



RESEARCH ARTICLE

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Key Points:

- Significant methane emissions of 37 kg s^{-1} were observed from a 4235 km^2 area of the southwestern Marcellus Shale region
- We estimate a mean CH_4 leak rate of 3.9% from O&NG operations in the SW Marcellus with a lower limit of 1.5% and an upper limit of 6.3%
- The estimated mean CH_4 leak rate exceeds the 2.4% tipping point relative to coal combustion for the methane GWP over a 20 year time horizon

Supporting Information:

- Supporting Information S1

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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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Abstract Natural gas production in the U.S. has increased rapidly over the past decade, along with concerns about methane (CH_4) leakage (total fugitive emissions), and climate impacts. Quantification of CH_4 emissions from oil and natural gas (O&NG) operations is important for establishing scientifically sound, cost-effective policies for mitigating greenhouse gases. We use aircraft measurements and a mass balance approach for three flight experiments in August and September 2015 to estimate CH_4 emissions from O&NG operations in the southwestern Marcellus Shale region. We estimate the mean $\pm 1\sigma$ CH_4 emission rate as $36.7 \pm 1.9 \text{ kg CH}_4 \text{ s}^{-1}$ (or $1.16 \pm 0.06 \text{ Tg CH}_4 \text{ yr}^{-1}$) with 59% coming from O&NG operations. We estimate the mean $\pm 1\sigma$ CH_4 leak rate from O&NG operations as $3.9 \pm 0.4\%$ with a lower limit of 1.5% and an upper limit of 6.3%. This leak rate is broadly consistent with the results from several recent top-down studies but higher than the results from a few other observational studies as well as in the U.S. Environmental Protection Agency CH_4 emission inventory. However, a substantial source of CH_4 was found to contain little ethane (C_2H_6), possibly due to coalbed CH_4 emitted either directly from coalmines or from wells drilled through coalbed layers. Although recent regulations requiring capture of gas from the completion venting step of the hydraulic fracturing appear to have reduced losses, our study suggests that for a 20 year time scale, energy derived from the combustion of natural gas extracted from this region will require further controls before it can exert a net climate benefit compared to coal.

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 [*U.S. Energy Information Administration (EIA), 2016a*] (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 [*U.S. EIA, 2016b*]. In June 2016, shale gas production accounted for about 48% of the total U.S. natural gas production, with the Marcellus Shale accounting for 39% of the total U.S. shale gas production. Therefore, the Marcellus Shale accounts for about 19% of the total U.S. natural gas production. Natural gas production in the U.S. was roughly $2.95 \times 10^{19} \text{ J yr}^{-1}$ (or $7.7 \times 10^{11} \text{ m}^3 \text{ yr}^{-1}$) in 2015 and is expected to rise to $1.18 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ by 2040 [*U.S. EIA, 2016c*]. In the Marcellus Shale region, the natural gas production was $1.33 \times 10^{10} \text{ m}^3 \text{ yr}^{-1}$ in 2010 and is expected to increase to $1.81 \times 10^{11} \text{ m}^3 \text{ yr}^{-1}$ 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 U.S. geopolitically by increasing U.S. energy security [*American Chemical Council, Economics and Statistics Department, 2013; U.S. EIA, 2016c*]. 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 ($\text{NO}_x = \text{NO} + \text{NO}_2$), sulfur dioxide (SO_2), particulate matter, carbon monoxide (CO), and mercury. The downsides of O&NG operations include the potential for surface

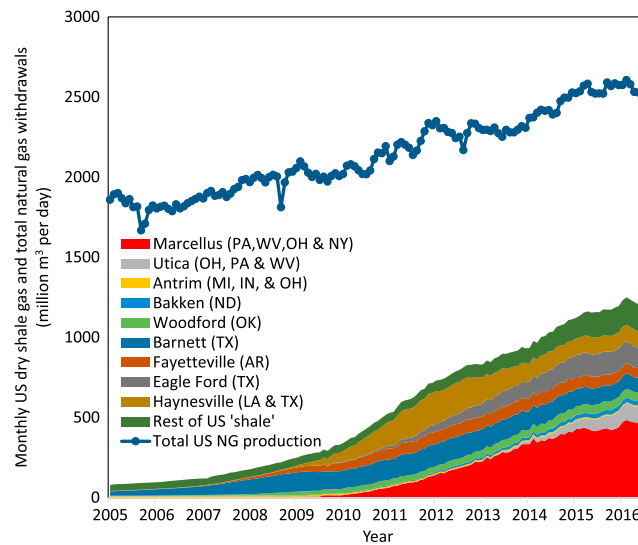


Figure 1. Monthly U.S. total natural gas (linked green dots) and dry shale gas (shaded area) withdrawals from January 2005 to July 2016. Data are adapted from <http://www.eia.gov> (accessed September 2016).

and groundwater contamination [Colborn et al., 2011; Rozell and Reaven, 2012; Finkel and Hays, 2013; Gordalla et al., 2013; Vidic et al., 2013] and air pollution [McDermott-Levy et al., 2013; Field et al., 2014]. Significant emissions of methane (CH₄), volatile organic compounds (VOCs), and NO_x into the atmosphere are associated with O&NG operations [Gilman et al., 2013; Bunch et al., 2014; Rich et al., 2014; Roy et al., 2014; Swarthout et al., 2015; Yuan et al., 2015]. In particular, the leakage of CH₄ is a significant concern for climate impact. In trapping infrared radiation, CH₄ is 86 times as potent as carbon dioxide (CO₂) over a 20 year time horizon and is 34 times as potent as CO₂ over a 100 year time horizon

(on a per mass basis with climate-carbon feedbacks) according to the Intergovernmental Panel on Climate Change [Intergovernmental Panel on Climate Change, 2013]. Quantifying emissions of CH₄ from O&NG operations is essential to establish scientifically sound, cost-effective policies for mitigating greenhouse gases (GHGs).

