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Methane Emissions From the Baltimore-Washington Area Based on Airborne Observations: Comparison to Emissions Inventories

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Key Points:
- An aircraft observation-based estimate indicates a mean CH_4 emission rate of 8.8 ± 2.1 kg/s for the Baltimore-Washington region
- CH_4 emission rates in the national and MD GHG inventories for this area are factors of 2.8 and 1.7 lower than observed, respectively
- Reconciliation of the wide range of CH_4 emissions estimates from landfills and the natural gas system is necessary

Supporting Information:
- Supporting Information S1

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Abstract Urban areas are responsible for a substantial fraction of anthropogenic emissions of greenhouse gases (GHGs) including methane (CH_4), with the second largest anthropogenic direct radiative forcing relative to carbon dioxide (CO_2). Quantification of urban CH_4 emissions is important for establishing GHG mitigation policies. Comparison of observation-based and inventory-based urban CH_4 emissions suggests possible improvements in estimating CH_4 source emissions in urban environments. In this study, we quantify CH_4 emissions from the Baltimore-Washington area based on the mass balance aircraft flight experiments conducted in Winters 2015 and 2016. The field measurement-based mean winter CH_4 emission rates from this area were 8.66 ± 4.17 kg/s in 2015 and 9.14 ± 4.49 kg/s in 2016, which are 2.8 times the 2012 average U.S. GHG Inventory-based emission rate. The observed emission rate is 1.7 times that given in a population-apportioned state of Maryland inventory. Methane emission rates inferred from carbon monoxide (CO) and CO_2 emission inventories and observed CH_4/CO and CH_4/CO_2 enhancement ratios are similar to those from the mass balance approach. The observed ethane-to-methane ratios, with a mean value of 3.3% in Winter 2015 and 4.3% in Winter 2016, indicate that the urban natural gas system could be responsible for ~40–60% of total CH_4 emissions from this area. Landfills also appear to be a major contributor, providing 25 ± 15% of the total emissions for the region. Our study suggests there are grounds to reexamine the CH_4 emissions estimates for the Baltimore-Washington area and to conduct flights in other seasons.

Plain Language Summary In this study methane emission rates were estimated for the Baltimore-Washington region based on airborne observations. The inferred methane emission rate is greater than the national greenhouse gas inventory by a factor of 2.8. Reconciliation of the wide range of CH_4 emissions estimates from landfills and the natural gas system is necessary.

1. Introduction

Urban greenhouse gas (GHG) emissions contribute about 70% of total emissions of anthropogenic GHGs (Intergovernmental Panel on Climate Change, IPCC, 2014; UN-HABITAT, 2011). Among the emitted GHGs, methane (CH_4) is the second most important GHG next to carbon dioxide (CO_2), contributing 0.48 W/m^2 (or 17%) globally to the total anthropogenic direct radiative forcing (Myhre et al., 2013). Over a 20-year time horizon, CH_4 is 86 times as potent as CO_2 in terms of global warming potential (IPCC, 2014) and represents an important climate change mitigation option in the near term due to its relatively short lifetime of about 10 years (Voulgarakis et al., 2013). Quantifying urban CH_4 emissions is thus important for establishing scientifically sound, cost-effective policies for mitigating climate change due to anthropogenic emissions of GHGs.

Major sources of urban CH_4 emissions include natural gas systems, landfills, and wastewater treatment facilities. Other CH_4 sources in urban areas are stationary combustion, enteric fermentation, and geologic seeps. A

small amount of CH_4 is also emitted from vehicular exhaust but this source only accounts for <0.2% of anthropogenic CH_4 emissions (Lipman & Delucchi, 2002; Nam et al., 2004). There have been several studies focusing on urban CH_4 emissions from natural gas delivery systems (Jackson et al., 2014; Lamb et al., 2015; McKain et al., 2015; Peischl et al., 2013; Phillips et al., 2013) and landfills (Cambaliza et al., 2017; Kumar et al., 2004; Mosher et al., 1999; Sekhavatjou et al., 2012) in urban areas. However, only a very few studies (Cambaliza et al., 2015; Heimburger et al., 2017; Lamb et al., 2016; Wunch et al., 2009) have focused on CH_4 emissions on an urban scale.

Discrepancies between observation-based (top-down) and inventory-based (bottom-up) estimates for CH_4 emissions were found in several recent studies (Lamb et al., 2016; Turner et al., 2016; Wunch et al., 2009), suggesting that sources of CH_4 in urban environments are poorly characterized and that more observations are needed to assess and reduce uncertainty in CH_4 emissions inventories (McKain et al., 2015). In this study, we quantify the emissions of CH_4 from the Baltimore-Washington area for the first time using a mass balance approach for flight experiments conducted in winters 2015 and 2016 as part of the Fluxes of Atmospheric Greenhouse Gases in Maryland (FLAGG-MD) and the Wintertime Investigation of Emissions, Reactivity, and Transport (WINTER) campaigns. Several important CH_4 sources within this urban environment are identified and their contributions are quantified. We compare the estimated CH_4 emission rates based on airborne observations to the existing CH_4 emissions inventories for this area. The overall objective of this study is to reduce the uncertainty in the GHG emission rate estimate as well as to provide science information to policy makers.

2. Experimental Description and Methods

2.1. Study Area

The FLAGG-MD study aims to quantify sources, sinks, and emission rates of CO_2 and CH_4 for the Baltimore-Washington metropolitan area, including Washington, DC, Central Maryland, and Northern Virginia (Figure 1). This area is the fourth most populated region in the United States (U.S.; U.S. Census Bureau, 2016). According to the U.S. Census Bureau (http://www.census.gov/quickfacts/table), the total population in the study area (designated as an orange rectangle in Figure 1) in 2015 was about 8.5 million, approaching megacity classification (10 million), including about 5.4 million living in Maryland, about 2.4 million in Virginia, and about 700,000 in Washington, DC. The Baltimore-Washington metropolitan area is located at the southwestern end of the northeast corridor of the United States and is surrounded by rural areas to the northwest and southeast with the Appalachian Mountains to the west and the Chesapeake Bay to the east (Figure 1). The oil and natural gas operations in the southwestern Marcellus Shale region are located about 300 km to the west/northwest of this region. Emissions of CH_4 from the Marcellus Shale and surrounding coal mines can influence the background levels of CH_4 in the air entering our study area when the wind is from the west or northwest. This work focuses on the use of aircraft observations to identify and quantify urban CH_4 emissions from the Baltimore-Washington metropolitan area. Emissions of CO_2 and nitrogen oxides (NO_x) from this area are presented in accompanying paper (Salmon et al., 2018).

