AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Atmospheres

RESEARCH ARTICLE

10.1002/2013JD021272

Key Points:

- Emissions from an oil and gas basin are estimated using airborne measurements
- Inventories underestimate hydrocarbon emissions by a factor of 2 or more

Supporting Information:

- Readme
- Supplemental Text S1, Tables S1 and S2, and Figures S1–S5

Correspondence to:
G. Pétron,
Gabrielle.Petron@noaa.gov

Citation:
Pétron, G., et al. (2014), A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin, *J. Geophys. Res. Atmos.*, *119*, 6836–6852, doi:10.1002/2013JD021272.

Received 28 NOV 2013
Accepted 30 APR 2014
Accepted article online 7 MAY 2014
Published online 3 JUN 2014

A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin

Gabrielle Pétron[1,2], Anna Karion[1,2], Colm Sweeney[1,2], Benjamin R. Miller[1,2], Stephen A. Montzka[2], Gregory J. Frost[1,2], Michael Trainer[2], Pieter Tans[2], Arlyn Andrews[2], Jonathan Kofler[1,2], Detlev Helmig[3], Douglas Guenther[1,2], Ed Dlugokencky[2], Patricia Lang[2], Tim Newberger[1,2], Sonja Wolter[1,2], Bradley Hall[2], Paul Novelli[2], Alan Brewer[2], Stephen Conley[4], Mike Hardesty[1], Robert Banta[2], Allen White[2], David Noone[1,5], Dan Wolfe[1], and Russ Schnell[2]

[1]Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA, [2]NOAA Earth System Research Laboratory, Boulder, Colorado, USA, [3]Institute for Arctic and Alpine Research, University of Colorado Boulder, Boulder, Colorado, USA, [4]Department of Land, Air and Water Resources, University of California, Davis, California, USA, [5]Department of Atmospheric and Oceanic Sciences, University of Colorado Boulder, Boulder, Colorado, USA

Abstract Emissions of methane (CH_4) from oil and natural gas (O&G) operations in the most densely drilled area of the Denver-Julesburg Basin in Weld County located in northeastern Colorado are estimated for 2 days in May 2012 using aircraft-based CH_4 observations and planetary boundary layer height and ground-based wind profile measurements. Total top-down CH_4 emission estimates are 25.8 ± 8.4 and 26.2 ± 10.7 t CH_4/h for the 29 and 31 May flights, respectively. Using inventory data, we estimate the total emissions of CH_4 from non-O&G gas-related sources at 7.1 ± 1.7 and 6.3 ± 1.0 t CH_4/h for these 2 days. The difference in emissions is attributed to O&G sources in the study region, and their total emission is on average 19.3 ± 6.9 t/h, close to 3 times higher than an hourly emission estimate based on Environmental Protection Agency's Greenhouse Gas Reporting Program data for 2012. We derive top-down emissions estimates for propane, *n*-butane, *i*-pentane, *n*-pentane, and benzene from our total top-down CH_4 emission estimate and the relative hydrocarbon abundances in aircraft-based discrete air samples. Emissions for these five nonmethane hydrocarbons alone total 25.4 ± 8.2 t/h. Assuming that these emissions are solely originating from O&G-related activities in the study region, our results show that the state inventory for total volatile organic compounds emitted by O&G activities is at least a factor of 2 too low for May 2012. Our top-down emission estimate of benzene emissions from O&G operations is 173 ± 64 kg/h, or 7 times larger than in the state inventory.

1. Introduction

As a result of its unique geology, the state of Colorado has had a long history of natural resources extraction [*Scamehorn*, 2002]. More recently, Colorado has experienced an unconventional fossil fuel production boom in coal bed methane, tight sand and shale natural gas, shale oil, and associated gas. Tar sands and shale oil development could be next (http://ostseis.anl.gov/eis/index.cfm). The Denver-Julesburg (D-J) Basin in NE Colorado produces both oil and natural gas (O&G) from mostly tight sand and shale formations. The formation extends eastward from the Rocky Mountains to western Nebraska and Kansas and northward from Denver, Colorado, to southern Wyoming. It has been actively explored and drilled since the 1970s. The most densely drilled region of the D-J Basin is located in Weld County, between Denver and Greeley (Figure 1).

With higher natural gas prices between 2004 and 2009 and, more recently, the discovery of crude oil in the Niobrara Shale [*Colorado Department of Natural Resources*, 2011], Weld County has been experiencing a drilling surge, with the addition of close to 10,000 new wells since 2005 [*Colorado Oil and Gas Conservation Commission* (*COGCC*), 2014] (see supporting information Figure S1). In 2012, Weld County was home to 24,000 active oil and gas wells that accounted for 74% of the oil (5.8 million m3 out of 7.8 million m3 or 36.5 out of 49 million barrels) and 13% of the natural gas (7.7 billion m3 out of 59.5 billion m3 or 272 billion cubic feet out of 2.1 trillion cubic feet) produced in Colorado [*COGCC*, 2014]. Garfield County (19.8 billion m3 or 700 Bcf) in the Piceance Basin in western Colorado and La Plata (11.1 billion m3 or 393 Bcf) and Montezuma (10.5 billion m3 or 370 Bcf) Counties in the San Juan Basin in southwestern Colorado were the top three natural gas producers in 2012 [*COGCC*, 2014].

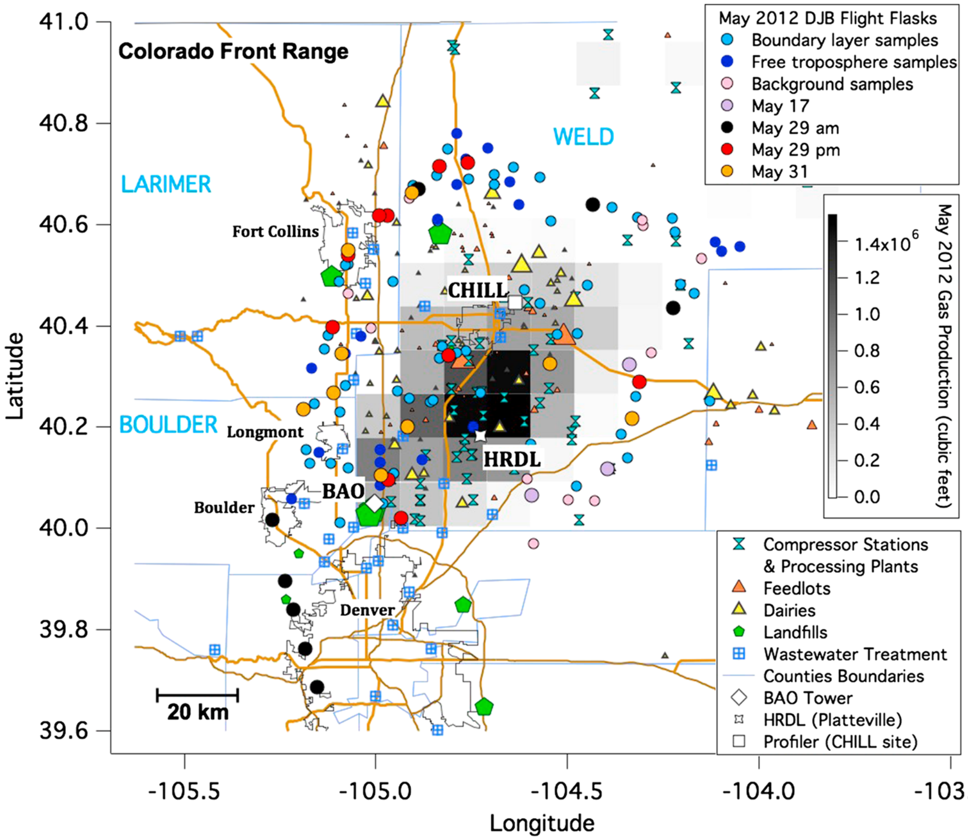

Figure 1. Map of Colorado's northern Front Range. Locations of ground-based meteorological measurements HRDL and CHILL and the BAO tower are shown in white symbols. The locations of the aircraft discrete air samples collected in May 2012 are shown with colored circles: light blue for boundary layer samples, dark blue for free troposphere samples, light pink for background samples, light purple, red, and orange for flights on three different days (17, 29, and 31 May 2012). Natural gas production in May 2012 (binned by township 6 × 6 km^2) is shown on a gray scale in the background. Compressor stations and processing plants are shown with blue hourglass symbols, feedlots with orange triangles, dairy farms with yellow triangles, landfills with green pentagons, and wastewater treatment plants with blue crossed squares. The size of the symbols for animal operations reflect their permitted capacity, and the size of the symbols for the landfills reflect the 2012 facility-level CH_4 emission estimates reported to the Environmental Protection Agency (EPA) Greenhouse Gas Reporting Program (GHGRP).

In 2007, a large region encompassing the Denver metropolitan area and most of the northern Front Range of Colorado was officially declared a nonattainment area (NAA) for the national ambient air quality standard for 8 h average ground-level ozone (O_3) (www.colorado.gov/cdphe/attainment). The urban corridor in the Front Range lies between the Rocky Mountains and the D-J Basin's O&G operations. Under stagnant and hot summer conditions, O_3 precursors (volatile organic compounds (VOCs) and nitrogen oxides) emitted by various sources accumulate and react, leading to elevated O_3 levels. Previous analysis found that O&G operations were responsible for 40% of the total mass of anthropogenic VOCs emitted in the NAA [*Colorado Department of Public Health and the Environment* (*CDPHE*), 2008]. As a result, since 2007 the Colorado Department of Public Health and the Environment (CDPHE) has implemented stricter VOC emission regulations for O&G sources in the Colorado Front Range NAA.