Table 1. A Survey of Estimates of Methane Leakage From Oil and Natural Gas Production Operations^a

Leakage as % of Production	Region	Method	Reference
10.1 ± 7.3% ^b	Bakken, North Dakota	Remote sensing	Schneising et al. [2014] and Peischl et al. [2016]
2.8–17.3%	Southwestern Pennsylvania	<i>Aircraft sampling-based mass balance</i>	Caulton et al. [2014]
17%	Los Angeles Basin, California	Aircraft measurements and emissions inventory	Peischl et al. [2013]
~12%	Eagle Ford, Texas	Remote sensing	Schneising et al. [2014] and Howarth [2015]
6.2–11.7%	Uintah, Utah	Aircraft sampling-based mass balance	Karion et al. [2013]
4.2–8.4%	Bakken Shale, North Dakota	Aircraft sampling-based mass balance	Peischl et al. [2016]
3.6%–7.9%	U.S. National	Estimates based on emission estimates from EPA and GAO reports	Howarth et al. [2011]
2.3–7.7%	Northeastern Colorado	Ground level ambient tall tower and mobile sampling	Pétron et al. [2012]
1.5–6.3%	Southwestern Pennsylvania and northern West Virginia	<i>Aircraft sampling-based mass balance</i>	<i>This work</i>
1.93%	U.S. National	U.S. EPA NEI 2014 and U.S. EIA total U.S. natural gas production in 2014	U.S. EPA [2016a] and U.S. EIA [2016a]
1.3–1.9%	Barnett, Texas	Aircraft sampling-based mass balance	Karion et al. [2015]
1.42%	U.S. national	Source sampling	Kirchgessner et al. [1997]
1.35%	Pennsylvania and West Virginia	<i>Ground facility-level source sampling</i>	Omara et al. [2016]
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]
0.18–0.41%	Northeastern Pennsylvania	<i>Aircraft sampling-based mass balance</i>	Peischl et al. [2015]

^aStudies are listed in approximate order from high to low leak rates. Studies in italic are those conducted in the Marcellus Shale region. Satellite-based measurements using SCIA [Schneising et al., 2014] were more reliable for the Bakken and Eagle Ford plays, where leakage was estimated as about 10% (3–17%) of total energy content.

^bThe Bakken value estimated by Peischl et al. [2016] by converting back from % total energy content losses is 39%.

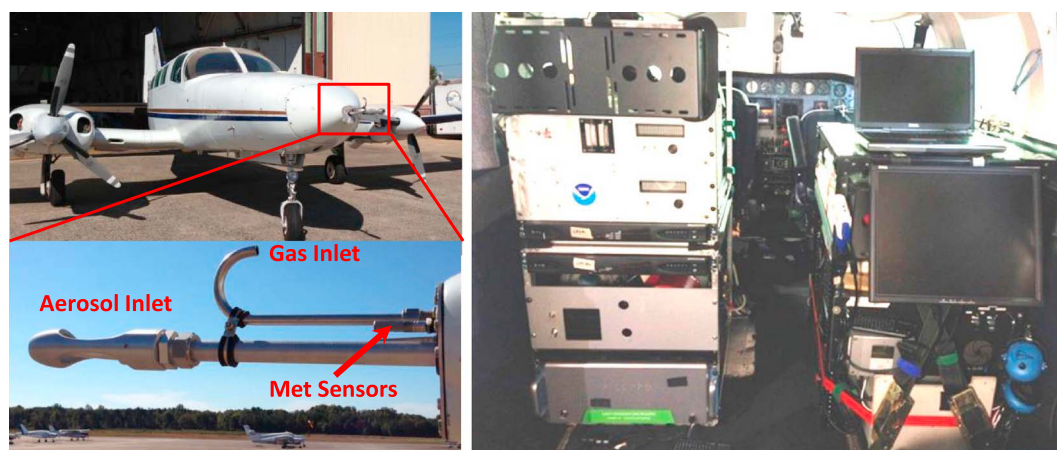


Figure 2. (left) Pictures showing the Cessna aircraft with gas and aerosol sample inlets. (right) Instrumentation inside the aircraft.

There have been several observation-based (top-down) studies to quantify emissions of CH_4 from O&NG fields in the U.S. [Pétron *et al.*, 2012; Allen *et al.*, 2013; Karion *et al.*, 2013; Peischl *et al.*, 2013; Caulton *et al.*, 2014; Schneising *et al.*, 2014; Lamb *et al.*, 2015; Marchese *et al.*, 2015; Peischl *et al.*, 2015; Zimmerle *et al.*, 2015; Omara *et al.*, 2016; Peischl *et al.*, 2016]. The estimated leakage rates of CH_4 obtained from these studies cover a wide range (Table 1) and have been the subject of some controversy [Howard *et al.*, 2015; Howard, 2015a, 2015b; Allen *et al.*, 2015; Howarth, 2015]. However, recent reports suggest that leakage per unit of natural gas production may be trending downward [Schneising *et al.*, 2014; Schwietzke *et al.*, 2014; Vinciguerra *et al.*, 2015; Schwietzke *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 and cattle 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 $\text{C}_2\text{H}_6/\text{CH}_4$ from well sites can vary widely [Goetz *et al.*, 2015], complicating the use of this metric.

There are also discrepancies in CH_4 leak rates between observation-based (top-down) and inventory-based (bottom-up) methods, 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, increasing substantially the database for such measurements. Leak 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 (Figure 2). The aircraft instrumentation listed in Table 2 includes separate gas and particle (Droplet Measurement Technologies, Boulder, CO) sample inlets and pressure/temperature/humidity sensors (Vaisala, Model PTU300) installed at the nose of the aircraft. Flight tracks were recorded using both a portable global positioning system (GPS) and an aircraft inertial navigation system (INS). Horizontal two-dimensional wind was obtained by a Garmin G600 system that uses information from the INS, GPS, and an air data computer. The aircraft was equipped with the following trace gas analyzers: (1) a Picarro cavity ring down spectrometer (Model G2401-m) for CH_4 , carbon dioxide (CO_2), carbon monoxide (CO), and water vapor (H_2O) measurements; (2) a Thermal Electron Model 49C ozone (O_3) analyzer based on UV absorption; (3) a Thermal Electron Model 43C sulfur dioxide (SO_2) analyzer based on pulsed fluorescence; and (4) a Los Gatos Research Model RMT-200 nitrogen dioxide (NO_2) analyzer based on cavity-enhanced absorption spectroscopy. The aircraft was also equipped with three instruments

Table 2. UMD Aircraft Instrumentation

Variable	Method	Sample Frequency
Position	GPS	1 s
Meteorology (T, RH, P, 2-D Wind)	Thermistor, Hygistor, Capacitance Manometer, Garmin G600 system	1 s
Greenhouse gas CO ₂ /CH ₄ /CO/H ₂ O	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/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	2 min

to measure aerosol optical properties, including a nephelometer (TSI Model 3563) to measure aerosol scattering, a particle soot absorption photometer (PSAP, Radiance Research) to measure absorption, and an aethalometer (Magee Model AE31) to measure black carbon.