2.2. Description of the Aircraft Observations

Two airplanes were used to quantify GHG emissions from the Baltimore-Washington area, the Purdue University's Airborne Laboratory for Atmospheric Research (ALAR, https://www.chem.purdue.edu/jafci/projects/alar.php) and the University of Maryland's Cessna 402B research aircraft (http://aosc.umd.edu/~flaggmd/). Urban CH_4 emission rates from the area are estimated from data collected by both aircraft using the mass balance approach. Figure 1 shows the paths of both aircraft for the flights conducted over the Baltimore-Washington area in winters 2015 and 2016. A typical flight experiment consists of both upwind and downwind transects at different altitudes to capture the urban CH_4 enhancement on the downwind side. Spirals and en route vertical profiles as well as low-altitude flyovers above regional airports were conducted to capture vertical mixing of CH_4 and the depth of the planetary boundary layer (PBL). Flights were primarily conducted in winter when biogenic uptake of CO_2 is expected to be minimum. A summary of the flight experiments is provided in Table S1 of the supporting information (SI).

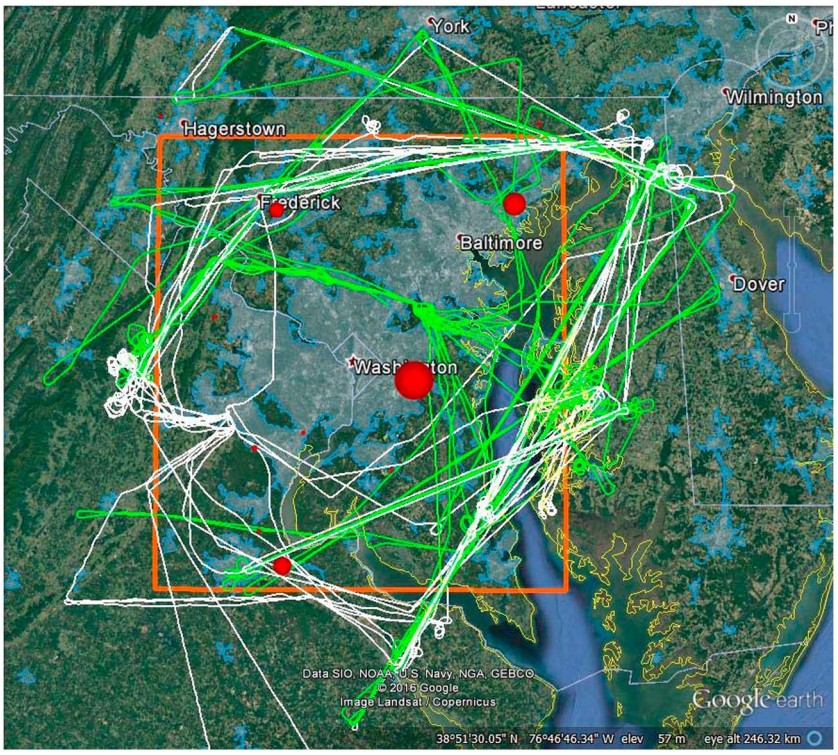

Figure 1. Flight paths of the Purdue's Duchess (white) and the University of Maryland's Cessna (green) aircraft over the Baltimore-Washington area in winters 2015 and 2016. Areas shaded in gray are urban areas from the U.S. census 2013. The orange rectangle represents the designated 130 × 156 km study area with coordinates for the four corners of (38°12′N, 77°42′W), (39°36′N, 77°42′W), (38°12′N, 76°12′W), and (39°36′N, 76°12′W). The red circles represent major landfills in the area. The diameter of each circle is approximately proportional to the estimated emission of CH_4 from each landfill based on our airborne observations.

The equipment on the Purdue Duchess aircraft included a global positioning system and inertial navigation system (GPS/INS), a Best Air Turbulence (BAT) probe for 3-D wind measurements, a Picarro cavity ring-down spectroscopy analyzer (Model G2301-m) for CH_4, CO_2, and water vapor (H_2O) measurements, and a Los Gatos Research Model RMT-200 nitrogen dioxide (NO_2) analyzer based on cavity enhanced absorption spectroscopy. Further details about the instrumentation on the Duchess have been provided elsewhere (Salmon et al., 2017, 2018).

The University of Maryland's Cessna aircraft was equipped with an instrument package to measure gaseous and particulate air pollutants. The aircraft instrumentation 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 GPS and an aircraft INS. Horizontal two-dimensional wind was calculated by a Garmin G600 system using the measured true heading, true airspeed, ground speed, and ground track angle (Conley et al., 2014). In October 2017 a measurement bias was discovered in the Garmin true heading that is based on the measured magnetic heading by a magnetometer on the Cessna. The Cessna wind measurement has been corrected for this error, as described in section S2.1 of the SI. In general the corrected Cessna winds agree with the winds observed by a wind profiler located in Beltsville, MD, and the winds from four models: the Weather Research and Forecasting Model (WRF 3 km), the North American Mesoscale Forecast System (NAM) 4 km, NAM 12 km, and the North American Regional Reanalysis (NARR). See Tables S2 and S3 of the SI for a detailed comparison.

The Cessna aircraft was equipped with the following trace gas analyzers: (1) a Picarro cavity ring-down spectrometer (CRDS, Model G2401-m) for CH_4, CO_2, carbon monoxide (CO), and H_2O measurements; (2) a modified Thermal Electron Model 49C ozone (O_3) analyzer based on UV absorption; (3) a modified Thermal Electron Model 43C sulfur dioxide (SO_2) analyzer based on pulsed fluorescence; and (4) a Los Gatos

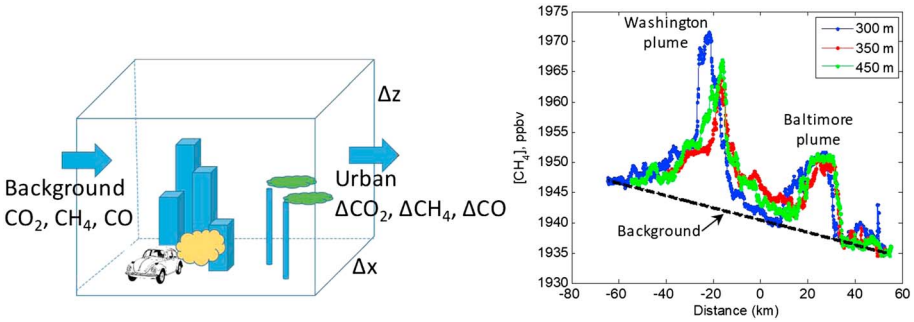

Figure 2. (left) The conceptual model of a mass balance approach to quantify greenhouse gas emissions from an urban environment. (right) Methane mixing ratios measured along three downwind flight transects at various altitudes on 13 February 2015. The thick black dashed line is the assumed CH_4 background defined from the interpolation of CH_4 levels measured at the edges of urban plumes in downwind transects. Enhancement of CH_4 was observed along the downwind transects of Baltimore and Washington, DC.