Atmospheric chemical measurements conducted throughout the northern Colorado Front Range between 2007 and 2010 showed elevated levels of several hydrocarbons found in natural gas and oil, including CH_4 and other light alkanes (ethane (C_2H_6), propane (C_3H_8), *i*-butane (iC_4H_{10}), *n*-butane (nC_4H_{10}), *i*-pentane (iC_5H_{12}), and *n*-pentane (nC_5H_{12})), and sometimes aromatics including the carcinogen benzene (C_6H_6) [*Eisele et al.*, 2009; *Pétron et al.*, 2012; *Lafranchi et al.*, 2013]. These measurements showed similar relative enhancements of nonmethane hydrocarbons (NMHCs) as those observed in the early 1990s by *Goldan et al.* [1995] [see *Pétron et al.*, 2012].

In February 2011, *Gilman et al*. [2013] and *Swarthout et al*. [2013] participated in a 3 week intensive measurement campaign at the National Oceanic and Atmospheric Administration (NOAA) Boulder Atmospheric Observatory (BAO) tower, on the southwest edge of the D-J Basin. They measured an extensive suite of VOCs in situ and in flasks near the surface and confirmed the likely large role played by O&G operations emissions in the Front Range summertime O_3 problem. *Gilman et al*. [2013] showed that effluents from O&G operations in the region during the campaign contributed over half of the total VOC reactivity with OH, the first step in the chemical oxidation chain leading to near-surface O_3 formation.

Pétron et al. [2012] and *Swarthout et al*. [2013] both attempted to constrain emissions of CH_4 and several NMHCs from O&G operations in Weld County. *Pétron et al*. [2012] used hydrocarbon dry air mole fractions measured in air samples collected daily (between fall 2007 and April 2010) at midday from a 300 m agl (meters above ground level) inlet at the NOAA BAO tower and bottom-up information (raw natural gas mean composition and flashing (degassing) emissions from oil storage tanks estimates provided by the State). *Pétron et al*. [2012] estimated that in 2008 fugitive emissions of raw natural gas were underestimated by a factor of 2. The likely leakage range fell within 2.3% to 7.7% of production (average 4%), compared to an estimated 1.6% based on inventory data [*Bar-Ilan et al*., 2008; *Pétron et al*., 2012]. *Pétron et al*. [2012] estimated that CH_4 and C_3H_8 annual emissions from O&G operations in Weld County in 2008 likely ranged between 71 and 252 Gg/yr (8–29 t/h) and 21 and 65 Gg/yr (2.4–7.4 t/h), respectively.

Swarthout et al. [2013] calculated emission rates for several alkanes and C_6H_6 based on the increase in NMHCs mixing ratios in air samples collected from a 22 m agl inlet at the NOAA BAO tower site in the nocturnal boundary layer during five nights with low surface winds in February 2011, assuming no vertical mixing and no chemical destruction. They extrapolated their BAO flux results to the Wattenberg Field and to Weld County (two different but largely overlapping subregions of the D-J Basin that both lie within the Colorado Front Range NAA), assuming emissions were homogeneous in space and could be scaled with surface area. Their extrapolated C_3H_8 emission estimates were 13 ± 3 Gg/yr (1.5 ± 0.3 t/h) using the Wattenberg Field surface area and 40 ± 4 Gg/yr (4.6 ± 0.5 t/h) using the larger surface area of Weld County. February 2011 oil and natural gas production statistics for the Wattenberg Field were 19% and 7% lower than production statistics for Weld County, while the *Swarthout et al*. [2013] surface area-based emission estimates for these two regions differed by a factor of 3. It is important to note that large areas in Weld County have no oil and gas operations (Figure 1), so it is not appropriate to simply scale the BAO results with surface area.

The emission estimates reported in *Pétron et al*. [2012] and *Swarthout et al*. [2013] relied in part on simple emission models with unverifiable assumptions [*Levi*, 2012; *Pétron et al*., 2013] and, in the case of *Swarthout et al*. [2013], on measurements with likely limited spatial representativeness. In this paper, we present results from an alternative top-down approach to estimate the total emissions of CH_4 and five NMHCs in Weld County on 2 days in May 2012.

The rest of the paper is organized as follows. In section 2 we describe the study region and the measurements during the intensive airborne campaign. Top-down regional emission estimates for CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 are presented in section 3. In section 4, we compare these results with inventories. In section 5, we conclude with a summary of the measurement-based results and their significance.

2. Experiment

2.1. Region of Study

The D-J Basin is a prolific fossil fuel reserve, with a stack of multiple sedimentary rocks in the form of sandstone and shale deposited in the Western Interior Basin of North America during the Cretaceous and now buried thousands of feet below the surface. Several of these rock formations contained deposits rich in marine organic matter [*Sonnenberg*, 2012]. The organic matter trapped in buried rocks underwent thermogenic decomposition in the deeper part close to the north/south axis of the D-J Basin and biogenic decomposition in some of the shallower parts on the eastern flank [*Fishman et al*., 2005; *Higley and Cox*, 2007; *Sonnenberg*, 2012].

Our study focuses on a 70 km × 85 km region in northeastern Colorado encompassing the highest density of the O&G production activities in the D-J Basin, mostly located in Weld County, north of Denver and east of Boulder and Larimer Counties (Figure 1). Most wells in the region produce what is referred to as wet or associated gas, which means natural gas coproduced with oil. Oil wells contribute close to 50% of the total natural gas produced in the region [*Pétron et al.*, 2013]. In addition to over 24,000 producing wells in 2012, Weld County was also home to more than 6000 oil or liquid condensate storage tanks (the vast majority located on well pads), 27 gathering compressor stations, 11 processing plants (CDPHE, personal communication, 2013), and over 1000 miles of natural gas transmission pipelines.

Every year, between several hundred and a few thousand new wells are drilled and completed (with hydraulic fracturing) in Weld County [*COGCC*, 2014]. Existing wells are sometimes refractured to target new natural gas and oil-bearing formations or to restimulate production from previously targeted zones. The American Petroleum Institute reports that the D-J Basin has the highest refracturing rate in the nation, 14%, versus 1% for the national average [*API/ANGA*, 2012].

Over 100 different oil- and gas-producing companies operate in the D-J Basin. A team of nine O&G inspectors at CDPHE is in charge of checking compliance for O&G permitted facilities. They typically inspect a subset of operations from larger companies every 3 years on average and from smaller companies every 5 years on average (CDPHE, personal communication, 2013).

There are other CH_4 sources in the region. Beef and dairy production is a major economic activity in Weld County, with over half a million head of cattle [*USDA*, 2012]. Enteric fermentation in ruminants and manure management facilities are known sources of CH_4 [*Johnson and Johnson*, 1995; *U.S. Environmental Protection Agency* (*EPA*), 2013a]. CH_4 is also emitted from a few large landfills and several wastewater treatment plants servicing the over 2 million people living in the northern Colorado Front Range.

2.2. Methods

The ground and airborne-based measurements conducted in the D-J Basin in May 2012 were similar to those carried out in the Uinta Basin of northeastern Utah in February 2012 and described in *Karion et al*. [2013]. Airborne measurements of CH_4 with a Cavity Ring Down Spectroscopic gas analyzer (Picarro Model # G2401-m) were conducted on 11 different days (12 flights) between 4 and 31 May 2012. Each flight lasted between 3 and 4 h. In-flight measurement repeatability of the CH_4 dry air mole fraction was ± 0.5 ppb (defined as the standard deviation of measurements of a standard gas at the measurement frequency of ~0.5 Hz), and total uncertainty of the measurements was ± 2 ppb (see section S1 in Text S1). The single-engine Mooney TLS aircraft was stationed at Boulder Municipal Airport, located in the southwest corner of the study region, which was the starting and ending point of each flight. A total of 118 discrete air samples (up to 12 on each individual flight) were collected on those flights and analyzed at the National Oceanic and Atmospheric Administration Earth System Research Laboratory Global Monitoring Division (NOAA ESRL GMD) in Boulder for 49 trace gases, including carbon monoxide (CO) and the following seven hydrocarbons: CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6H_6, and acetylene (C_2H_2).

In May 2012, NOAA ESRL also deployed a boundary layer wind profiler and a high-resolution Doppler lidar (HRDL) at two different locations in the basin; both provided vertically resolved measurements of horizontal wind speed and direction and boundary layer height at 20 to 30 min resolution [*Grund et al.*, 2001]. Meteorological measurements (surface temperature and turbulent heat flux) conducted by the University of Colorado near the NOAA BAO tower outside Erie, Colorado, were used to assess the surface energy budget and the resulting vertical mixing within the planetary boundary layer (PBL) on the 2 days retained for a mass-balance flux calculation. All measurements are described in further detail in Text S1.

