvania and northern West Virginia, the use of natural gas rather than coal for combustion will result in a smaller climate impact than coal over the next few decades. This calculation assumes that there are no significant emissions for natural gas transported from this region to power plants. The rates of CH_4 emissions listed in Table 1 are currently the subject of intense study and debate (Allen et al., 2013; Alvarez et al., 2012; Brandt et al., 2014; Cathles, 2012; Howard et al., 2015; Howarth, 2014, 2015; Howarth et al., 2011). For example, Howard (2015a) and Howarth (2015) have argued that Allen et al. (2013) might have underestimated CH_4 emissions and hence obtained an erroneously low CH_4 emission rate. The validity of the study by Allen et al. (2013) is still an ongoing point of contention (Alvarez et al., 2016, 2018; Guglielmi, 2018). It is noteworthy that there is considerable temporal variability in CH_4 emission rates in shale gas production regions, which could lead to variability in these estimates (Lavoie et al., 2017). Given the current low cost of natural gas, a purely economic driver to reduce the atmospheric release of CH_4 does not exist. Thus, existing regulatory approaches must be maintained in order for energy derived by the combustion of natural gas to remain a net climate benefit, relative to energy derived from coal combustion.

Initial regulations have been implemented in the United States in stages starting in 2012, focusing on reducing the emissions of VOCs (U.S. EPA, 2012). For example, the dominant source of VOC emissions during well development is the completion-venting step of the hydraulic fracturing (or fracking) process, in which the fracking fluids and solid-phase proppants are brought to the surface. Roy et al. (2014) estimated these emissions to be 3.8 and 21 tons of VOC per dry or wet well drilled in the Marcellus Shale, respectively (Roy et al., 2014). Beginning in October 2012, operators were required to capture or flare the gases, and from January 2015 onward, only capturing was allowed. However, wells considered exploratory or wells to determine the boundary of a natural gas field are exempt from these regulations.

The CH_4 leak rate per unit of natural gas production may have been trending downward in recent years (Schwietzke et al., 2016; U.S. EPA, 2018; U.S. EIA, 2018a; Vinciguerra et al., 2015) due to the new regulations that affected onshore oil and gas production (U.S. EPA, 2012; Healey & Pergande, 2014) These regulations have likely contributed to the recent apparent leveling off of the C_2H_6-to-total nonmethane organic carbon ratio observed at the U.S. EPA's PAMS in Essex, Maryland (Figure 8) during 2012–2015 (Vinciguerra et al., 2015). In October 2013, continuous bleed pneumatic devices at production facilities were required to limit gas venting to 6 standard cubic feet per hour (~0.17 m^3/hr; U.S. EPA, 2012). While occurring in the 2013 calendar year, these reductions would likely not have been observable at the Essex monitoring station until 2014 because the PAMS measurements are only made during June through August. Gas production storage tanks with an expected VOC emission rate of 6 tons/year or more were required to reduce VOCs by 95% by April 2014 for tanks commissioned after April 2013, or by April 2015 for older storage tanks. In January 2015, the completion venting procedure (i.e., clearing fluid and debris from a well before production) required removal of VOC emissions through reduced emissions completion (REC) processing and could no longer be flared (U.S. EPA, 2015). In May 2016, the U.S. EPA issued a new set of clean air standards specifically limiting CH_4 emissions from new and modified sources in the oil and gas industry (U.S. EPA, 2016). The implementation of these newer regulations is expected to further reduce CH_4 and other air pollutants emitted from O&NG operations. Improvements in the natural gas delivery system and changes in ethane to methane ratios in natural gas delivered could also affect the trend in ethane at the Essex site.