Research Model RMT-200 NO_2 analyzer based on cavity enhanced absorption spectroscopy. The aircraft was also equipped with three instruments 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 aerosol absorption, and an Aethalometer (Magee Model AE42) to measure black carbon. Calibrations for CH_4, CO_2, and CO were conducted both inflight and on ground using an onboard calibration system with standards certified at National Institute of Standards and Technology (NIST). Grab canisters were also used to collect whole air samples to measure volatile organic compounds (VOCs), including ethane that is used in this study, by Gas Chromatography-Flame Ionization Detector (GC-FID). The GC-FID was calibrated by a NIST-traceable standard with a measurement precision of ±10% for VOCs.

2.3. Mass Balance Approach

A mass balance approach is used to estimate total CH_4 emissions from the Baltimore-Washington area with assumptions of constant emissions, consistent wind speed, and wind direction, and stationary PBL depth during a given experiment with a duration of 4–5 hr (White et al., 1976; Cambaliza et al., 2014). Wind carrying background levels of CH_4 into the urban area encounters and advects CH_4 emissions out of the study area (Figure 2). Horizontal transects are flown roughly perpendicular to the prevailing wind direction downwind of the urban area, and local enhancements in CH_4 above background are intercepted and detected. The CH_4 emission rate from the area can be calculated using equation (1):

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

where, $[C]_{ij}$ is the concentration of CH_4 at a downwind location (x_i, z_i); $[C]_b$ is the background concentration detected at the edges of the downwind urban plume; $U_{\perp ij}$ is the perpendicular wind speed at a downwind location of (x_i, z_i); $[-x, +x]$ defines the horizontal width of the plume from the study area; and $[0, z]$ defines the mixing layer depth. We calculated the emission rate for each transect, then averaged the rates to come up with a rate for a given flight day.

The mean relative uncertainty of emissions found using the mass balance analysis of aircraft observations was estimated to be ±33%, based on a square root of the sum of squares combination of the following individual uncertainties: ±18% for the background CH_4 mixing ratio measured at the edges of downwind transects, ±20% for perpendicular wind speed ($U_\perp$), ±15% for the mixing layer height (Δz), ±6% for the plume width (Δx), and ±10% for the variation in the fluxes at different altitudes. A detailed uncertainty analysis for the estimation of CH_4 emission rate is presented in section S2 of the SI.

2.4. HYSPLIT Back Trajectory Simulation

Back trajectories are used to illustrate the transport history associated with the sampled air parcels and to identify CH_4 point sources like landfills. Back trajectory simulations were conducted with the starting

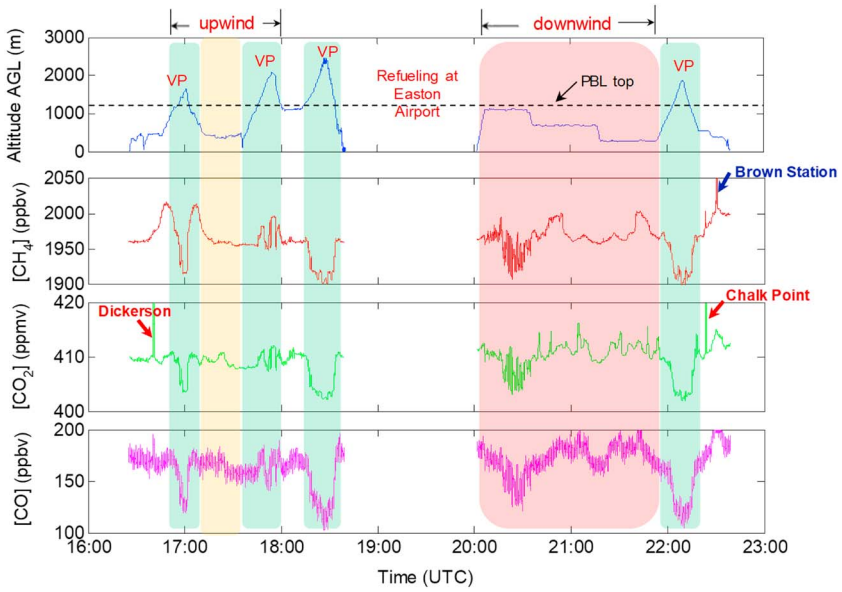

Figure 3. Time series of altitude, CH_4, CO_2, and CO mixing ratios measured in the upwind (yellow shaded) and downwind (light-red shaded) transects as well as during vertical profiles (VP, light-green shaded) in a mass balance experiment conducted on 20 February 2015. Noticeable isolated spikes of highly elevated CH_4 and CO_2 correspond to emissions from two power plants (Dickerson and Chalk Point) and a landfill (Brown Station), as indicated.

locations and times initialized along the upwind and downwind transects, using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, Version 854) model (Stein et al., 2015) and meteorological data from the North American Mesoscale (NAM) Forecast System model (Janjic, 2003; Janjic et al., 2001). The NAM wind fields have a horizontal resolution of 12 km, 26 vertical levels up to 20,000 m (including 9 levels under 2,000 m), and a temporal resolution of 3 hr.

3. Results

3.1. Aircraft Observations

We conducted a total of 10 mass balance flight experiments in winter 2015 and 5 experiments in winter 2016. Observations from a typical mass balance experiment shown in Figure 3 include one upwind transect followed by three downwind transects (in some flights only two downwind transects were carried out). Interpolation of mean mixing ratios of CH_4 observed on the edges of the urban plume along the downwind transects was used as background CH_4 (as shown in Figure 2) for the air parcels entering the study area. Enhancements of CH_4 in the downwind transects were calculated from the downwind CH_4 mixing ratios after subtracting the background CH_4.

Spirals and en route vertical profiles were conducted along both upwind and downwind transects to characterize the vertical variation of the CH_4 mixing ratio and to determine the PBL height. Figure S4 shows typical vertical profiles of CH_4, CO_2, water vapor, and potential temperature within and above the PBL. Air within the PBL was generally well mixed and the mixing layer height was determined as the altitude where the CH_4 mixing ratio reaches its free-tropospheric background level, the water vapor mixing ratio drops off, and the potential temperature increases rapidly (Figure S4).

The HYSPLIT back trajectories shown in Figure S5 demonstrate an example of the paths of air parcels passing through the Baltimore-Washington area and sampled at the downwind transects as well as the influence of the upwind Marcellus Shale area on the CH_4 background. The variability of background when the Marcellus Shale is upwind depends on wind direction and wind speed on a given day. The influence is likely taken into account in the background calculated as the averages on edges of the downwind urban plume and interpolated along the plume (Figure 2). Usually three downwind transects were conducted in each mass balance flight experiment and they illustrate the repeatability and relative uniformity of CH_4 plumes observed within the PBL (Figure 2).