To put the intensive aircraft campaign results into a broader context, we compare the airborne flask measurements with long-term measurements of flask air samples collected daily from the 300 m agl inlet of the NOAA BAO tower since fall 2007. To filter the BAO data by wind sector, we use 30 s wind speed and direction measurements collected by the NOAA ESRL Physical Sciences Division at the tower 300 m agl level (www.esrl.noaa.gov/psd/technology/bao).

The aircraft and BAO discrete air samples discussed here were all analyzed by NOAA ESRL GMD for CH_4 using a gas chromatography GC-flame ionization detector [*Dlugokencky et al.*, 1997], for CO using resonance fluorescence at ~150 nm with a repeatability of ± 0.4 ppb [*Novelli et al.*, 1998] and for 43 other compounds including the six nonmethane hydrocarbons mentioned above using a GC-mass spectrometry (MS) [*Montzka et al.*, 1993; *Pétron et al.*, 2012; *Lafranchi et al.*, 2013]. The GMD analyses of NMHCs in aircraft and BAO samples are reported on the same calibration scale: C_6H_6 on NOAA-2006 and all other hydrocarbons (besides CH_4) on

NOAA-2008. See also section S2 in Text S1 for more information on the NOAA CH_4 calibration scale and results from a NMHC interlaboratory measurement comparison, which GMD participated in.

3. Results and Discussion

3.1. Total CH_4 Emission Mass-Balance Estimates

In the mass-balance approach used here, airborne measurements of CH_4 dry air mole fraction (moles of CH_4 per mole of dry air) are combined with ground-based wind speed and direction measurements to estimate total CH_4 mass fluxes in and out of a region of the atmosphere surrounding O&G producing wells in the D-J Basin (Figure 1). The resulting top-down CH_4 flux reflects an aggregate emission from all CH_4 sources within the region for several hours on the days of the measurements (see section S6 in Text S1 for more details). Given the short transit time between the emission sources and our measurements ($<$ 0.5 day) and a global CH_4 lifetime close to 9 years, atmospheric chemical losses of CH_4 are insignificant and are not considered here. In the rest of this section, we describe the main atmospheric measurements used to derive the total top-down CH_4 flux estimates on 29 and 31 May 2012.

A first estimate of CH_4 emissions from the D-J Basin is made using two separate downwind transects at two different altitudes 150 m apart on 29 May (Figure 2, Table S1, and section S6 in Text S1). On that day the average winds in the planetary boundary layer (PBL) are from the SE at 3.7 ± 0.9 m/s, and the downwind transects on the western side of the region show a 90 km long CH_4 plume with enhancements spanning 10 to 35 ppb over background (1881 ± 4 ppb). The highest enhancements in CH_4 ($>$20 ppb above background) occur downwind of the most active oil and natural gas production area in the basin (centered around Platteville, Colorado; Figure 1). The top of the PBL during the downwind transect on 29 May is located at 3600 m above sea level (m asl, ~2100 ± 230 m agl).

On 31 May, the airplane first sampled clockwise the outer perimeter of the part of the O&G basin with the densest distribution of wells and then conducted transects in the middle of the region (Figure 3). The upwind CH_4 level in the PBL on that day is 1870 ± 4 ppb (Figure 3c). CH_4 enhancements measured in the downwind plume range from 10 to 100 ppb above the upwind background level (Figure 3c). Winds in the PBL on 31 May are from the NE as indicated by the 6 h back trajectory of the air mass derived from the HRDL wind measurements, averaged with height within the PBL (black line and diamonds, Figure 3a). On that day, the average wind speed in the PBL during the 6 h prior to the downwind plume measurement is 3.1 ± 1.1 m/s.

The top of the convective boundary layer during the downwind transect on 31 May is located at 3000 m asl (~1500 ± 230 m agl), as defined by the altitude of the sharp gradient in both the trace gas mole fractions and potential temperature measured during an aircraft vertical profiling spiral from 19:15 to 19:39 GMT on the western (downwind) side of the D-J Basin, north of Longmont, Colorado (Figure 3b). Variability in the CH_4 mole fraction visible in this downwind vertical profile is caused by horizontal variability in CH_4 mole fraction from local sources over the 4–6 km wide spiral that the aircraft conducted as it performed a vertical profile (Figure S3).

The total CH_4 emission for the area encircled by each flight is estimated using the mass-balance approach and the chemical and physical measurements described above and in Text S1. The mass-balance calculation yields 25.8 ± 8.4 t h^{-1} on 29 May (this value represents an average of the two downwind flight segments at two aircraft altitudes) and 26.2 ± 10.7 t h^{-1} on 31 May (Table 1). We have propagated the measured variability of the various parameters in the mass-balance equation to quantify the 1σ uncertainty on the total CH_4 emissions estimate on each day (section 6 in Text S1 and Tables S1 and S2). Because the estimates on these two different days are independent, the 1σ uncertainty on the average top-down CH_4 flux (26.0 t/h) for the 2 days is 6.8 t h^{-1}, or close to 26% of the total flux, which is lower than the uncertainties of 33–41% derived on each day.

3.2. CH_4 Source Attribution

The top-down CH_4 fluxes derived above encompass all CH_4 sources in the area located between the downwind and upwind transects for each flight. We do not have enough information to quantitatively partition the emissions between the various CH_4 sources based on the airborne measurements alone. Here we estimate CH_4 emissions from agricultural operations, landfills, and wastewater treatment plants located within our mass-balance region based on available bottom-up information. We use emission factors from the

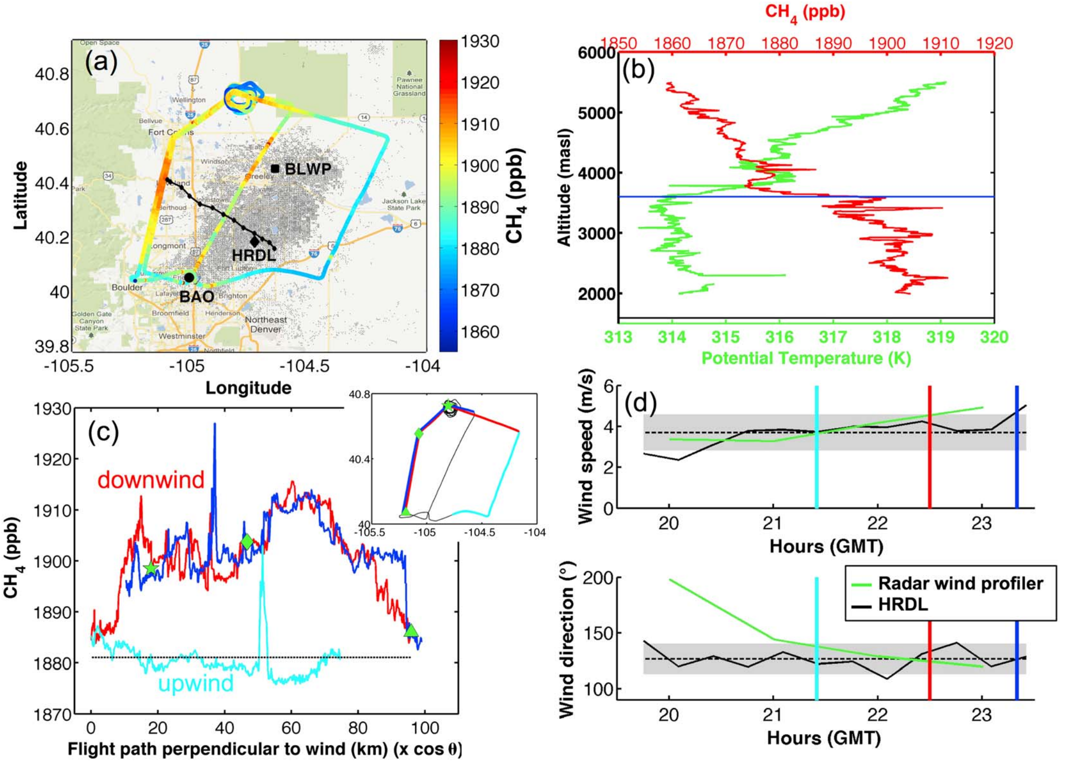

Figure 2. Measurements used on 29 May 2012 CH_4 flux calculation. (a) Map of flight track color-coded with CH_4 mole fraction, 4 h back trajectory of the downwind air mass (from HRDL winds, black line and dots), and the locations of oil and gas wells (gray dots). (b) Vertical profiles of CH_4 mole fraction (red, top axis) and potential temperature (green, bottom axis) measured during a spiral at the northernmost point of the flight track, during the red-colored downwind segment (indicated by green star in inset of Figure 2c); blue line indicates the top of the planetary boundary layer (PBL), and the black line at the bottom shows the mean ground level for the region. (c) CH_4 mole fraction as a function of distance along the flight track perpendicular to the mean wind direction. The average upwind mole fraction (1881 ± 4 ppb CH_4, black dashed line) derived from the upwind measurements (light blue line) is subtracted from the two downwind segments (dark blue, flown at ~2000 m asl (~400 m agl), and red, before they are integrated along the flight path perpendicular to the wind direction; the downwind segments were flown at ~2150 m asl (~550 m agl)) along the western and northern sides of the flight track; the upwind measurements (light blue) were made in the southeast and eastern portions of the track (inset) at 2000 m asl (400–600 m agl depending on ground elevation). A narrow large CH_4 plume was sampled in the upwind leg, most likely from a local point source given its narrow width. Green symbols in the figure correspond to locations indicated with same symbols in inset map. (d) Wind (top) speed and (bottom) direction from HRDL, averaged through the PBL (black, with dashed line indicating the average used in the calculation and gray bar indicating the uncertainty derived in section S6 in Text S1); green line indicates the same measurement from the radar wind profiler near Greeley. Light blue, red, and dark blue vertical lines indicate the average times of the upwind and two downwind legs, corresponding to the same colors in Figure 2c. Local (daylight savings) time was GMT 6 h.

literature, activity or inventory data compiled by the state of Colorado, and annual facility-level emission estimates reported to the Environmental Protection Agency (EPA) Greenhouse Gas Reporting Program (GHGRP) for 2012 [*EPA*, 2013b].