Mixing ratios of CH₄, CO₂, CO, and water vapor were measured with the Picarro analyzer at a frequency of 0.5 Hz. Ambient air from the nose of the aircraft was pulled through a rear-facing perfluoroalkoxy Teflon tube (OD = 0.95 cm and ID = 0.64 cm) at a total flow rate of 10 L min⁻¹ (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 with a sampling flow rate of 0.40 standard liters per minute. During each flight experiment, five to six stainless steel canisters were used to take whole air samples and the canisters were then sent to the Maryland Department of Environment's Air Toxics and Photochemical Assessment Monitoring Station (PAMS) Analytical Laboratory for the analysis of VOCs based on gas chromatography with flame ionization detection (GC-FID). Other trace gas and particulate matter analyzers installed in the aircraft have been used in the past; additional details regarding current and previous measurement methodologies have been documented in previous publications [Taubman *et al.*, 2006; Hains *et al.*, 2008; Brent *et al.*, 2013; He *et al.*, 2014, 2016].

For the flights over the Marcellus Shale, the Picarro analyzer was calibrated for CH₄, CO₂, 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 ppm for CO₂, 0.2 ppb for CH₄, and 4.2 ppb for CO (standard deviations (1 σ) of 0.5 Hz data over 5 min). The accuracies stated in the manufacturer's specifications are about 0.1 ppmv for CO₂, 1 ppbv for CH₄, and 10 ppbv for CO.

2.2. Flight Experiments

The UMD Cessna 402B aircraft was used to perform three mass balance field experiments over the Marcellus Shale region in southwestern Pennsylvania and northern West Virginia on 25 August, 29 August, and 14 September 2015 (Figure 3). In each mass balance experiment, multiple vertical profiles and transects were flown upwind (generally to the west) and downwind (generally to the east) of natural gas operations, perpendicular to the wind direction. The enhancement in CH₄ concentration relative to background was captured. Flights over the Marcellus Shale region usually started at approximately noon to minimize mixing layer growth throughout the duration of the experiments. Typically, one upwind transect and three downwind transects were conducted, during times when the mixing layer height was approximately constant. Each of the 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 either at the end of the first flight or in the second flight after the airplane had been refueled.

We defined a 77 km \times 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°36'W), and (40°06'N, 79°48'W). This area covers most of our flight

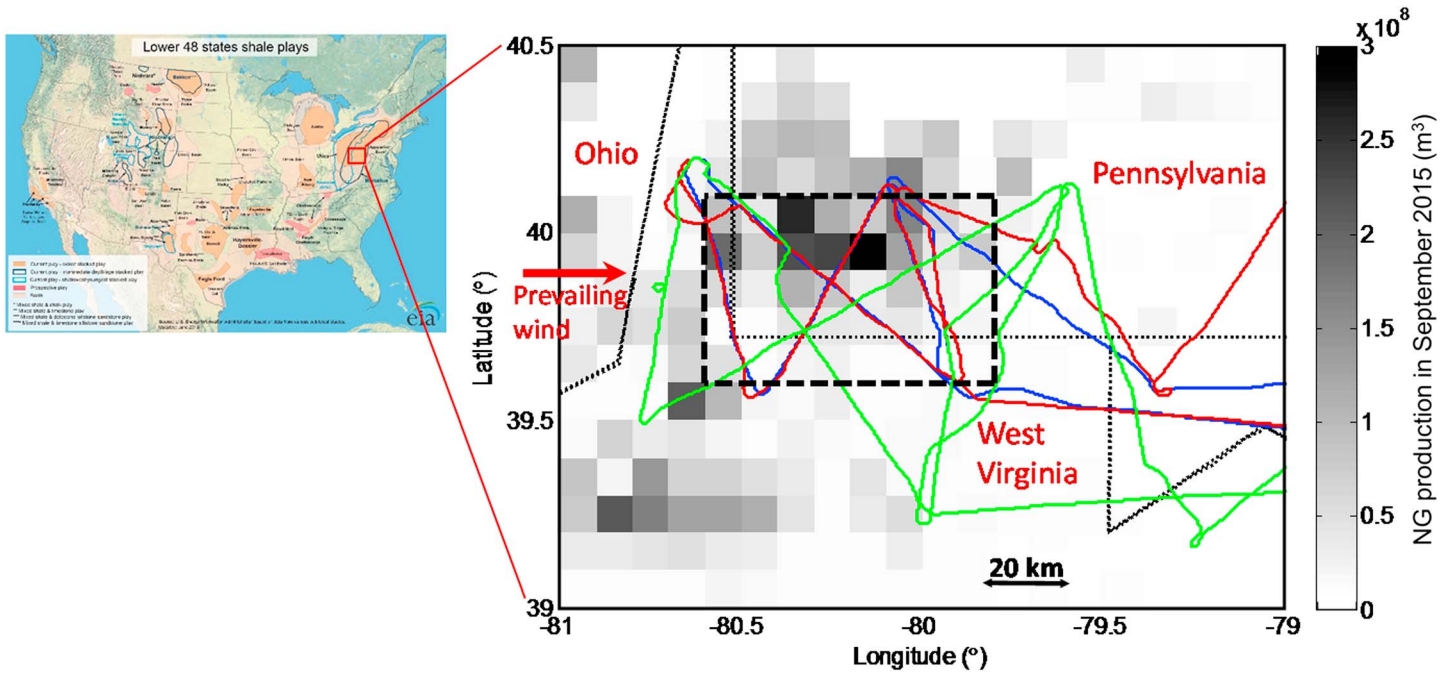


Figure 3. Location of the surveyed area and three flight paths (blue, red, and green) for three mass balance experiments conducted on 25 August, 29 August, and 14 September 2015, respectively. The black dashed rectangle represents a 77 km × 55 km area that covers the surveyed oil and natural gas operation region. Monthly Marcellus natural gas productions are 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.

tracks in the Marcellus Shale region and represents the majority of natural gas production in the area where Pennsylvania, West Virginia, and Ohio come together (Figure 3). In August 2015, the natural gas production from this surveyed area was $6.96 \times 10^7 \text{ m}^3$, representing 16% of the total Marcellus Shale natural gas production and 2.8% of the total U.S. natural gas production.