Table 1
CH_4 and CO Emission Rates (ER) Estimated Based on the Mass Balance Flights Conducted During FLAGG-MD in Winter 2015

Flight date[a]	CH_4 ER (kg/s)	CO ER (kg/s)
2/6/2015	4.56	7.67
2/13/2015	2.10	5.60
2/18/2015	9.69	—[c]
2/19/2015	14.2[b]	15.9
2/20/2015	4.36	11.5
2/23/2015	10.5	9.80
2/24/2015	13.3	39.2
2/25/2015	5.98	9.24
2/27/2015	10.1	—[c]
3/11/2015	12.0	—[c]
Mean ± 1σ	8.66 ± 4.17	14.0 ± 11.5

Note. FLAGG-MD = Fluxes of Atmospheric Greenhouse Gases in Maryland. [a]Date is formatted as month/day/year. [b]Mean CH_4 emission rate determined by the Cessna and Duchess. Both research aircraft flew on this day. [c]Only the Duchess flew, without a measurement of CO.

3.2. CH_4 and CO Emissions Based on Mass Balance Approach

Mass balance flights on 15 days (10 days in winter 2015 and 5 days in winter 2016) were used to calculate the emissions of CH_4 and CO. Data are not used for individual flight transects that did not capture the full width of the Baltimore-Washington urban plume. The CH_4 and CO emission rates estimated by the mass balance approach are shown in Table 1 for winter 2015 and Table 2 for winter 2016.

There are significant variations in the emissions rates from flight to flight (Table 1). The CH_4 emission rates from the Baltimore-Washington area were 8.66 ± 4.17 kg/s in winter 2015 and 9.14 ± 4.49 kg/s (mean ±1σ standard deviation) in winter 2016. From the 15 independent flight days in Tables 1 and 2, the estimate of CH_4 emission rate is about 8.82 ± 2.08 kg/s (95% confidence interval, CI). The CO emission rates were 14.0 ± 11.5 kg/s in winter 2015 and 15.4 ± 7.8 kg/s in winter 2016. The average CH_4 emission rate derived from the aircraft wind observations agrees with that derived from the modeled winds, within the uncertainty of the mass balance approach (see section S3 of the SI). The mass balance emission estimates are more variable for 2016 than those found for 2015, mainly due to the winds in winter 2016 being more variable than in winter 2015.

Using the mass balance approach and upwind transects for the flights on 13, 19, 20, and 23 February 2015 when winds were mainly from northwest, we estimate CH_4 fluxes from the Marcellus Shale into the Baltimore-Washington area were 3.98, 4.15, 8.39, and 11.4 kg/s, respectively, with a mean and standard deviation of 6.98 ± 3.58 kg/s. This mean CH_4 flux is smaller than but comparable to the observed CH_4 flux out of the Baltimore-Washington area. No significant dependence between CH_4 flux and wind direction was observed (Figure S7). The mean flux of CH_4 (12.0 kg/s) estimated from three flights with southerly winds and thus little Marcellus influence was actually larger than the CH_4 flux (5.8 kg/s) estimated from all other flights by a factor of 2, further suggesting the influence of upwind Marcellus emissions has likely been taken into account in our definition of the background.

3.3. CH_4 Emissions From Landfills

There are 14 landfills in the study area. We surveyed 11 of them by carrying out downwind transects of the landfill plumes and estimated emissions using the same mass balance approach described above. The highest observed emission rate of CH_4 came from the Brown Station Sanitary Landfill (and nearby old closed landfills), located in Maryland, about 20 km to the east of downtown Washington, DC (the large red circle in Figure 1). Each year the landfill accepts ~250,000 tons of municipal solid waste (MDE, 2014). The landfill has been operating since 1968 and is expected to be closed in 2022 [USEPA GHGRP, 2017]. The landfill is equipped with a CH_4 collection system with a reported collection efficiency of about 84% (MDE, 2014). Several downwind transects at various altitudes and different distances away from the Brown Station landfill during the Winter 2015 flights were conducted to quantify the precision of emissions found using the mass balance approach. A representative CH_4 plume measured downwind of the Brown Station landfill plume is shown in Figure 4. A significant enhancement of CH_4, up to 120 ppbv larger than background, was observed in the plume about 13 km downwind of the landfill. Roadside Surveys of the Brown Station landfill using a mobile Picarro analyzer suggest large enhancement of CH_4 in the plumes downwind of this landfill (section S4 of the SI).

Table 2
CH_4 and CO Emission Rates (ER) Estimated Based on the Mass Balance Flights Conducted During FLAGG-MD in Winter 2016

Flight date[a]	CH_4 ER[b] (kg/s)	CO ER (kg/s)
2/8/2016	14.2	24.5
2/12/2016	4.46	10.9
2/17/2016	13.0	5.69
2/18/2016	5.16	13.6
2/19/2016	8.74	22.4
Mean ± 1σ	9.14 ± 4.49	15.4 ± 7.8

Note. FLAGG-MD = Fluxes of Atmospheric Greenhouse Gases in Maryland. [a]Date is formatted as month/day/year. [b]Mean emission rates measured by the two research aircraft.

The same aircraft-based mass balance approach as described above was used to quantify the emissions of CH_4 from the Brown Station landfill. Table 3 reports observed background CH_4, enhancements of CH_4 in the plumes, mean wind speed and direction, and PBL heights for nine flights conducted in Winter 2015. The emission rate of CH_4 from the Brown Station landfill inferred from these nine flights is 0.50 ± 0.11 kg CH_4/s

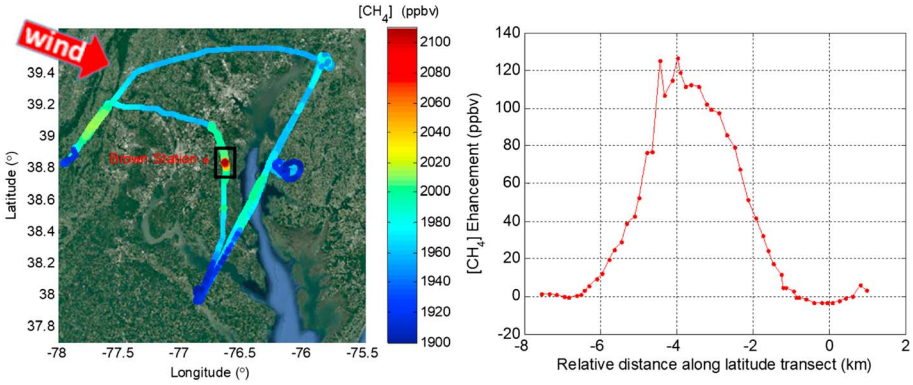

Figure 4. (left) A map showing flight track on 20 February 2015 colored with observed CH_4 mixing ratios and the location of the Brown Station landfill. A CH_4 plume was observed along the flight track downwind of the landfill. The black rectangle denotes the part of the flight with CH_4 data depicted in the right panel. (right) Enhancement of CH_4 above the nearby baseline, which reflects urban emissions, as a function of relative distance along the latitudinal transect of the plume.