Cattle feeding and dairy and egg production are major economic activities in the NE Front Range. Enteric fermentation in ruminants is the largest agricultural source of CH_4 in the region. Our study region encompasses more than 100 animal feeding and dairy permitted operations in Weld County, 11 operations in Larimer County, and 2 small operations in Boulder County. We derive CH_4 emission estimates for these operations using 2012 cattle head count statistics provided by the state of Colorado [*NASS*, 2014] and the 2007 Agricultural Census statistics for sheep and poultry [*USDA*, 2012]. More than 97% and 100% of beef and dairy permitted capacities in Weld County are within the study region, respectively, and so we choose to round the percent number for beef cattle up to 100% and use total beef and dairy head counts in Weld County. For Larimer County, 5.5% and 52% of beef and dairy permitted capacities are within the study region. These fractions are used to prorate the total Larimer County cattle statistics.

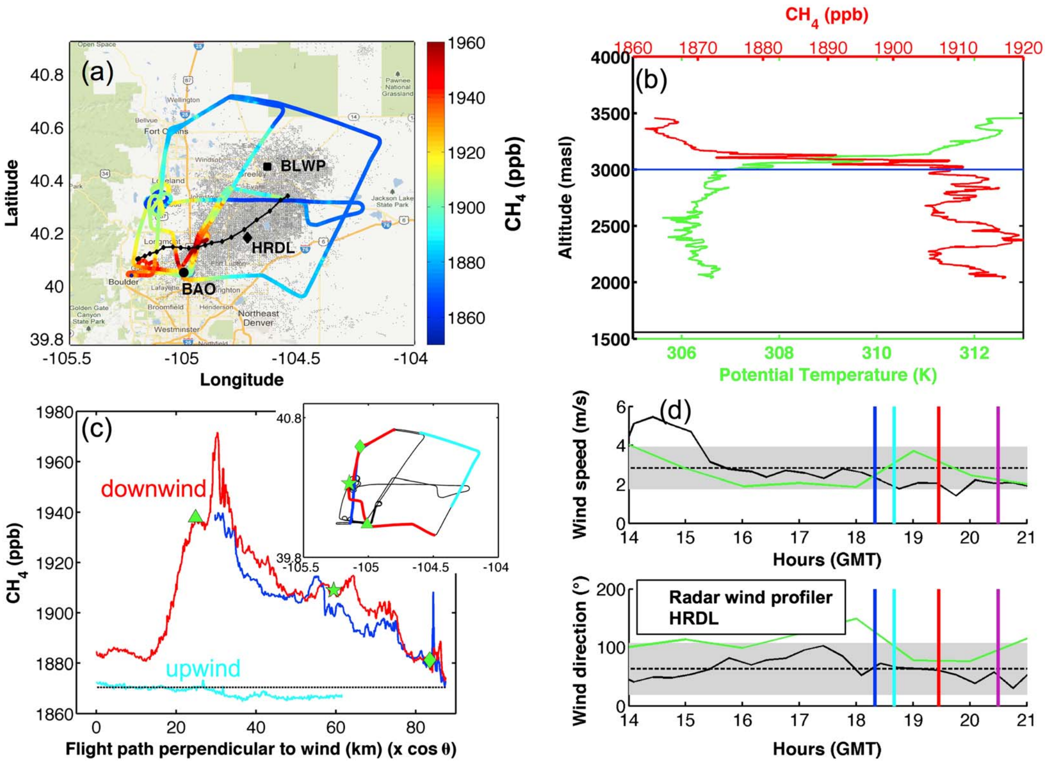

Figure 3. Same as Figure 2 but for measurements used in 31 May 2012 CH_4 flux calculation. (c) One downwind segment (red, flown at 2020 m asl (~500 m agl)) was integrated for the flux calculation after the background mole fraction (1870 ± 4 ppb CH_4, black dashed line) was subtracted. The upwind measurements (light blue), sampled in the northeastern portion of the track (inset) at 2000 m asl (~400 magl), were used to define the background condition for the flux calculation. The dark blue line shows the mole fraction along the earlier downwind segment at the same altitude that captured only part of the plume. (d) The purple line indicates the average time of a second descending profile, shown in Figure S4.

In 2012, according to the state of Colorado Agricultural Statistics, Weld (Larimer) County was home to 50,000 (12,000) beef cows and 70,000 (12,000) dairy cows, and the total number of cattle and calves was 565,000 (51,000). Between 2008 and 2013, the interannual variability in these statistics is ≤12%. We assume that a total of 51,000 beef cows and 76,000 dairy cows were in our study region in May 2012.

We assume that 80% of the beef cows in Weld and Larimer Counties had calved by the time we conducted our campaign in May [*EPA*, 2014, Table A-179, Annex 3], and we use the US national statistics on cattle population [*EPA*, 2014, Table A-178, Annex 3] to derive head counts for calves and replacement heifers in dairy farms. We use the ratios of bulls to cows reported for Colorado in 2012 (5.6%) and the total number of cows in

Table 1. CH_4 Emission Estimates for Weld County for 29 and 31 May 2012

CH_4 Emissions (t/h)		29 May[a]	31 May	Average[b]
Total measurement-based estimates		25.8 ± 8.4 (33%)	26.2 ± 10.7 (41%)	26.0 ± 6.8 (26%)
Non-O&G sources—inventory-based estimates (see text and Tables 2 and 3 for details)	Animals	3.9 ± 0.7	3.9 ± 0.7	
	Animals waste	0.7 ± 0.2	0.7 ± 0.2	
	Landfills	1.5 ± 1.5	0.7 ± 0.7	
	Municipal wastewater plants	0.5 ± 0.15	0.5 ± 0.15	
	Industrial wastewater plant	0.5 ± 0.15	0.5 ± 0.15	
	Total nonoil and gas sources	7.1 ± 1.7	6.3 ± 1.0	
Remaining balance: O&G sources		18.7 ± 8.6	19.9 ± 10.7	19.3 ± 6.9

[a] The value from 29 May is the average of calculations from two separate downwind legs.
[b] The variance of the average flux is calculated as the sum of the individual day variances divided by 4.

Table 2. Bottom-Up Information and CH_4 Emission Estimates (t/h) From Livestock Operations, Enteric Fermentation in Ruminants (E1), and Manure Management (E2 and E3) in the Region Encompassed by the 29 and 31 May 2012 Flights[a]

Source	Enteric Fermentation					Manure			
Livestock	Head Count[b] (× 1000)	EF1[c]	SD[c]	E1 (t/h)	SD[d]	EF2[e]	E2 (t/h)	EF3[f]	E3 (t/h)
Cattle in feedlots	308	4.3	1.4	1.32	0.51	0.23	0.07	0.97	0.30
Beef cows	51	7.8	1.6	0.40	0.11	0.23	0.01	0.97	0.05
Beef cows calves	41	1.0	0.2	0.04	0.01	0.23	0.01	0.97	0.04
Beef stockers	10	5.7	1.2	0.06	0.02	0.23	<0.01	0.97	0.01
Beef heifers	10	7.1	1.4	0.07	0.02	0.23	<0.01	0.97	0.01
Bulls	7	10.0	2.0	0.07	0.02	0.23	<0.01	0.97	<0.01
Dairy cows	76	18.3	3.7	1.39	0.36	6.16	0.47	2.74	0.21
Dairy cows calves	38	3.2	0.7	0.12	0.03	0.23	0.01	1.76	0.07
Replacement heifers 7–11 months	11	5.6	1.1	0.06	0.02	0.23	<0.01	1.76	0.02
Replacement heifers 12–23 months	27	7.9	1.6	0.21	0.06	0.23	<0.01	1.76	0.04
Sheep	200	0.9[e]	0.2	0.18	0.05	0.003	<0.01	0.066	0.01
Poultry (mostly egg layers)	3,000	na	na	-	-	0.014	0.04	0.025	0.08
Total	-	-	-	3.9	0.7	-	0.6	-	0.8

[a] Units for the emissions factors EF1, EF2, and EF3 are g/head/h (10^6 g = 1 t). The derivation of the head count for each animal category is provided in the main text.

[b] Estimated based on 2012 Colorado Agricultural Statistics for county-level total numbers of beef cows, dairy cows, and other cattle and calves, rounded 2007 Agricultural Census statistics for poultry and sheep totals and calves production and cattle replacement statistics from US EPA 2013.