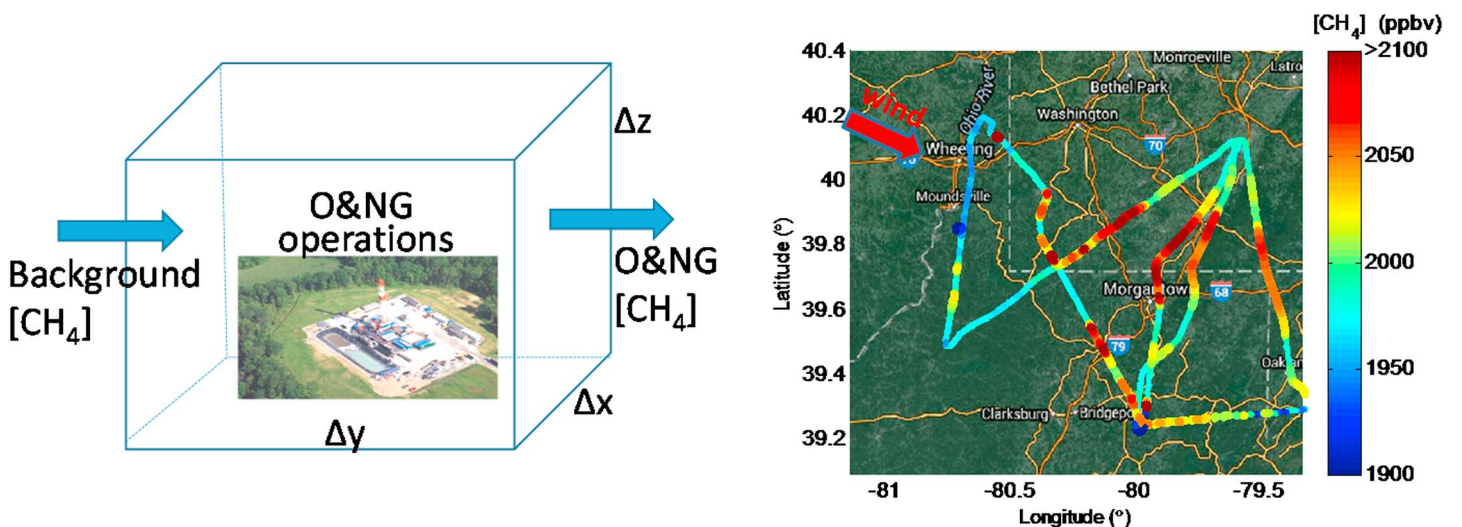


Figure 4. (left) The conceptual model of a mass balance approach to quantify methane emissions from an O&NG operation area. (right) Methane mixing ratios measured along the flight track on 14 September 2015. An enhancement of CH₄ was clearly observed along the downwind transects.

2.3. Mass Balance Approach

A mass balance approach was used to quantify the CH₄ emissions from the surveyed area. This method relies on the assumptions of constant emissions and stationary planetary boundary layer (PBL) depth during a given experiment and is robust for the estimate of total emissions from a given area [White *et al.*, 1976; Cambaliza *et al.*, 2014]. Wind carrying background concentrations of CH₄ blows over the Marcellus Shale area, where it picks up CH₄ emissions (Figure 4). Horizontal transects are flown perpendicular to the prevailing wind direction downwind of the natural gas extraction area, and enhancements in CH₄ above background are intercepted and detected. The CH₄ emission rate from the area can be calculated using equation (1) [White *et al.*, 1976]:

$$\text{Emission Rate} = \int_0^z \int_{-x}^{+x} ([C]_{ij} - [C]_b) x U_{\perp ij} dx dz \quad (1)$$

where, $[C]_{ij}$ is the concentration of CH₄ at a downwind location (x_i, z_j) ; $[C]_b$ 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 mixing layer height.

There are several sources of uncertainty associated with parameters used in the mass balance approach (equation (1)). We estimate the uncertainties (2σ) in the measurements used in equation (1) to be $\pm 20\%$ for the enhancement of the CH₄ mixing ratio ($[C] - [C]_b$) measured downwind, $\pm 20\%$ for perpendicular wind speed (U_{\perp}), $\pm 10\%$ for the mixing layer height (Δz), and $\pm 20\%$ for the plume width (Δx). The combined uncertainty in CH₄ emission rate estimation using equation (1) is about $\pm 36\%$. This uncertainty is slightly larger than the averaged uncertainty ($\pm 31\%$, 2σ) estimated for the mass balance approach during the INFLUX study [Cambaliza *et al.*, 2014] because of greater uncertainties in the wind fields and mixing layer height due to orographic effects in our study area. Uncertainties in emissions of CH₄ from coal mines and other non-O&NG sources contribute an additional uncertainty to the range of possible CH₄ leak rates inferred from active O&NG operations in our study area.

2.4. 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's Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) [Draxler and Rolph, 2016; Stein *et al.*, 2015] and meteorological data from the North American Mesoscale Forecast System model [Janjic *et al.*, 2001; Janjic, 2003], with a horizontal resolution of 12 km, 26 vertical levels up to 20,000 m (including nine levels under 2000 m), and a temporal resolution of 3 h.

2.5. Other Data Sets Used in This Study

Pennsylvania well locations and natural gas production data were obtained from the Pennsylvania Department of Environmental Protection (http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/OG_Well_Prod_Status, accessed July 2016). West Virginia well locations and natural gas production data were obtained from the West Virginia Department of Environmental Protection (<http://www.dep.wv.gov/oil-and-gas/databaseinfo/Pages/default.aspx>, accessed July 2016). Ohio well locations and natural gas production data were obtained from the Ohio Department of Natural Resources (<http://oilandgas.ohiodnr.gov/production>, accessed July 2016).

Locations of known point sources of CH₄, 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 November 2016). As shown in Figure 1, the total shale gas and natural gas production data were obtained from the Energy Information Administration (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 CH₄ molar fraction of 0.877 ± 0.084 in natural gas was derived from this study, for 80 samples collected in the survey area [Román-Colón and Ruppert, 2014].

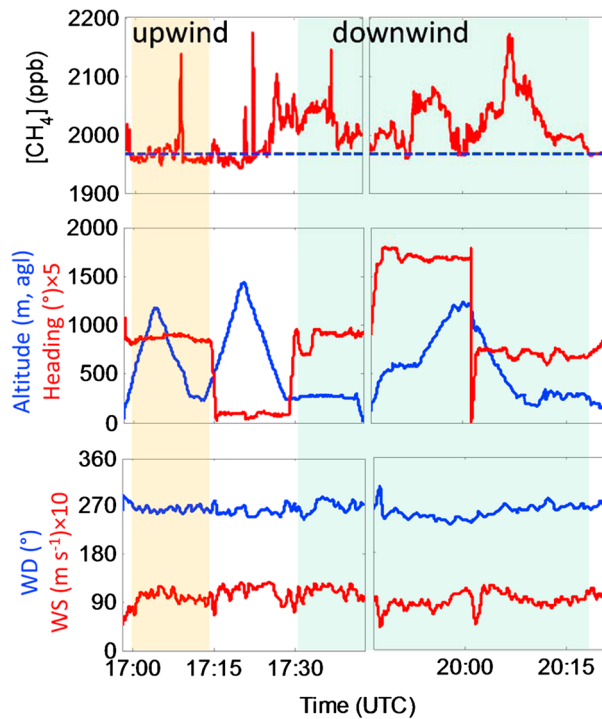


Figure 5. (top) Time series of CH₄ mixing ratio, (middle) altitude above ground level (agl) and aircraft heading, and (bottom) wind direction (WD) and wind speed (WS) measured in the upwind transect (yellow shaded) and downwind plumes (green shaded) during a mass balance experiment on 25 August 2015. The blue dashed line indicates the average mixing ratio of CH₄ in the upwind transect.