(Table 3), which accounts for about 6% of the total inferred CH_4 emissions from the Baltimore-Washington area. Because the emission rates from the Brown Station landfill were measured at different downwind distances, ideally, they should be the same assuming the CH_4 emission rate of the landfill is constant during a given flight. The variation in the emission rates in Table 3 is thus a measure of the precision of the mass balance approach (Cambaliza et al., 2014; 2015). A variability of ~21% (1σ standard deviation of the mean CH_4 emission rate in each flight) in the emission rate of CH_4 emission from the Brown Station landfill was observed flight to flight, which could be caused by different CH_4 emission rates from the landfill under various meteorological (Lu & Kunz, 1981; Xu et al., 2014; Young, 1992) and surface/subsurface conditions as well as deviations from the assumption that the plume is well mixed within the PBL.

If we assume the emission rate we observed in winter is representative for the entire year, the annual CH_4 emission rate from the Brown Station landfill would be 15,600 metric tons CH_4/year. This rate is a factor of 9 larger than the rate of 1,740 metric tons/year from the Brown Station landfill reported by the EPA's Greenhouse Gas Reporting Program (GHGRP) for 2015. Additionally, the CH_4 emission rate from this landfill was 4,850 metric tons/year for 2014 in the GHGRP, which is still lower than the observed CH_4 emission rate by a factor of 3.2. It is unclear why the emission rate of CH_4 for this landfill given by the EPA GHGRP decreased dramatically from 2014 to 2015. According to the GHGRP, annual CH_4 emissions from the Brown Station landfill have been decreasing from 2010 and 2016, from 11,300 metric tons in 2010 to 1,750 metric tons in 2016 (section S7 of the SI).

Emissions of CH_4 from other landfills in Maryland and Virginia within our study area have also been estimated, and the results are summarized in Table 4. Also listed in Table 4 are the CH_4 emission rates reported by the

Table 3
Mean Measurements Along the Transects Downwind of the Brown Station Landfill Used in Equation (1) to Derive CH_4 Emission Rates (ER) From This Landfill During the Flights in Winter 2015

Flight date	Mean $[CH_4]_{bkg}$ (ppbv)	Mean $[CH_4]_{enhanced}$ (ppbv)	Mean WS (m/s)	Mean WD (°)	PBL height (m AGL)	Number of plumes	CH_4 ER (kg/s) mean ± 1σ
2/6/2015	1,950	1,990	8.85	221	520	3	0.412 ± 0.359
2/13/2015	1,957	1,970	7.09	261	1,400	4	0.443 ± 0.171
2/19/2015	1,990	2,025	15.07	287	1,100	3	0.524 ± 0.473
2/20/2015	2,003	2,024	6.59	255	1,250	2	0.467 ± 0.091
2/23/2015	1,938	1,955	11.38	320	1,400	3	0.552 ± 0.212
2/24/2015	1,978	2,005	6.49	175	800	2	0.743 ± 0.605
2/25/2015	1,960	1,977	6.11	252	1,400	3	0.452 ± 0.147
2/27/2015	1,986	1,999	7.79	317	1,530	3	0.385 ± 0.160
3/11/2015	2,005	2,029	8.55	332	620	2	0.499 ± 0.500

Note. The error bars in the last column show the variation (1σ) of CH_4 emission rates obtains during different transects in a given flight. The distances between the landfill and downwind transects ranged roughly from 10 to 30 km. Date is formatted as month/day/year.

Table 4
Estimated Mean CH_4 Emissions From the Landfills in the Study Area in Maryland (MD) and Virginia (VA) Using the 2015 Aircraft Observations

Landfill (# of transects/flights)	Mean ± 1σ CH_4 emission mass balance approach (kg CH_4/s)	EPA GHGRP 2015 (kg CH_4/s)	Maryland GHG inventory 2014 (kg CH_4/s)
Brown Station (27/10)	0.497 ± 0.106	0.054	0.090
Eastern Sanitary (12/5)	0.213 ± 0.250	0.072	0.099
Quarantine Road (15/7)	0.053 ± 0.064	0.053	0.257
Harford Waste (5/5)	0.141 ± 0.078	0.088	0.038
Reichs Ford (2/1)	0.316 ± 0.066	0.095	0.027
Route 40 West (3/3)	0.101 ± 0.119	0.111	0.149
Charles County (14/7)	0.130 ± 0.078	0.087	0.051
Cecil Central (2/1)	0.048 ± 0.043	0.064	0.035
Frederick Regional (7/5)	0.180 ± 0.093	0.082	N/A (in Virginia)
King George (6/2)	0.170 ± 0.202	0.375	N/A (in Virginia)
Stafford County (3/2)	0.192 ± 0.098	0.040	N/A (in Virginia)
MD landfill total	1.50 ± 0.80	0.624	0.747
MD + VA landfill total	2.04 ± 1.20	1.12	N/A

Note. The error bars in the second column show the variation (1σ) of CH_4 emission rates for different flights. Also shown are the emission data reported by the U.S. EPA's GHGRP for 2015 and the state of Maryland GHG inventory for 2014. EPA = U.S. Environmental Protection Agency; GHGRP = Greenhouse Gas Reporting Program; GHG = greenhouse gas.

EPA's GHGRP and state of Maryland GHG inventory (where appropriate). The total observed CH_4 emission rate for all 11 landfills is 2.04 ± 1.20 kg CH_4/s, which is greater than the total emission rate in the US EPA's GHGRP by a factor of 1.8 ± 1.0. The total emission rate from the eight landfills in Maryland is 1.51 ± 0.80 kg CH_4/s, which exceeds the state of Maryland's CH_4 inventory for these landfills by a factor of 2.0. The emission rate of CH_4 from the Brown Station landfill itself accounts for a quarter of the total observed rate from these landfills, but it constitutes a much smaller fraction of both national and state inventories.

Due to airspace restrictions in the Washington, DC area, we were not able to survey a few landfills in Virginia that are close to the DC area. To calculate total CH_4 emissions from the landfills in the study area, we added the emission values for these unsurveyed landfills in the GHGRP and then multiplied the sum by a factor of 1.8. The total CH_4 emissions from all landfills in this study area are estimated to be about 2.26 ± 1.33 kg CH_4/s, with 1.50 ± 0.80 kg CH_4/s from the landfills in Maryland (based on the aircraft observations) and 0.753 ± 0.529 kg CH_4/s from the landfills in Virginia based on both the observations for landfills we surveyed and the EPA GHGRP data for landfills we did not survey. This suggests the landfills contribute about 25 ± 15% of the total inferred CH_4 emissions in our study area.

Note the flight experiments were conducted in winter. It is possible that there are some seasonal variations in CH_4 emissions from landfills and the estimated CH_4 emission rates in winter in this study may not be representative of other seasons. Ground-based studies have shown that CH_4 emissions from landfills are higher in winter than in summer mainly due to lower biological CH_4 oxidation in winter (Borjesson & Svensson, 1997; Christophersen et al., 2001; Rachor et al., 2013) and can be influenced by changes in barometric pressure, soil temperature, soil moisture, and wind (Lu & Kunz, 1981; Rachor et al., 2013; Xu et al., 2014; Young, 1992). On the other hand, a model simulation of a landfill in Indianapolis, Indiana shows a monthly minimum CH_4 emission rate of 0.16 kg/s in March and a maximum of 0.24 kg/s in January (Cambaliza et al., 2017). Further observations of CH_4 emissions from this area in other seasons and under different meteorological conditions are needed to further assess the emission inventories.