[c] Cattle emission factors (EF1) based on *Johnson and Johnson* [1995, Table 2]. Standard deviation (SD) on EF1 is set to 20% except for feedlot cattle including stockers, where it is 33%.

[d] The emission estimate standard deviation takes into account the prescribed standard deviation of emission factor EF1 and 20% uncertainty in head count for each animal category.

[e] Source for EF2 emission factors used to derive emission estimates E2 [*IPCC*, 2000].

[f] Source for EF3 emission factors used to derive emission estimates E3 [*CDPHE*, 2002].

our study region to estimate the total number of bulls (~7000). We use these estimates and the constraint on the total cattle head counts to estimate the total number of feedlot cattle in the study region at 308,000 head.

These figures for total beef and dairy cattle agree to within 10% with the total permitted capacity for dairy cattle (167,000 heads) and beef cattle (405,000 heads in large feedlots with > 1000 heads each; and 6000 heads in <1000-head operations) in the study region (CDPHE, personal communication). We assume a 20% uncertainty on the total head count for all animal categories and a 20% uncertainty on the emission factors for all categories except for feedlot cattle (33%) (see details in Table 2).

For each animal category, we use an average emission factor from *Johnson and Johnson* [1995], which is still one of the most exhaustive references for US cattle. The emission factors we use are similar to values reported or used in more recent publications on North American cattle (see *EPA* [2013a, Table A-182], *Stackhouse et al.* [2011], *Kebreab et al.* [2008], and *Westberg et al.* [2001], for example). The total bottom-up emission estimate from enteric fermentation in cattle in Weld County in May 2012 amounts to an average of 3.8 ± 0.7 t/h (Table 2).

Another source of agricultural CH_4 from animal husbandry comes from animal manure disposal systems. Emissions from livestock manure depend in large part on how animal solid waste is managed [*Lodman et al.*, 1993; *Steed and Hashimoto*, 1994]. Dry aerobic management systems result in lower conversion of organic matter in the manure to CH_4, while the diversion of waste with water into anaerobic lagoons can result in very efficient conversion to CH_4 [*EPA*, 1999, 2009]. In Colorado's arid climate, animals are kept in dry lots for many feedlot and dairy operations [*Sharvelle and Loetscher*, 2011] and manure is removed mechanically and composted nearby.

EPA [2013a] uses a detailed emission model to derive CH_4 manure emissions for US operations, which we cannot downscale as we do not have detailed information on waste management practices for the facilities in the region of interest. Instead, we use emission factors from two reports, *IPCC* [2000] and *CDPHE* [2002]. The two reports have very different emission factors for dairy farms and beef operations (EF2 and EF3 in Table 2), and the final total CH_4 emissions for all animal operations are 0.6 and 0.8 t/h, respectively. It is possible that *CDPHE* [2002] emission factors reflect Colorado's practices better. In Colorado, a small percentage of total dairy farm waste is managed with anaerobic lagoons, a more common practice in the US Midwest. *EPA*

Table 3. Hourly CH_4 Emission Estimates for the Five Major Landfills Operating in the Region Encompassed by the Flights Based on Annual Estimates Reported for 2012 [*EPA*, 2013b]

Facility	Latitude	Longitude	2012 Emissions (t/h)
North Weld Sanitary Landfill	40.585°	−104.826°	0.50
Central Weld Sanitary Landfill (closed)	40.349°	−104.806°	0.16
Denver Regional Landfill (closed) [a]	40.022°	−105.028°	0.51[b]
Denver Regional North Landfill (closed)[a]	40.031°	−105.032°	0.02[b]
Front Range Landfill	40.022°	−105.009°	0.25[b]
Total Upwind on 29 May 2012			1.44
Total Upwind on 31 May 2012			0.66

[a] These two closed (no longer in operation) landfills have recovery systems.
[b] The last three landfills were beyond the downwind transect for the 31 May flight.

[2013a] reports a 2σ relative uncertainty of −18% to +20% on manure management CH_4 emissions from all cattle in the US inventory for 2011. We assume that the uncertainty is larger at the regional scale than for the national scale. We use the average of the two inventory-based estimates (0.7 t/h) with a 1σ uncertainty 0.2 t/h.

The flux region encompassed by the 29 May 2012 flight has two active landfills and three closed landfills, two of which have a CH_4 recovery system (see Figure 1 and Table 3). Only the two landfills in the northern half of Weld County are within the flux region of the 31 May flight: the three southernmost landfills are south (downwind) of the flight “downwind” transects. Based on annual facility-level emissions reported to the EPA GHGRP for 2012 [*EPA*, 2013b], we calculate hourly average emission estimates for these five landfills (Table 3) and assume that these emission magnitudes are representative of both days in May 2012. The bottom-up estimates for CH_4 emissions from landfills total 1.7 t/h on 29 May and 0.7 t/h on 31 May. There are no uncertainty estimates reported in the EPA GHGRP, but field measurements around landfills have shown how emission rates depend on the soil microclimate and surface meteorological conditions including surface pressure [*Czepiel et al*., 1996; *Mosher et al*., 1999; *Czepiel et al*., 2003; *Bogner et al*., 2011]. For landfill emissions of CH_4 in the national inventory, EPA reports a 2σ relative uncertainty of −54% to +46% [*EPA*, 2013a]. Much of this uncertainty is due to the lack of measurements to assess the efficiency of installed methane recovery and/or flaring systems. Given the lack of validation for this estimate, a 1σ uncertainty of 100% for both days is used in our analysis.

Another smaller source of CH_4 in the region is from anaerobic digestion of sludge by bacteria at municipal and industrial wastewater treatment facilities. There are 11 municipal facilities in the region sampled by the May 2012 flights: 5 in Larimer County (out of 6), 5 in Weld County (out of 9), and 1 in Boulder County (in Longmont). To estimate the CH_4 emissions from these facilities, we use the projected state-level estimate for 2010 (3.59 t/h) derived by *Strait et al*. [2007] and scale it by the fraction of the state population residing in Weld County, Larimer County and the city of Longmont, which is 12.7% in 2010. We then use the relative increase in population from 2010 to 2012 (4%) to scale the 2010 estimate and obtain an estimate for total CH_4 emissions in 2012 for these 11 facilities of 0.47 t/h. The methodology followed by *Strait et al*. [2007] is based on the EPA State GHG Inventory Tool, which is very similar to the method used by EPA for the national-level greenhouse gas (GHG) inventory [*EPA*, 2013a]. There is also a large industrial wastewater facility associated with the JBS Swift slaughterhouse in Greeley. The facility processes close to 400 head of cattle into beef per hour, and its reported CH_4 emissions from its wastewater treatment in 2011 equal 0.47 t/h [*EPA*, 2013b]. The industrial wastewater plant did not report emissions to the GHGRP for 2012 even though it was still in operation; therefore, we use the reported emissions for 2011 assuming operations did not change. The 2σ uncertainty reported by *EPA* [2013a] for national CH_4 emissions from wastewater treatment facilities ranges between −29% and +28%. We use 29% as the 1σ relative uncertainty (or 0.14 t/h) in the regional scale emission estimates for both municipal and industrial wastewater plants.

A few additional processes in the region contribute a small amount to the total CH_4 flux. Based on flux measurements in the D-J Basin reported by *Klusman and Jakel* [1998], we calculate that the natural flux of CH_4 from natural microseepage in the region likely amounts to less than 0.1 t/h. The Fort St. Vrain 969-MW natural-gas-fired power plant near Platteville was found by our airborne measurements to have no detectable CH_4 emissions. Two aircraft transects passing ~2 km to the west of the power plant on 31 May

2012 include distinct CO_2 plumes (not shown) downwind of the power plant with no coincident detectable CH_4 enhancements. Abandoned coal mines are another possible source of CH_4 in the area. Over 200 small coal mines were exploited in the Front Range in the Boulder-Weld coal field in an arc extending from Marshall south of Boulder toward Frederick north of Denver [*Roberts et al.*, 2001]. Coal mines in this area have been closed since at least 1978 and, unlike those in the Piceance Basin in Western Colorado, are not categorized by the EPA as being in a gassy coal basin [*EPA*, 2004]. Some of our flight transects through the region sampled downwind of some of these mines locations, and our in situ CH_4 analyzer did not detect any noticeable CH_4 enhancement. We surmise that emissions from these mines are likely to be insignificant, because they are covered mines and have not been previously noted as major sources. They are not included in our analysis.

The total bottom-up hourly average CH_4 flux for non-O&G sources in the study region is estimated to be 7.1 ± 1.7 t CH_4/h on 29 May and 6.3 ± 1.0 t CH_4/h on 31 May (Table 1). The uncertainties on the non-O&G emission estimates are added in quadrature to obtain the 1σ uncertainty for the total non-O&G emissions. When we subtract these fluxes from the top-down estimates of the total CH_4 flux in the region on 29 and 31 May 2012, we are left with an average flux of 19.3 ± 6.9 t CH_4/h (1σ uncertainty) attributable to O&G operations, or 75% of the total top-down regional CH_4 emission estimate (Table 1).

3.3. Light Alkanes and Benzene Correlations

Dry air mole fractions for CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6H_6, C_2H_2, and CO were measured by NOAA ESRL GMD in 118 discrete air samples collected in flasks on the 12 flights conducted in the D-J Basin in May 2012 (Figures 1 and 4). Air samples were typically acquired to ascertain hydrocarbon mole fractions in upwind legs, in the free troposphere above the PBL, and downwind of (and within) the D-J Basin.