3. Results

3.1. Aircraft Observations

Observations from a typical mass balance experiment shown in Figure 5 include one upwind transect followed by three downwind transects, all flown at an airspeed of about 70 m s⁻¹. The mean mixing ratios observed in the upwind transects were used as CH₄ background for the air parcels entering the surveyed area. CH₄ enhancements in the downwind transects were calculated from the downwind CH₄ mixing ratios after subtracting the CH₄ background.

En route vertical profiles were conducted along both upwind and downwind transects in order to characterize the vertical variation of CH₄ mixing ratio. The PBL height was generally the same in the upwind and downwind transects. Figure 6 shows a typical vertical profile of CH₄ and CO₂, potential temperature, and water vapor within the mixing layer. Air within the PBL was generally well mixed. Therefore, the mixing layer

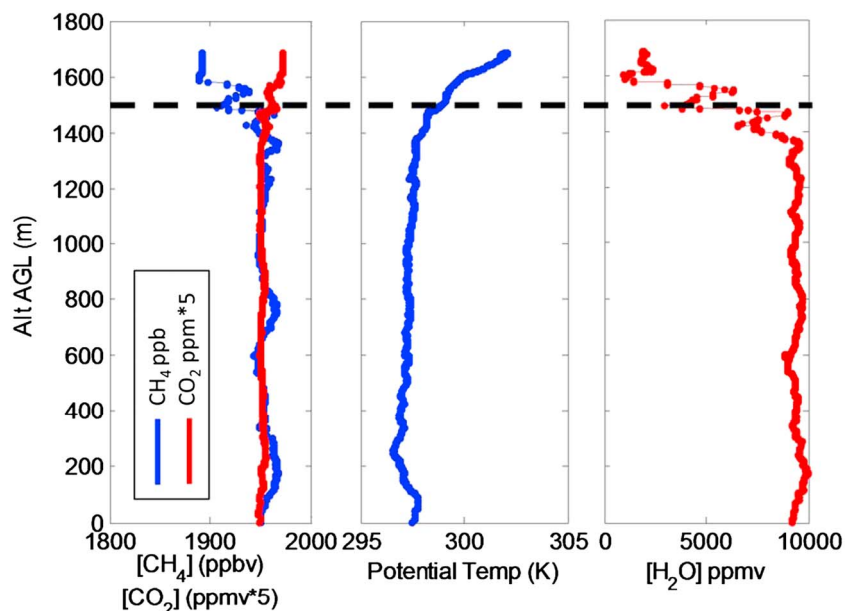


Figure 6. [CH₄], [CO₂], potential temperature, and H₂O mixing ratio during a vertical profile on 14 September 2015. The dashed line indicates the top of the mixed layer (PBL).

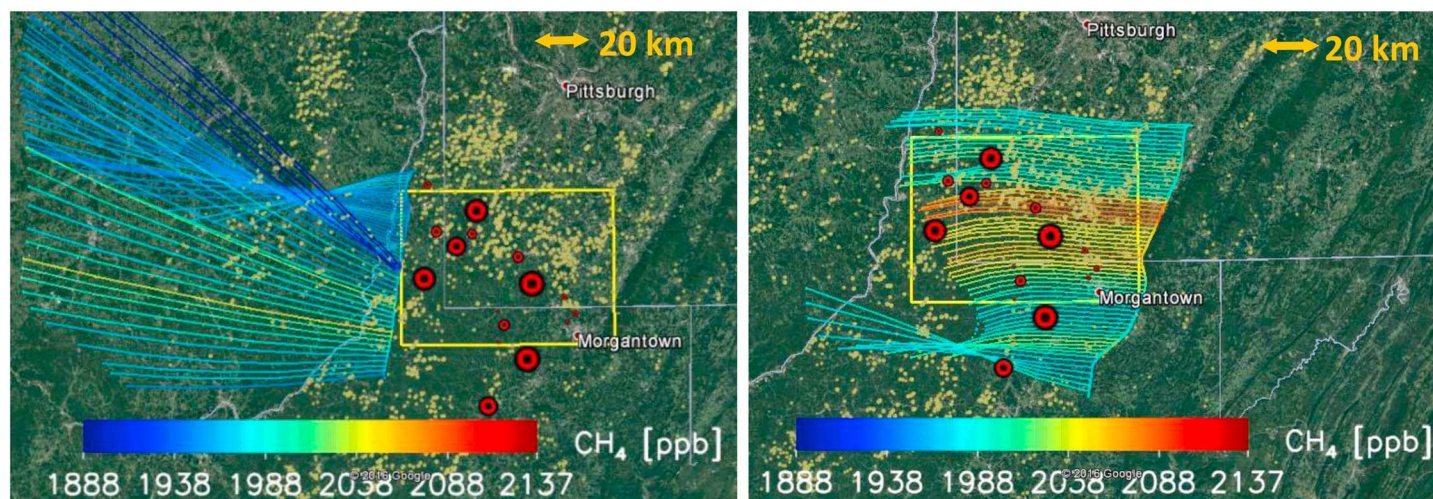


Figure 7. (left) Upwind and (right) downwind transects and HYSPLIT 6 h back trajectories initiated from the flight transects, at 20 s intervals. The transects are colored with in situ measured CH₄ mixing ratios, and each back trajectory has the same color as its starting point on the transect. Thick 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 size of each dot approximately proportional to the CH₄ emission from each coal mine.

height (i.e., the dashed line in Figure 6) can be obtained as the altitude where the CH₄ mixing ratio reaches its free tropospheric background level of about 1890 ppbv, water vapor mixing ratio drops to a significantly smaller value compared to the abundances measured at lower altitudes, and potential temperature begins to increase rapidly.

The HYSPLIT back trajectories shown in Figure 7 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 CH₄ mixing ratios observed within the PBL, at different time and locations.