3.4. Using CH_4/CO and CH_4/CO_2 Ratios to Estimate CH_4 Emission Rates

Emissions of CO and CO_2 from the Baltimore-Washington urban area have been estimated in various emission inventories. For example, the Emissions Database for Global Atmospheric Research (EDGAR) v4.3.1 estimates that the CO emission rate from this area was 0.459 million metric tons/year or 14.6 kg/s in 2010, which agrees within the uncertainty to the observed CO emission rate (14.6 ± 9.8 kg/s) for Winters 2015 and 2016. The US EPA's GHG Inventory (GHGI) estimates that CO_2 emissions from this area are about 102 million metric tons/year or 3,230 kg/s for 2014 (US EPA, 2014). Because many CO, CO_2, and CH_4 sources are collocated in urban areas, good correlations between CH_4 and CO as well as CH_4 and CO_2 are expected. Such behavior

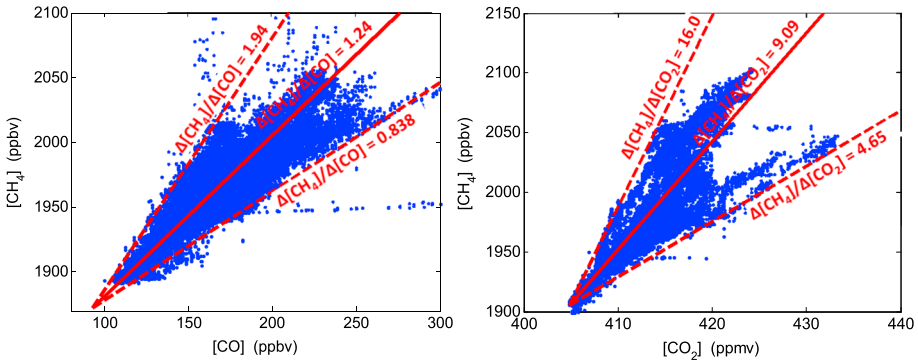

Figure 5. Scatter plot of observed CH_4 versus CO (left) in winter 2015 and CH_4 versus CO_2 (right) in winter 2016 over the Baltimore-Washington area. The solid red lines show the mean $\Delta[CH_4]/\Delta[CO]$ in parts per billion by volume per parts per billion by volume and $\Delta[CH_4]/\Delta[CO_2]$ in parts per billion by volume per parts per million by volume and red dashed lines indicate the upper and lower limits of the slopes. Observations with extremely high CH_4 (e.g., mainly in landfill plumes), CO (e.g., during takeoffs and landings), and CO_2 (in power plant plumes) are excluded from the slope estimate.

was observed during our study, as shown in Figure 5. Using the CO and CO_2 emission rates estimated in the inventories and observed CH_4-to-CO and CH_4-to-CO_2 ratios, we can estimate the CH_4 emissions according the following relation (Hsu et al., 2010; Wunch et al., 2009):

$$CH_4\ \text{Emission Rate} = \Delta[CH_4]/\Delta[X] \times [X\ \text{emission rate}] \quad (2)$$

where X = CO or CO_2. With the $\Delta[CH_4]/\Delta[CO]$ in Figure 5, we can infer the total CH_4 emissions from the Baltimore-Washington area to be 10.3 kg CH_4/s (with a range from 7.06 to 16.0 kg CH_4/s according to the minimum and maximum $\Delta[CH_4]/\Delta[CO]$ in Figure 5) based on the EDGAR CO inventory for 2010. This emission rate is inferred to be 12.0 kg CH_4/s (with a range from 5.29 to 19.2 kg CH_4/s according to the minimum and maximum $\Delta[CH_4]/\Delta[CO_2]$ in Figure 5) based on the US EPA CO_2 emission estimate for 2014 (US EPA, 2014) that are scaled to population in our study area. If we use the CO_2 emission rate of 4,230 kg/s estimated based on the aircraft observations, the inferred CH_4 rate would be 14.0 kg CH_4/s (with a range from 7.06 to 24.7 kg CH_4/s). The emission rates of CH_4 inferred in this manner are compared to both top-down and bottom-up estimates in section 3.6.4. Similar slopes of CH_4 versus CO_2 in 2015 and CH_4 versus CO in 2016 were observed, although the data were slightly more scattered in 2015 (Figure S15 in the SI). The CH_4/CO_2 ratios given by the national GHG inventory and EDGAR are significantly underestimated compared to the CH_4/CO_2 ratios observed in this study.

The observed CO to CO_2 mole ratio calculated from the Winter 2016 measurements is 0.53% as shown as the black line in Figure 6, which is in good agreement with the CO to CO_2 mole ratio (0.58%) observed at an I-95 near-road site located in Laurel, Maryland, in the middle of the Baltimore and Washington area (red line, Figure 6). The observed CO to CO_2 ratio is lower than the ratio of 0.93% given in the EDGAR 2010 emission inventory for this area, possibly because the CO emission rate in the EDGAR 2010 inventory is too high or its CO_2 emission rate is too low. Salmon et al. (2018) found higher CO emissions in the EPA National Emissions Inventory (NEI) 2011 and 2014 than observed for our study area.

3.5. Ethane/Methane Ratio

To understand the CH_4 source attribution in the Baltimore-Washington area, one approach to use is the ethane-to-methane (C_2H_6-to-CH_4) ratio. Figure 7 shows the ethane versus methane mixing ratios observed in the grab sample canisters collected during flights over the Baltimore-Washington area in winters 2015 and 2016. The slopes of the best fit line to the C_2H_6 versus CH_4 data are 3.30 ± 0.35% in winter 2015 and 4.31 ± 0.63% in winter 2016. The mean C_2H_6-to-CH_4 mole ratio in the monthly grab samples of natural gas was 8.40% (with a weighted mole fraction of 0.9110 for CH_4 and 0.0765 for C_2H_6) in February 2015 and 7.81% (with a mole fraction of 0.9183 for CH_4 and 0.0717 for C_2H_6) in February 2016. These monthly grab samples were taken from natural gas delivered by Baltimore Gas & Electric Company (BGE, unpublished data) at