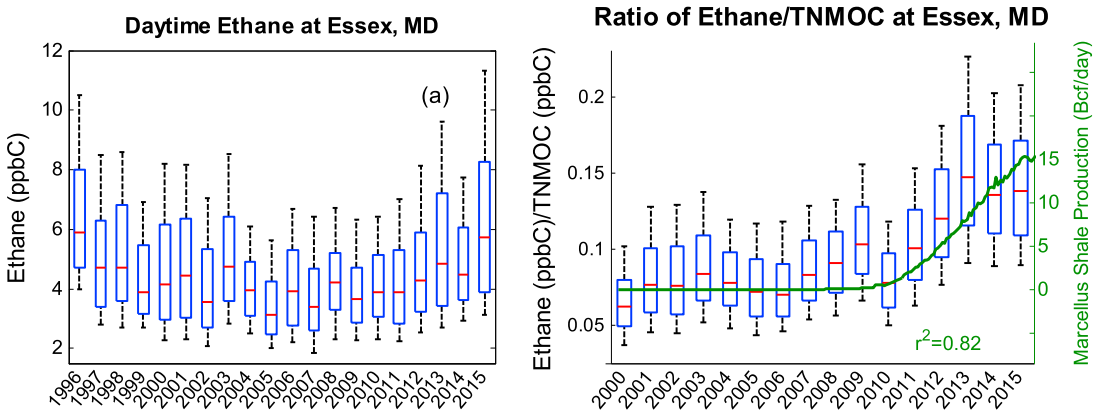

Figure 8. Hourly daytime ethane mixing ratio in units of parts per billion carbon (ppbC) (a) and the ratio of ethane to total nonmethane organic carbon (TNMOC) (b) observed at Essex, MD, shown by box and whisker plots. The box provides the 25th and 75th percentiles, with the median represented by the red bar, and the whiskers extend to the 10th and 90th percentiles. In addition, the natural gas production rates from the Marcellus Shale are shown in green in (b). A strong correlation of the C_2H_6 to TNMOC ratio versus the Marcellus Shale natural gas production was observed with an r^2 value of 0.82.

5. Conclusions

We conducted three flight-based mass balance experiments over the Marcellus Shale in southwestern Pennsylvania and northern West Virginia in August and September 2015. We calculate the mean emissions of CH_4 to the atmosphere, from the 77-km × 55-km surveyed area, to be 21.2 kg CH_4/s (or 0.668 Tg CH_4/year) with an overall uncertainty of ±33% in the mass balance approach, showing strong evidence of localized emissions of CH_4 from this region. Two additional flights conducted in the same area in 2016 indicated the mean emissions of CH_4 to be 29.0 kg CH_4/s (section S5).

Based on the total natural gas production and CH_4 emissions in the sectors other than O&NG operations, we estimate a mean CH_4 emission rate from the O&NG operations in our surveyed area to be 1.1% of the total natural gas production. Using the uncertainties in the mass balance approach and CH_4 emissions from sources other than O&NG, we estimate the lower limit as 0% and the upper limit as 3.5% (Table 4). This emission rate is broadly consistent with the results from several other recent studies based on atmospheric observations, including the U.S. EPA GHG inventory estimate for CH_4 emissions. Our best estimate of the CH_4 emission rate does not exceed the break-even point of 2.4% (based on the global warming potential of CH_4 over a 20-year time horizon), beyond which natural gas becomes worse with respect to climate forcing compared to coal. Our mean estimated emission rate indicates a climate impact of CH_4 combustion below that of coal, but the full range includes values above this point. Hence, the production of energy from CH_4 extracted from our surveyed area with current technologies is a climate benefit, over the next two decades, if our measured emission rate is representative of typical conditions for extraction in the Marcellus Shale and other shale gas basins. This conclusion is reversed if downstream leakage exceeds 1.3% of natural gas production or if the bulk of the CH_4 from coalbeds results from drilling for O&NG, or if the upper limit of our CH_4 emission rate (i.e., 3.5%) turns out to be close to the actual value. Although new regulations on the completion-venting step of the hydraulic fracturing appear to have improved emission rates, further actions are needed in order to reduce natural gas losses.

There appears to be a substantial source of CH_4 from processes in this Marcellus Shale area that contain little C_2H_6. Limited VOC measurements from canisters filled during these flights show that the observed C_2H_6-to-CH_4 ratio was 2.3%, which is smaller than the C_2H_6-to-CH_4 ratio of 6.7% in the natural gas samples at the wells for this region. The lower C_2H_6-to-CH_4 ratio in the atmosphere is likely due to the emissions of coalbed natural gas that contains little C_2H_6, emitted either directly from coal mines or from wells that drilled through coalbed layers. The uncertainty in the C_2H_6-to-CH_4 ratio leaves open the possibility that coal mines dominate CH_4 emissions in the southwestern Marcellus region.

This work demonstrates that a flight-based mass balance approach is a valuable tool for estimating CH_4 emissions from O&NG operations. More of such observations are needed to assess the consistency of

results across different regions, to better quantify CH_4 emissions for inventories, as well as to characterize and reduce uncertainties of CH_4 emissions associated with the mass balance approach.

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