3.2. Methane Emission Rate Estimate

Highly spatially resolved observations of CH₄ and wind during the flight experiments in this study allow us to calculate atmospheric mass emission rate of CH₄ from the surveyed area. Using the measurements in the three mass balance experiments, the mean and standard deviation of the CH₄ emission rate (Table 3) were determined to be $36.7 \pm 1.9 \text{ kg CH}_4 \text{ s}^{-1}$ (or $1.32 \pm 0.07 \times 10^8 \text{ g CH}_4 \text{ h}^{-1}$) from the surveyed area using equation (1). This emission rate in the surveyed area in 2015 is a factor of 1.8 higher than the CH₄ emission rate ($20.8 \text{ kg CH}_4 \text{ s}^{-1}$) in the U.S. CH₄ National Emission Inventory (NEI) for 2012 [Maasakkers *et al.*, 2016]. For each mass balance experiment, we analyzed each transect separately assuming that CH₄ was mixed well within the PBL and then averaged the emission rates derived from three downwind transects. We conducted three additional mass balance flight experiments in summer 2016. The mean CH₄ emission rate was $37.1 \pm 13.0 \text{ kg CH}_4 \text{ s}^{-1}$ in 2016, very similar to that in 2015, even though the number of drilled and completed

Table 3. Mean Measurements and Their Standard Deviations (1σ) Along the Transects Used in Equation (1) to Derive CH₄ 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 ⁻¹)	WD (deg)	PBL Height (m AGL)	CH ₄ E.R. (kg s ⁻¹)
8/25/2015	1967 ± 22	2023 ± 39	9.7 ± 1.4	260 ± 12	2200	38.35
8/29/2015	2016 ± 16	2119 ± 50	6.4 ± 1.4	226 ± 13	1950	37.14
9/14/2015	1960 ± 28	2032 ± 37	9.6 ± 1.2	283 ± 12	1500	34.59

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

Flight Date	Observed CH ₄ E.R. ^a (kg s ⁻¹)	Coal Mining CH ₄ E.R. ^a (kg s ⁻¹)	NG Distribution CH ₄ E.R. ^a (kg s ⁻¹)	Enteric Fermentation CH ₄ E.R. ^a (kg s ⁻¹)	Landfills CH ₄ E.R. ^a (kg s ⁻¹)	O&NG CH ₄ E.R. (kg s ⁻¹)	NG Production ^b (m ³ s ⁻¹)	CH ₄ Leak Rate
8/25/2015	38.35 ± 13.81	15.04 ± 2.26	0.09 ± 0.03	0.06 ± 0.01	0.03 ± 0.02	23.13 ± 13.99	918.1	4.24 ± 2.57%
8/29/2015	37.14 ± 13.37	15.04 ± 2.26	0.09 ± 0.03	0.06 ± 0.01	0.03 ± 0.02	21.92 ± 13.56	918.1	4.02 ± 2.49%
9/14/2015	34.59 ± 12.45	15.04 ± 2.26	0.09 ± 0.03	0.06 ± 0.01	0.03 ± 0.02	19.37 ± 12.56	956.5	3.41 ± 2.21%

^aE.R. = emission rate. A 36% uncertainty is used for the observed total CH₄ emission rate. As the uncertainties in Table 1 of *Maasackers et al.* [2016], the following uncertainties are estimated in the CH₄ emission rates: ±15 for coal mining, ±30% for NG distribution, ±18% for enteric fermentation, and 64% for landfills.

^bThe mean natural gas production within the surveyed area in August and September 2015 at 1 atm and 288.7 K. A CH₄ molar fraction of 0.877 ± 0.084 in natural gas [*Román-Colón and Ruppert*, 2014] in this area is used to derive total amount of CH₄ in natural gas.

wells in 2016 were half of their 2015 number (<http://www.eia.gov/petroleum/drilling/#tabs-summary-3>). The details of these additional flights are provided in section 4 of the supporting information. These results obtained with the new flights buttress the CH₄ emission estimate for this area.

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

Here we attempt to relate the CH₄ emission rate found from the three mass balance experiments (Table 3) to leakage from natural gas production. As described in section 2, we must account for emissions of atmospheric CH₄ from other sources in the survey region, e.g., 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 Greenhouse Gas Reporting Program (GHGRP, <http://ghgdata.epa.gov>, 2015) were used to derive the CH₄ 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 CH₄ emissions from surface and abandoned coal mines in the surveyed area to be approximately 0.05 and 0.35 kg CH₄ s⁻¹, respectively, based on a gridded national inventory for U.S. CH₄ emissions [*Maasackers et al.*, 2016]. We have included CH₄ emissions from surface and abandoned coal mines in the total CH₄ 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] and must be considered when weighing the net climate impact of natural gas system. The estimates of CH₄ emissions from natural gas distribution pipes and cattle (enteric fermentation) are described in the supporting information. Note that CH₄ 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.

The column labeled O&NG CH₄ emission rate in Table 4 is the difference between the observed total CH₄ emission rate and the four other CH₄ emission sources. Our estimate for CH₄ emissions of 19.4–23.1 kg s⁻¹ from the O&NG operations in the surveyed area is a factor of 2.4–2.9 greater than the 2014 EPA GHG Inventory estimate of 7.9 kg CH₄ s⁻¹ from petroleum and natural gas systems in the surveyed area (2014 EPA GHG inventory, Tables 3-36 and 3-44), assuming that inventory CH₄ emissions scale with natural gas production across the country (i.e., the natural gas production from the surveyed area accounts for 2.8% of total U.S. natural gas production). The mean observed CH₄ emission rate (21.6 ± 1.9 kg CH₄ s⁻¹) from the O&NG operations in the surveyed in 2015 is a factor of 6.3 higher than that (3.44 kg CH₄ s⁻¹) in the U.S. CH₄ NEI for 2012 [*Maasackers et al.*, 2016], even though total natural gas production from the Marcellus Shale has increased only by a factor of 2.3 from 2012 to 2015.

With the derived CH₄ emissions from the surveyed area, the CH₄ leakage fraction from O&NG operations is estimated to be 3.4% to 4.2%, based on the total natural gas production and CH₄ emissions from sectors excluding O&NG operations in this area (Table 4). This fractional leakage spans the estimated range on the three flight experiments conducted in 2015. As stated in section 2.3, besides the uncertainty of 36% in the mass balance approach, additional errors, including the one associated with CH₄ emissions from coal mining, arise from uncertainties in other sources shown in Table 4. Using these uncertainties, a propagated error of 13.4 kg s⁻¹ or 62% is estimated for the CH₄ emission rate from the O&NG operations, which results in a mean uncertainty of ±2.4% in the CH₄ leak rate. Thus, we estimate the mean CH₄ leak rate to be 3.9% with a lower limit of 1.5% and an upper limit of 6.3%.