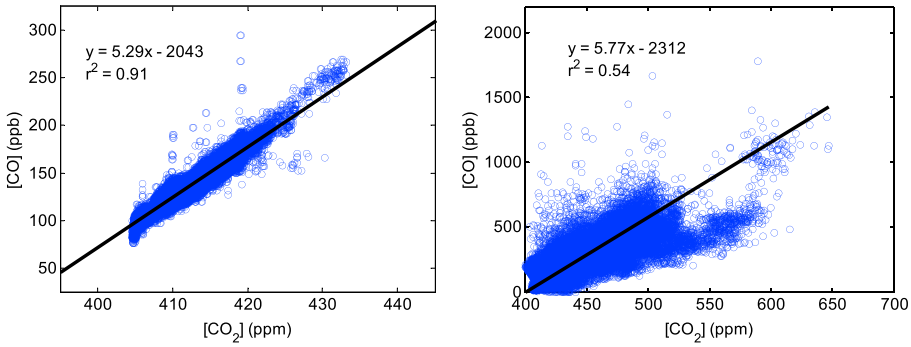

Figure 6. (left) Observed CO versus CO_2 (blue circles) and its linear regression (the thick black line) during FLAGG-MD in winter 2016. The CO to CO_2 mole ratio is 0.53%, which equals 5.29 ppb/ppm × 100. (right) The observed CO versus CO_2 (blue circles) and its linear regression (the thick black line) at an I-95 near-road site located in Laurel, Maryland. FLAGG-MD = Fluxes of Atmospheric Greenhouse Gases in Maryland.

three gate stations to Baltimore City and all or part of 10 Central Maryland counties. Because other major CH_4 sources like landfills, enteric fermentation, and waste water treatment emit little ethane, it is reasonable to use the observed C_2H_6-to-CH_4 mole ratio in the air compared to the ratio in the natural gas system to infer that the contribution of the natural gas system to the total area-wide emission rate of CH_4 was 39 ± 15% in winter 2015 and 55 ± 21% in winter 2016. We can then infer that the natural gas system in the study area emitted 3.40 ± 1.70 kg CH_4/s in winter 2015 and 5.04 ± 2.52 kg CH_4/s in winter 2016. These CH_4 emission rates from the natural gas system represent 1.1 ± 0.6% of the natural gas delivered to all customers in the study area in February 2015 and 2.1 ± 1.0% in February 2016 (section S6 of the SI). These percentage numbers are similar to leakage rates estimated for Los Angeles of 0.7% (Peischl et al., 2013) and 2% (Wennberg et al., 2012) and for Boston of 2.7% by (McKain et al., 2015).

We note there are limited C_2H_6 measurements in the VOC samples collected during the flights and the C_2H_6-to-CH_4 mole ratio in the pipeline line is from monthly grab samples. This may introduce some uncertainties in the inferred contribution of the natural gas system to the total area-wide CH_4 emission. Continuous measurements of both C_2H_6 and CH_4 would be beneficial for advancing the use of ethane to better quantify the role of leaks from the natural gas system.

3.6. Comparison to Emission Inventories

3.6.1. Comparison to the Maasakkers CH_4 Inventory for 2012

Using the gridded U.S. national CH_4 inventory for 2012, the CH_4 emissions from the Baltimore-Washington area within the yellow outline in Figure 1 are estimated to be about 3.09 kg CH_4/s (Maasakkers et al.,

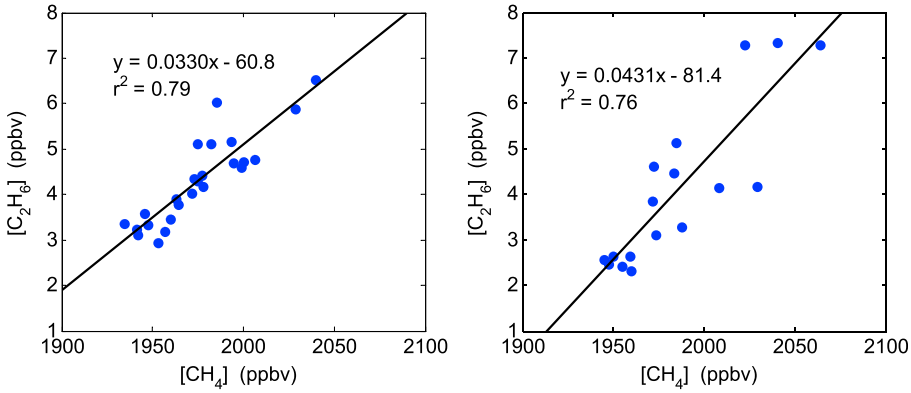

Figure 7. Ethane versus methane over the Baltimore-Washington region in winters of 2015 (left) and 2016 (right). Individual points represent measurements from the whole air samples. The solid lines show a linear regression best fit to the data.

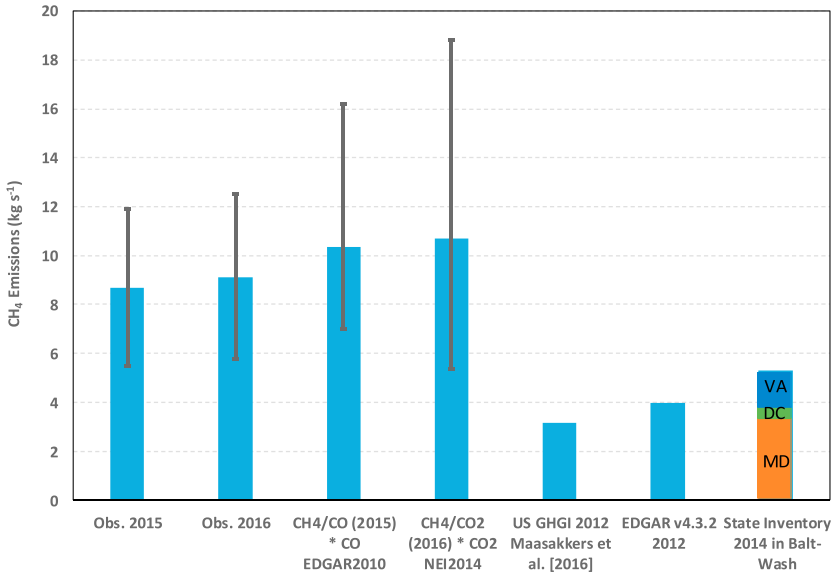

Figure 8. Summary of top-down and bottom-up CH_4 emissions from the Baltimore-Washington area. The four leftmost estimates are based on our aircraft (i.e., top-down) data; the other three values are from previously published (i.e., bottom-up) inventories.

2016), a factor of 2.8 smaller than the 8.82 kg CH_4/s emission rate estimated from the aircraft observations for winters 2015 and 2016 (Figure 8). Annual emission rates in the Maasakkers CH_4 inventory for 2012 are used for all sectors except the following six: stationary combustion, petroleum, natural gas production, manure management, rice cultivation, and field burning. For these six sectors, monthly emission rates in the Maasakkers CH_4 inventory for 2012 are available and used for comparison. Landfills are responsible for about half (49%) of the total emissions of CH_4 in this area according to the source attribution in this CH_4 inventory for 2012, even though the magnitude of CH_4 emissions from landfills is under estimated. Our observations indicate that the study area's landfills contribute about 25% of the total CH_4 emissions. Other important CH_4 sources in this area, as reported by the Maasakkers CH_4 inventory, include natural gas transmission and distribution (21%), enteric fermentation and manure management (12%), mobile and stationary combustion (8%), and waste water treatment (8%; Figure S12).