Mole fractions of all the light alkanes in flask air samples collected directly downwind of O&G operations in the D-J Basin are elevated above background levels measured in upwind legs and in the free troposphere. The 97 air samples collected by the airplane in the PBL (below 3000 m asl) have an average mole fraction and 1σ mole fraction variability of 1891 ± 24 ppb for CH_4 and 4.3 ± 3.2 ppb for C_3H_8, compared to 1854 ± 10 ppb for CH_4 and 0.46 ± 0.58 ppb for C_3H_8 in the 21 air samples collected by the airplane above 3000 m asl.

In Figure 4, we show correlation plots for the hydrocarbons' dry air mole fractions measured in the aircraft flasks. Correlation slopes for the 97 PBL air samples are derived using an orthogonal distance regression (ODR) with a 2 ppb uncertainty for the CH_4 measurements, a 5% uncertainty for the NMHC measurements, and no constraint on the *y* intercept. The slopes, the attached 1σ uncertainties, and R^2 are reported in Table 4. Below, we discuss CH_4 and C_3H_8 mixing ratios correlation in the aircraft samples. Then we describe another strong feature of this data set, which relates to the very tight correlations between the C_{3-5} alkane mixing ratios. We also report on the analysis of C_6H_6 mixing ratios correlations with C_3H_8 and C_2H_2 mixing ratios. Finally, the May 2012 flight results are compared with other measurements conducted at the NOAA BAO facility.

CH_4 and C_3H_8 in the aircraft PBL air samples are correlated, with an R^2 of 0.66 and a CH_4-to-C_3H_8 correlation slope of 6.2 ppb/ppb (Figure 4). From flight to flight, CH_4 "background" mole fractions in the upwind aircraft flasks range between 1846 and 1876 ppb, while the enhancements above background in downwind flasks ranged between 1 and 104 ppb. The flight-to-flight variability in the upwind CH_4 mole fraction can be as high as on e third of the downwind enhancement signals we want to interpret. C_3H_8 mole fractions in upwind aircraft flasks range between 0.16 and 1.80 ppb, while the enhancements in all other PBL flasks range between 0.09 and 15 ppb (Figure 4).

To remove the influence of the varying background (upwind) mole fractions from flight to flight, we derive enhancements of CH_4 and C_3H_8 above background for each flask air samples collected below 3000 m asl on 11 different flights. For each flight, we define the measured CH_4 and C_3H_8 background mole fractions as the level measured in one flask air sample collected in the PBL upwind of the O&G operations out of a maximum of 12 flasks collected during each flight. For one flight, we do not have a background air flask sample. The correlation slope of CH_4 and C_3H_8 enhancements for the 76 remaining PBL aircraft samples (using the same assumptions as above) is 6.1 ± 0.4 ppb CH_4/ppb C_3H_8. The higher R^2 (0.80) compared to the correlation of absolute CH_4 and C_3H_8 mole fractions is an indication that removing the flight-to-flight varying background is important when interpreting CH_4 and C_3H_8 mixing ratios measurements from multiple days. We consider this latter slope of 6.1 ± 0.4 ppb/ppb to reflect the overall ratio of CH_4 to C_3H_8 total emissions in the study region in May 2012.

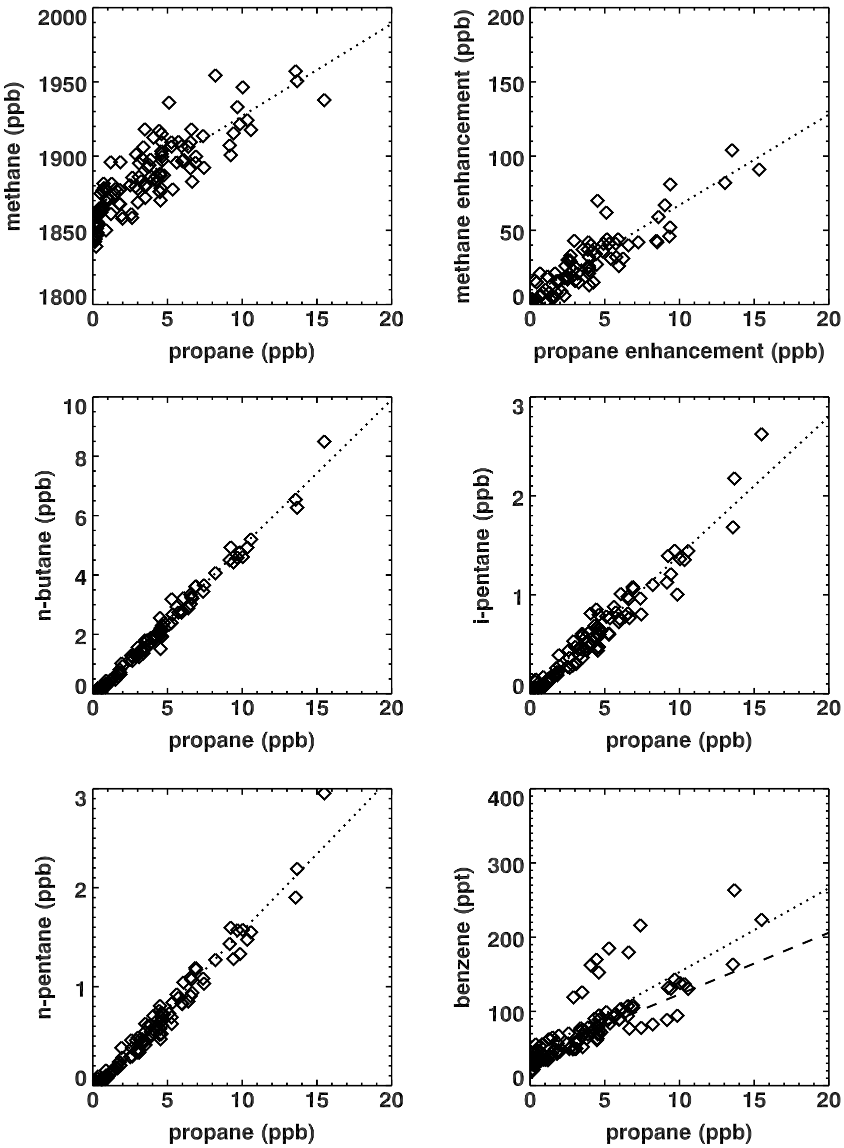

Figure 4. Correlation plots for different hydrocarbon versus propane mixing ratios (or enhancements above background as noted) in flasks sampled by aircraft in the boundary layer. The dotted lines show the correlation slopes of the single regression as reported in Table 4. The dashed line in the benzene to propane figure shows the multiregression slope also reported in Table 4. All the data come from the NOAA GMD multiple species analysis by GC-MS of discrete air samples collected with the aircraft on different days in the Denver-Julesburg Basin in May 2012.

The tight correlations between the C_{3-5} alkane mixing ratios for all samples collected in the PBL by the airplane ($R^2 \geq 0.99$) with the same slopes for all flight data suggest that these gases are emitted by the same sources located in the study region and at a fairly constant ratio, as concluded by *Pétron et al.* [2012]. None of the nonmethane light alkanes measured correlates with either CO or C_2H_2 ($R^2 < 0.2$), which shows that these gases are emitted by noncombustion processes.

For all 97 aircraft PBL flask samples, C_6H_6 correlates well with both C_3H_8 (O&G source) and C_2H_2 (mobile combustion source) ($R^2 = 0.65$ in both cases) (Figures 4 and S5). Using a multilinear regression to explain C_6H_6 variability, we find that the regression coefficients a_{C3H8} (8.3 ± 0.4 ppt/ppb) and a_{C2H2} (0.39 ± 0.02 ppt/ppt) are lower than the single regression correlation slopes we report in Table 4. The R^2 values for the correlation of aircraft ($[C_6H_6] - a_{C2H2}{*}[C_2H_2]$)-to-$C_3H_8$ and ($[C_6H_6] - a_{C3H8}{*}[C_3H_8]$)-to-$C_2H_2$ are 0.85 and 0.88, respectively. This increase in the R^2 compared to the single regression correlation coefficient suggests that the variability in the C_6H_6 enhancements is mostly due to these two different sources.