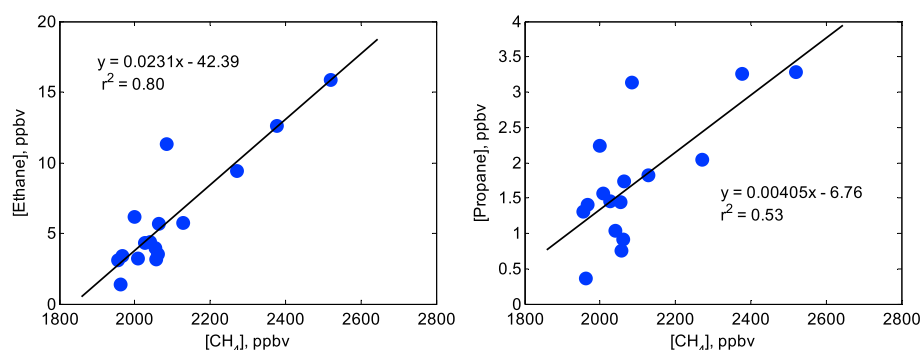


Figure 8. (left) Ethane (C₂H₆) versus CH₄ and (right) propane (C₃H₈) versus CH₄ over the surveyed Marcellus Shale area in southwestern Pennsylvania and northern West Virginia in August/September 2015. The solid lines show the linear regression.

3.4. Correlation Between Methane and Ethane/Propane

In the limited 16 VOC samples collected during the three flight experiments, strong correlations between CH₄ and C₂H₆ and between CH₄ and propane (C₃H₈) were observed (Figure 8), confirming that the CH₄ enhancements observed during the flights may primarily be 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., Pétron *et al.*, 2012; Karion *et al.*, 2013; Smith *et al.*, 2015; Peischl *et al.*, 2015, 2016]. In a survey done by USGS in 2014 [Román-Colón and Ruppert, 2014], 80 samples were collected from different wells located within our study region. The mean molar composition of natural gas was found to be 87.7% CH₄, 5.88% C₂H₆, 2.02% C₃H₈, 2.40% nitrogen, and 2.0% other compounds. Thus, the average ethane-to-methane molar ratio for the samples collected directly from the wells in the surveyed area is 6.7%. This ratio is greater than the slope (2.3%) of the C₂H₆ versus CH₄ correlation plot in Figure 8 derived from our VOC canister samples (hereafter C₂H₆-to-CH₄ ratio). Studies have found that coal mines do not emit significant C₂H₆ and the C₂H₆-to-CH₄ ratio in the emissions from coal mines is much lower than that in the natural gas [Kim, 1973]. Results in Table 4 suggest that coal mining and O&NG operations are two dominant CH₄ emission sources in this region. Potentially, we could use the ethane-to-methane ratio observed in the ambient air and the ratio in the natural gas to infer the relative contributions to methane emissions from these two sources. By this measure, it might be inferred that coal mining accounts for 66% of the total CH₄ emissions and O&NG operations account for the remaining 34%, resulting in a CH₄ leak rate of 2.3%, which falls between the lower and upper limits of the leak rates (i.e., 1.5–6.3%). For an extreme assumption with zero emissions from coal mining, the inferred CH₄ leak rate would be 6.6%, which is slightly greater than the upper limit of 6.3%. However, there is considerable uncertainty and variability in the observed ethane-to-methane ratio due to the limited number of canisters collected for VOC measurements in each flight experiment as shown in Figure S1. The variability occurs likely because emissions from coal mining and from O&NG were not always well mixed in the atmosphere at the locations where the VOC samples were collected. In addition, the variability of background ethane and methane concentrations can interfere with the slope of the combined data set, which could be different from the slopes for individual flight experiments. Therefore, quantitative use of the ethane-to-methane ratio awaits further measurements.

One likely reason for our observations of a smaller C₂H₆-to-CH₄ ratio is the emission of coalbed CH₄ that has a lower C₂H₆-to-CH₄ ratio [Kim, 1973]. There are significant emissions of natural gas from coal mines in the surveyed area. According to U.S. EPA's GHGRP, the U.S. CH₄ NEI for 2012 [Maasackers *et al.*, 2016], and observed total CH₄ emission rate, CH₄ emissions from the coal mines account for about 39% of the total CH₄ emissions from our surveyed area (Table 4). A ground-based survey in the southwestern Marcellus indicated substantially more CH₄ from O&NG operations than from coalbed methane wells [Johnson and Heltzel, 2016]. Caulton *et al.* [2014] also identified several shale well pads in our surveyed area with high CH₄ emissions. These well pads were identified as in the drilling phase, a preproduction stage previously assumed to have little or no CH₄ emissions. These wells accounted for only 1% of the wells in their study area but had 6–9% of the CH₄ emissions from all sources [Caulton *et al.*, 2014]. The high CH₄ emissions from this stage are

likely due to the drilling through coalbed layers, which would be associated with little emissions of C_2H_6 . 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 emissions of coalbed CH_4 [Lyon *et al.*, 2015].

4. Discussion

The average CH_4 emission rate from the surveyed area of the Marcellus Shale was $36.7 \pm 1.9 \text{ kg } CH_4 \text{ s}^{-1}$ or $8.7 \pm 0.4 \text{ g } CH_4 \text{ km}^{-2} \text{ s}^{-1}$. This CH_4 emission rate is broadly consistent with the results ($2.0\text{--}14 \text{ g } CH_4 \text{ km}^{-2} \text{ s}^{-1}$) of Caulton *et al.* [2014] but larger than the results ($1.2 \pm 0.6 \text{ g } CH_4 \text{ km}^{-2} \text{ s}^{-1}$) of Swarthout *et al.* [2015], both studies conducted in the Marcellus Shale region in southwestern Pennsylvania. Caulton *et al.* [2014] conducted nine flights in June 2012, and Swarthout *et al.* [2015] collected whole air samples throughout an 8050 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 rate of $0.4 \text{ g } CH_4 \text{ km}^{-2} \text{ s}^{-1}$ of Peischl *et al.* [2015] obtained from the Marcellus Shale region in northeastern Pennsylvania. However, it should be noted that observational aircraft studies are generally based upon a limited number of transects, two in the case of Peischl *et al.* [2015] and 16 in our study.

The CH_4 leak rate as a percentage of natural gas production was estimated to be $3.9 \pm 0.4\%$ (mean $\pm 1\sigma$ standard deviation). This leak percentage is much greater than the leak rate of $0.18\text{--}0.41\%$ estimated for the Marcellus Shale region in northeastern Pennsylvania by Peischl *et al.* [2015] 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 median leak rate of 11% for conventional wells and 0.13% for unconventional wells and a mean leak rate of 1.35% [Omara *et al.*, 2016]. One possible reason for the different leak rates in 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 infrastructure and conventional wells in southwestern Pennsylvania and northern West Virginia. These older unconventional wells tend to have higher leak rates according to a recent study in the same area [Omara *et al.*, 2016]. In addition, compared to northern Pennsylvania, the NG extracted from southwestern Pennsylvania is wetter and contains more nonmethane hydrocarbons, which requires more separation and gas processing and can lead to more CH_4 leaks.