3.6.2. Comparison to a State Emissions Inventory

The Maryland Department of Environment (MDE) publishes state-wide emission inventories of GHG, including CH_4. MDE estimates that the state-wide yearly CH_4 emissions were 1.18×10^5 metric tons in 2014 (MDE, 2014) or 3.74 kg CH_4/s or 6.22×10^{-4} kg·s^{-1}·person^{-1}. Assuming the CH_4 emissions scale with population, we infer a total CH_4 emission rate of 5.29 kg/s from the Baltimore-Washington area, which has a total population of 8.50 million. This is smaller than the observed CH_4 emission rate by a factor of 1.7, although we are comparing winter data to an annual average. The MDE CH_4 inventory suggests that attribution of CH_4 emissions by source in Maryland for 2014 is different from that in the U.S. CH_4 inventory for 2012, with 24% from the natural gas system, 22% from landfills (similar to our analysis, 25%), 17% from enteric fermentation and manure management, 16% from wastewater treatment, and the rest from other minor sources (Figure S13).

3.6.3. Comparison to EDGAR

EDGAR (http://edgar.jrc.ec.europa.eu) includes a gridded global CH_4 emission inventory with a spatial resolution of 0.1° × 0.1°. The total CH_4 emissions from the Baltimore-Washington area are estimated to be 3.98 kg CH_4/s in the EDGAR v4.3.2 CH_4 emission inventory for 2012 (Janssens-Maenhout et al., 2017; Figure S10). This emission rate is larger than the value in the U.S. CH_4 inventory 2012 but is smaller than the inferred CH_4 emission rate based on the state of Maryland CH_4 inventories for 2014. The EDGAR CH_4 emission rate is also lower than the observed CH_4 emission rate by a factor of 2.2. There may be an issue with EDGAR emissions as the CH_4 sources are mainly allocated based on population instead of source locations (Maasakkers et al., 2016). The gridded points with large CH_4 emissions are generally located in the urban areas with large population. We note that there are no significant CH_4 emissions from the grids in the EDGAR4.3.2 CH_4 emission inventory

where three landfills (Brown Station, Eastern Sanitary, and King George) are located, even though large CH_4 emissions were observed from these landfills (Figure S10 and Table 4).

The source attribution of CH_4 emissions given by EDGAR4.3.2 shows 53% from solid waste landfills, 26% from the wastewater treatment, but only 9% from the natural gas system, and the rest from other minor sources (Figure S10). Again, our aircraft observations indicate about 25% is actually occurring from landfills. We note that CH_4 emissions from the natural gas sector in EDGAR4.3.2 for 2012 in our study area were significantly reduced compared to EDGAR4.2 for 2010, as discussed in section S5 of the SI.

3.6.4. An Overall Comparison of Top-Down/Bottom-Up Emissions

Figure 8 shows a summary of CH_4 emissions based on the aircraft mass balance experiments, in the three CH_4 inventories as well as inferred from the CO and CO_2 inventories and observed CH_4-to-CO and CH_4-to-CO_2 ratios. The observed CH_4 emission rates from the Baltimore-Washington study area using the mass balance approach applied to aircraft data (first two values in Figure 8) are similar to those inferred from the observed CH_4/CO and CH_4/CO_2 ratios applied to the EDGAR and U.S. NEI emission inventories of CO and CO_2, respectively (section 3.4). However, emissions of CH_4 from both of our methods are larger than the global, national, and state CH_4 emission inventories by a factor of ~1.7 to 2.8. Our analysis of data near 11 landfills indicates this source contributes about 25 ± 15% of the overall emissions, and comparison of the observed C_2H_6 to CH_4 ratio suggests leakage from the natural gas system is responsible for about 40-60% of the emitted CH_4, the latter being significantly underestimated in the inventories. The remaining emissions are from enteric fermentation and manure management, wastewater treatment, and other minor sources.

With observed emission rates of 8.66 kg/s for CH_4 and 4,230 kg/s for CO_2 from the Baltimore-Washington study area in Winter 2015, the radiative forcing of climate due to CH_4 is about 18% of the radiative forcing due to CO_2, over a 20-year time horizon. Given the dominance of the natural gas system (40–60%) and landfills (25 ± 15%), the reduction of future emission of CH_4 from these sources would result in a significant reduction of the total GHG burden originating from the Baltimore-Washington region.

4. Conclusions

We conducted the first aircraft mass balance experiments over the Baltimore-Washington area in winters 2015 and 2016 and estimated the average CH_4 emission rates to be 8.66 ± 4.17 kg/s in winter 2015 and 9.14 ± 4.49 kg/s in winter 2016 (mean ±1σ standard deviation of multiple flights). Comparing our winter data to annual averages, these observed emission rates are a factor of 2.8 larger than the emission rate inferred from the U.S. CH_4 inventory for 2012 and a factor of 1.7 larger than the population-apportioned emissions estimated from the state of Maryland CH_4 inventory. The mass balance estimated of CH_4 emissions are similar to values of CH_4 emissions inferred from CO emissions in the EDGAR inventory for 2010 and the CO_2 emissions in the U.S. EPA GHGI for 2014 coupled with the observed CH_4/CO and CH_4/CO_2 ratios, lending credence to the accuracy of our empirical top-down estimates. Fifteen independent observations and agreement among three methods adds confidence to the estimate of about 8.82 ± 2.08 kg/s (95% CI).

We have shown that the major CH_4 sources in this area are landfills and the natural gas system. Emissions of CH_4 from numerous landfill facilities in the area were quantified using the mass balance approach. Based on the observations in winter 2015, the observed total CH_4 emission from the landfills in Maryland are greater than the U.S. EPA's GHGRP emission rate by a factor of 1.8 and the state of Maryland CH_4 inventory by a factor of 2.0. A large CH_4 point source was identified to be the Brown Station landfill or nearby facilities, which accounts for about 6% of total CH_4 emissions from this area and has a CH_4 emission rate an order of magnitude greater than that given in the U.S. EPA's GHGRP and state of Maryland inventories. The measured ethane-to-methane ratios in the limited canister samples collected during the flights, with a mean of 3.3% in winter 2015 and 4.3% in winter 2016, indicate that ~40–60% of CH_4 emissions in this area are from the natural gas system.

Overall CH_4 is responsible for ~18% of the total climate radiative forcing due to CO_2 in the Baltimore-Washington study area over a 20-year time horizon. Quantification of urban CH_4 emissions is thus important for mitigating anthropogenic GHG emissions. More top-down observations, especially mass balance observations in other seasons, perhaps coupled with continuous measurements of ethane, are needed to better quantify CH_4 emissions from urban areas. Such measurements would be useful for

further assessment of inventories of CH_4 emissions, to understand the reason for differences in CH_4 emissions from various estimates, and to establish scientifically sound and cost-effective policies for mitigating future release of CH_4 guided by such program like the Maryland Climate Change Plan.

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