Table 4. Summary of Correlation Slopes (ppb/ppb) Between Various Hydrocarbons' Dry Air Mole Fractions Measured in Air Samples Collected With the Aircraft in May 2012[a]

	This Study—Boundary Layer Samples Only			BAO 2008–2012 NE Sector May–June (85 Samples)			BAO 2007–2012 NE Sector November–April (919–988 Samples[b])			G13 BAO Feb 2011 Multiregression		S13 BAO Feb 2011		
Data Sets Species	Slope	SD	R^2	Slope	SD	R^2	Slope	SD	R^2	Slope	SD	Slope	SD	R^2
CH_4 to C_3H_8 enhancements	6.1	0.3	0.81	-	-	-	-	-	-	-	-	-	-	-
CH_4 to C_3H_8	6.2	0.5	0.66	8.1	0.8	0.56	8.9 ± 0	0.2	0.89	-	-	-	-	-
nC_4H_{10} to C_3H_8	0.495	0.007	1.00	0.475	0.007	1.00	0.438	0.003	1.00	0.563	0.004	0.46	0.01	0.96
iC_5H_{12} to C_3H_8	0.140	0.004	0.99	0.131	0.005	0.93	0.131	0.002	0.99	0.168	0.002	0.13	0.005	0.91
nC_5H_{12} to C_3H_8	0.156	0.003	0.99	0.146	0.005	0.94	0.137	0.002	0.99	0.190	0.002	0.13	0.005	0.92
C_6H_6 to C_3H_8	11.3×10^{-3}	0.9×10^{-3}	0.65	8.7×10^{-3}	0.8×10^{-3}	0.62	8.7×10^{-3}	0.3×10^{-3}	0.79	-	-	6.3×10^{-3}	0.4×10^{-3}	0.79
C_6H_6 to C_2H_2	0.54	0.04	0.65	0.35	0.06	0.33	0.38	0.01	0.82	-	-	0.39	0.01	0.94
C_6H_6 to C_3H_8 (multiregression)	8.3×10^{-3}	0.4×10^{-3}	0.85[c]	7.5×10^{-3}	0.7×10^{-3}	0.66	5.3×10^{-3}	0.2×10^{-3}	0.91	4.3×10^{-3}	0.1×10^{-3}	-	-	-
C_6H_6 to C_2H_2 (multiregression)	0.39	0.02	0.88[c]	0.23	0.04	0.35	0.222	0.007	0.88	0.166	0.005	-	-	-

[a] These slopes are compared with results from a similar analysis by GMD of midday samples collected from the NOAA BAO tower 300 m level (2007–2012) for the NE wind sector. The last two columns provide emission ratios reported by *Gilman et al.* [2013] (abbreviated G13) and *Swarthout et al.* [2013] (abbreviated S13) for VOC measurements at 22 m at BAO during a 3-week intensive campaign in February 2011.

[b] The number of valid BAO samples for each pair of trace gases varied and was within the range provided in the column header.

[c] R^2 for the residuals.

The hydrocarbon correlation slopes for the aircraft samples are now compared with results from three different BAO data sets. In Table 4, we report correlation slopes for the GMD long-term midday flask samples collected at the 300 m agl level of the BAO tower (calculated using the same ODR technique). The last two columns in Table 4 also show results presented in *Gilman et al.* [2013] and *Swarthout et al.* [2013] on VOC measurements collected during a 3 week intensive campaign at BAO in February 2011. We filter the GMD BAO data set to keep air samples coming from the NE only (flasks with prior 30 min mean wind from a direction of 0–140° and a mean wind speed > 2.5 m/s). The BAO NE data are also filtered by time of year: data from May and June 2008–2012 are compared with the May 2012 aircraft data, and data from November to April 2007–2012 are compared with the wintertime results reported by *Gilman et al.* [2013] and *Swarthout et al.* [2013] (denoted G13 and S13, respectively, in Table 4). *Gilman et al.* [2013] and *Swarthout et al.* [2013] report their VOC measurements on different calibration scales than GMD. They also sampled day and night closer to the surface, which may make some of their measurements less representative of a large area because the highest mole fraction enhancements tend to occur at night when winds are lower.

For the GMD data sets, nC_4H_{10}-to-C_3H_8, iC_5H_{12} -to-C_3H_8 and nC_5H_{12}-to-C_3H_8 correlation slopes for the aircraft PBL samples are 4–7% higher than the BAO NE May and June samples slopes. Conversely, the CH_4-to-C_3H_8 enhancements slope for the airplane PBL samples is 23% lower that the BAO NE May and June samples slope. The overall mix of hydrocarbon sources located within the footprints of the airplane and BAO samples have different chemical compositions, especially in terms of CH_4 relative to other light alkanes. This difference may reflect a higher contribution of hydrocarbon emissions related to oil and liquid condensate production (enriched in NMHCs relative to CH_4) in

Table 5. Emission Estimates for Methane and Five Nonmethane Hydrocarbons in Weld County Based on Aircraft Measurements in May 2012

Compound	Total Emissions (t/h) 2 Days in May 2012	Method
CH_4	26.0 ± 6.8	Mass-balance estimate
C_3H_8	11.8 ± 3.8	Based on CH_4 to C_3H_8 mixing ratios enhancements slope
nC_4H_{10}	7.7 ± 2.6	Based on C_3H_8 total emissions estimate and nC_4H_{10} to C_3H_8 mixing ratios slope
iC_5H_{12}	2.7 ± 0.9	Based on C_3H_8 emissions estimate and iC_5H_{12} to C_3H_8 mixing ratios slope
nC_5H_{12}	3.0 ± 1.0	Based on C_3H_8 emissions estimate and nC_5H_{12} to C_3H_8 mixing ratios slope
C_6H_6	0.17 ± 0.06	Based on C_3H_8 emissions estimate and C_6H_6 to C_3H_8 multiregression coefficient
Total for measured NMHC	25.4 ± 8.2	Sum of C_3H_8, nC_4H_{10}, iC_5H_{12} , nC_5H_{12} and C_6H_6 emissions

the air masses sampled with the aircraft. The $C_{3–5}$ alkane correlation slopes we report for BAO NE winter samples are closer to the slopes reported by *Swarthout et al*. [2013] and 22–28% lower than the slopes reported by *Gilman et al.* [2013]. At this time, it is not clear if the different calibration scales and sampling procedures between the three groups may explain some of the differences in correlation slopes observed.

The C_6H_6-to-C_3H_8 multivariate slopes for the May 2012 aircraft flasks and the BAO NE May–June flasks agree within their calculated 1 sigma: 8.3 ± 0.4 ppt/ppb and 7.5 ± 0.7 ppt/ppb, respectively. The multiregression slope we report for the BAO NE winter samples (5.3 ± 0.2 ppt/ppb) is 29% lower than the BAO NE May–June slope. It is in between the multiregression slope reported by *Gilman et al*. [2013] (4.3 ± 0.1 ppt/ppb) and the emission ratio reported by *Swarthout et al*. [2013] (6.3 ± 0.4ppt/ppb) for February 2011. These different measurements suggest that the relative strength of the C_6H_6 and C_3H_8 emissions from O&G sources in the region site may vary over time and space.

3.4. Light Alkanes and Benzene Measurement-Based Regional Emission Estimates

In this section we derive top-down estimates of light alkane and C_6H_6 emissions. We first scale the average CH_4 regional total top-down emission estimate (26.0 ± 6.8 t/h) obtained with the mass-balance approach with the inverse of the CH_4-to-C_3H_8 enhancements slope obtained for the aircraft flask samples. The total relative uncertainty in the C_3H_8 emission estimate is the sum of the relative uncertainty in the total CH_4 emission estimate and the relative uncertainty in the CH_4-to-C_3H_8 slope. The resulting total C_3H_8 mean hourly emission estimate for May 2012 is 11.8 ± 3.8 t/h.

Top-down emission estimates for n-C_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 are calculated by scaling the C_3H_8 top-down emission estimate with the NMHC-to-C_3H_8 slopes reported in Table 4 for the aircraft flask samples. Uncertainty estimates again reflect the uncertainty in the C_3H_8 top-down emission estimate and the slopes. The resulting nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 mean hourly emission estimates for May 2012 are 7.7 ± 2.6 t/h, 2.7 ± 0.9 t/h, 3.0 ± 1.0 t/h, and 173 ± 64 kg/h (1 kg = 0.001 t), respectively.

Gilman et al. [2013] attributed 100% of the light alkane ($C_{3–5}$) mixing ratio enhancements above background they observed at BAO in February 2011 to O&G operations emissions. We too assume that the emission estimates we derived above for these nonmethane light alkanes can be entirely attributed to O&G sources in the study region. For C_6H_6, we use the slope from the multiple regression analysis to isolate the contribution from O&G sources alone (see previous section). The top-down emission estimates for C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 are summarized in Table 5 and add up to 25.4 ± 8.2 t/h.

This small suite of NMHCs measured by GMD in the aircraft flasks represent a subset of the nonmethane and nonethane hydrocarbons emitted by O&G sources. C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 represent on average 77% of the total NMHC mass in raw natural gas from the Wattenberg field and between 68% and 88% of the total NMHC mass in flashing emissions from oil and liquid condensate storage tanks [see also *Pétron et al*., 2012, supporting information Figure S4; CDPHE, personal communication]. In the CDPHE inventory, as in other air quality emission inventories, ethane is not included in sum of the NMHC due to its low reactivity and low impact on local air quality.

Other NMHC reported in composition profiles for raw natural gas and flashing emissions from storage tanks, which GMD did not measure in the aircraft samples, are i-butane (iC_4H_{10}), alkanes with six carbons or more (C_{6+}), toluene, ethylbenzene, and xylenes [*Pétron et al*. 2012, supporting information]. GMD is currently developing a new GC-MS system to measure several of these gases in future discrete air samples. In order to estimate emissions for the NMHCs not analyzed by GMD, one could use the *Gilman et al*. [2013] and *Swarthout et al*. [2013] BAO VOC measurements, assuming they are representative of the mean emission ratios in Weld County.