A leak rate of 2.4% for a 20 year time horizon based on the global warming potential of CH_4 is the “tipping point,” beyond which natural gas becomes worse with respect to climate forcing than coal. The tipping point calculation, described in the supporting information, 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 . At our measured leak rate of $3.9 \pm 0.4\%$ 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 relatively greater climate impact over the next few decades. The rates of CH_4 leakage listed in Table 1 are currently the subject of intense study and debate [Howarth *et al.*, 2011; Cathles, 2012; Alvarez *et al.*, 2012; Allen *et al.*, 2013; Brandt *et al.*, 2014; Howard *et al.*, 2015; Howarth, 2014, 2015]. 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 leakage rate. The validity of the study by Allen *et al.* [2013] is still an ongoing point of contention [Alvarez *et al.*, 2016]. Given the current low cost of natural gas, a purely economic driver to reduce the atmospheric release of CH_4 by leakage does not exist. Thus, regulatory approaches are needed in order for energy derived by the combustion of natural gas to be a net climate benefit, relative to energy derived from coal combustion.

Initial regulations have been implemented in the U.S. in stages starting in 2012, focusing on reducing the emissions of VOCs [U.S. Environmental Protection Agency (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 t of VOC per dry or wet well drilled in the Marcellus Shale, respectively [Roy *et al.*, 2014]. Beginning in October 2012, operators

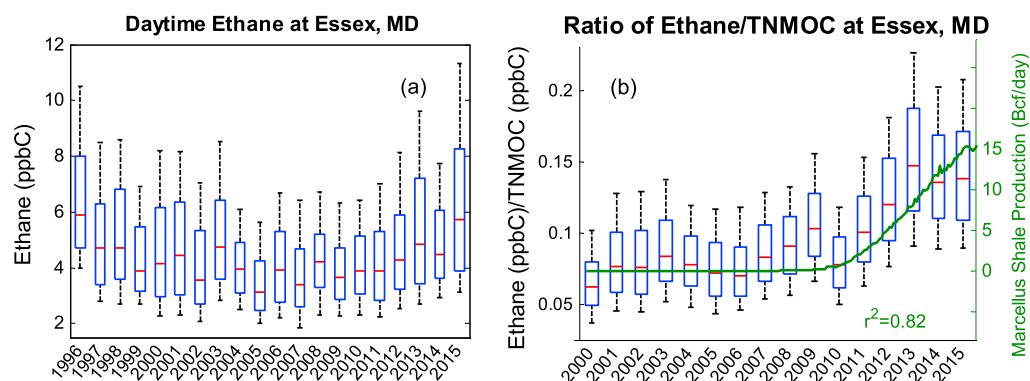


Figure 9. (a) Hourly daytime ethane mixing ratio in units of parts per billion carbon (ppbC) and (b) the ratio of ethane to total nonmethane organic carbon (TNMOC) observed at Essex, MD, shown by box and whisker plots. The box provides the 25th and 75th percentiles, with the median represented by the 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 Figure 9b. A strong correlation of the C_2H_6 to TNMOC ratio versus the Marcellus production was observed with an r^2 value of 0.82.

were required to capture or flare the gases, and from January 2015 onward, only capturing was allowed. Wells considered exploratory, or wells to determine the boundary of a natural gas field are exempt from these regulations though.

The CH_4 leak rate per unit of natural gas production may have been trending downward in recent years [Vinciguerra *et al.*, 2015; Schwietzke *et al.*, 2016], due to the new regulations that affected onshore oil and gas production [U.S. EPA, 2012; Healey and Pergande, 2014]. These regulation might have contributed to the recent leveling off of the C_2H_6 -to-total nonmethane organic carbon (TNMOC) ratio observed at the U.S. EPA's Photochemical Assessment Monitoring Station (PAMS) in Essex, Maryland (Figure 9), during the past 3 years [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 ($\sim 0.17 \text{ m}^3 \text{ h}^{-1}$) [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 5.4 t yr^{-1} or more were required to reduce VOCs by 95% by April 2014 for vessels 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 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, 2016b]. The implementation of these newer regulations is expected to further reduce CH_4 and other air pollutants emitted from O&NG operations.

5. Conclusions

We conducted three flight-based mass balance experiments over the Marcellus Shale in southwestern Pennsylvania and northern West Virginia during August and September 2015. We calculate the mean $\pm 1\sigma$ emissions of CH_4 to the atmosphere, from the $77 \text{ km} \times 55 \text{ km}$ surveyed area, to be $(1.32 \pm 0.07) \times 10^8 \text{ g } CH_4 \text{ h}^{-1}$ (or $1.16 \pm 0.06 \text{ Tg } CH_4 \text{ yr}^{-1}$), showing strong evidence of large emissions of CH_4 from this region.

Based on the total natural gas production and CH_4 emissions in the sectors other than O&NG operations in this area, we estimate an averaged CH_4 leak rate from the O&NG operations in our surveyed area to be $3.9 \pm 0.4\%$ of the total natural gas production. Using extreme values for coalbed CH_4 emissions, we estimate the lower limit as 1.5% and the upper limit as 6.3%. This leak rate is broadly consistent with the results from several other recent studies based on atmospheric observations but higher than results reported in a few other different studies that also use atmospheric observation data as well as the U.S. EPA emission inventory estimate for CH_4 leakage. Our best estimate of the CH_4 leak rate exceeds the

tipping point of 2.4% (based on the global warming potential of CH₄ over a 20 year time horizon), beyond which natural gas becomes worse with respect to climate forcing compared to coal. Hence, the production of energy from CH₄ extracted from our surveyed area with current technologies is a climate detriment, over the next two decades, if our measured leak rate is representative of typical conditions for extraction in the Marcellus Shale. Although new regulations on the completion venting step of the hydraulic fracturing appear to have improved relative leak rates, further actions are needed in order to reduce natural gas losses.

There appears to be a substantial source of CH₄ from processes in this Marcellus Shale area that contain little C₂H₆. Limited VOC measurements from canisters filled during flight show that the observed C₂H₆-to-CH₄ ratio was 2.3%, which is smaller than the C₂H₆-to-CH₄ ratio (6.7%) in the natural gas samples at the wells for this region. The lower C₂H₆-to-CH₄ ratio in the atmosphere is likely due to the emissions of coalbed natural gas that contain little C₂H₆, emitted either directly from coal mines or from wells that drilled through coalbed layers. The uncertainty in the C₂H₆-to-CH₄ ratio leaves open the possibility that coal mines dominate CH₄ emissions in the southwestern Marcellus region.

This work demonstrates that a flight-based mass balance approach is a valuable tool for estimating CH₄ emissions from O&NG operations. More of these kinds of observations are needed to assess the consistency of results across different regions, to better quantify CH₄ emissions for inventories, as well as to characterize and reduce uncertainties of CH₄ leakage associated with the mass balance approach.

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