4. Comparison With Inventory-Based Emissions Estimates

4.1. Nonmethane Hydrocarbons

CDPHE has developed bottom-up methods to track VOC emissions from O&G sources, which rely on both permit data and empirical equations. Flashing emissions of volatile compounds occur every time "new" oil or liquid condensate is dumped from the on-site separator into a storage tank. In the CDPHE inventory these emissions are treated as an area source proportional to oil and liquid condensate production. We use the May 2012 total oil and liquid condensate production volume for Weld County and an empirical equation described in *Wells* [2012] and *Bar-Ilan and Morris* [2012] to estimate the flashing emissions from storage tanks in Weld County. The empirical equation developed by CDPHE uses an emission factor of 13.7 lb VOC per barrel of oil or liquid condensate produced and assumes an overall emission reduction factor of 53% from the mandatory use of flares or vapor recovery units in the NAA [*Wells*, 2012]. Hourly emissions from oil and liquid condensate storage tanks in Weld County in May 2012 are estimated at 11.8 t/h. Other sources, including compressor engines, truck liquid loading, produced water storage tanks, etc., add 1.14 t/h (D. Wells, personal communication, 2014), while drill rigs, completion, and recompletion add another estimated 0.12 t/h (projected from WestJump (2008) [*Bar-Ilan and Morris*, 2012] to May 2012). In Weld County, according to the state inventory, the bulk of total O&G VOC emissions come from uncaptured or unburned flashing emissions at oil and liquid condensate storage tanks. The bottom-up total VOC emission estimates from O&G sources add up to 13.1 t/h. No uncertainties are available for this estimate. The bottom-up total is about half of the top-down total emission we derive for C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 in May 2012 (25.4 ± 8.2 t/h) alone.

In the CDPHE inventory of C_6H_6 sources, highway and nonroad vehicles are responsible for close to 90% of the total C_6H_6 emissions in the Front Range ozone nonattainment area, or 139 kg/h in 2011 (the 2012 estimate is not available yet). The CDPHE inventory estimate of C_6H_6 emissions from O&G operations in Weld County in 2012 amounts to 25.2 kg/h: 17.9 kg/h from oil and liquid condensate storage tanks and 7.3 kg/h from other O&G sources, including produced water tanks, crude oil and condensate loading and transportation, natural gas dehydration and processing operations, flares, and compressor engines. This official estimate is 7 times lower than our average top-down estimate (173 ± 64 kg/h). Taking into account the 1 sigma uncertainty in our estimate, there is 68% chance that the inventory underestimates these emissions by a factor of 4 to 9. Our results indicate that C_6H_6 emissions from O&G operations in Weld County may be as large or even larger than vehicle emissions. This finding stresses the need for further work to better understand and track the substantial "missing" sources of C_6H_6 (and potentially other hazardous air pollutants) in O&G production and processing operations [*Pétron et al*., 2012].

4.2. Methane

To date, neither the state of Colorado nor EPA provides complete, up-to-date, and spatially resolved (county or smaller scale) inventories of CH_4 sources. The most detailed and regionally relevant information source for CH_4 emissions from O&G sources is the EPA Greenhouse Gas Reporting Program (GHGRP), which collects emissions data from the largest sources of GHG in the US under the Consolidated Appropriations Act of 2008 [*EPA*, 2013b].

The GHGRP Subpart W covers almost all segments of petroleum and natural gas systems from production, processing, transmission compression, storage, and distribution besides emissions from stationary fuel combustion covered by Subpart C (http://www.epa.gov/ghgreporting/documents/pdf/infosheets/OnshorePetroleumNaturalGasSystems.pdf). Owners of O&G facilities emitting more than 25,000 t CO_2 equivalent/yr (from single point sources or as an aggregate for operations over an O&G basin) are required to report annual GHG emissions data to the EPA following specified methods to promote consistency across operators. Smaller operators and a few source categories do not report emissions data to the GHGRP Subpart W. For example, natural gas gathering compressors do not report to the program at this time. Despite these obvious limitations, it is currently the most detailed and basin-specific inventory of GHG emissions. In November 2013, the GHGRP made public the second year of emissions data reported to Subpart W for operations during 2012.

Twelve large oil and gas producers in the D-J Basin (out of 269 operators) report basin-level CH_4 emissions for their area distributed operations to the GHGRP. Their reported CH_4 emissions total 6.7 t/h for an average day in 2012. The two largest sources categories are pneumatic devices and pumps (3.8 t/h) and other equipment leaks from well pads (2.1 t/h). Reported emissions from other operations at well pads including liquid unloading, oil and liquid condensate storage tanks, and completions and workovers total 0.55, 0.15 and 0.14 t/h, respectively [*EPA*, 2013b]. Eleven facilities (large natural gas processing plants and transmission compressor stations) in Weld County also report facility-level GHG emissions to the GHGRP, and their aggregated CH_4 emission estimate for an average day in 2012 is 0.2 t/h.

Weld County is the largest O&G producing county by far in the D-J Basin. Here we use the assumption that the GHGRP area source emission estimates reported for the D-J Basin can be scaled by O&G production (expressed in Btu) to derive estimates of emissions for all O&G operators in Weld County in 2012, and we use heat contents for natural gas of 1.021 million Btu per thousand cubic feet and for oil of 5.871 million Btu per barrel of oil. In 2012, the 12 operators in D-J Basin reporting emissions to the GHGRP produced an equivalent of 5.07 × 1014 Btu, while all operators in Weld County produced an equivalent of 5.01 × 1014 Btu. We scale the GHGRP reported D-J Basin emissions total by 0.989 (= 5.01 × 1014/5.07 × 1014) and derive an estimated total emissions of 6.6 t CH_4/h for all O&G area sources in Weld County on an average day in 2012.

To account for all sources, emissions from large point sources (compressors and processing plants) not reporting to the GHGRP should also be added. It is not clear, however, how to scale the 0.2 t/h reported for a subset of 11 such facilities. With a simple scaling of 30/11, we get an estimate of 0.5 t CH_4/h for the identified 30 large O&G point sources in the study region (out of 38 total facilities in the state inventory for Weld County).

Overall there is a large gap between the CH_4 emissions we estimate based on the GHGRP data for O&G operations in Weld County for an average day in 2012 (7.1 t/h) and the 19.3 ± 6.9 t/h average top-down estimate we derive for 2 days in May 2012.

Following CDPHE bottom-up calculations for VOCs flashing emissions from storage tanks, hourly average CH_4 flashing emission estimates in Weld County in May 2012 range between 0.9 and 5.9 t/h based on 16 different flashing emissions composition profiles, with an average of 2.8 t/h. The GHGRP reported CH_4 emissions from oil and liquid condensate storage tanks in the D-J Basin in 2012 total 0.15 t/h and may be underestimated.

One clear limitation of this comparison has to do with the different temporal coverage of the top-down (daytime for 2 days) and bottom-up (annual) emission estimates. It is beyond the scope of this paper to derive an emission inventory for the same time period represented by our measurements, i.e., a midday snapshot on 2 days in May 2012. Further coordinated work to reconcile CH_4 and NMHC emissions estimates based on inventory models and atmospheric measurements studies at different spatial and temporal scales is needed to better characterize how O&G sources impact air quality and climate.

Several studies have expressed CH_4 emissions from O&G systems in terms of the fraction of produced CH_4 (or natural gas) lost to the atmosphere [*U.S. Environmental Protection Agency/Global Reporting Initiative* (*EPA/GRI*), 1996; *Shorter et al.*, 1997; *Pétron et al.*, 2012; *Peischl et al.*, 2013; *Karion et al.*, 2013; *Allen et al.*, 2013]. We estimate that the fraction of gross natural gas production from oil and gas wells lost to the atmosphere in Weld County in May 2012 is 4.1 ± 1.5 %. This number is close to the middle scenario (4%) reported by *Pétron et al.* [2012] for 2008 for the same region. Our current measurements do not allow us to separate the emissions contributions from oil production versus natural gas production. Our total loss rate is substantially lower than the 8.9 ± 2.8 % (1σ) loss rate reported by *Karion et al.* [2013] for the Uinta Basin gas field in northeastern Utah for one mass-balance flight conducted in February 2012.

5. Conclusions

This study presents estimates of total emissions of methane (CH_4), propane (C_3H_8), *n*-butane (nC_4H_{10}), *i*- and *n*-pentane (iC_5H_{12} and nC_5H_{12}), and the carcinogen benzene (C_6H_6) from the most densely drilled region of the Denver-Julesburg oil and natural gas basin in Weld County in May 2012. Our estimation approach is based on aircraft in situ continuous (CH_4) and discrete (CH_4, NMHCs) chemical measurements and ground-based wind profilers.

Our top-down total hourly average emission rates for CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, and nC_5H_{12} are 26.0 ± 6.8, 11.8 ± 3.8, 7.7 ± 2.6, 2.7 ± 0.9, and 3.0 ± 1.0 t/h, respectively. Based on the lack of correlation we observe between these alkanes and combustion tracers (CO, C_2H_2) in the airborne flask samples along with previous analysis of NMHC observations in the Basin [*Gilman et al*., 2013], we attribute 100% of these nonmethane emissions to oil and natural gas operations. We also derive a top-down average emission estimate for C_6H_6 emissions from oil and natural gas operations of 173 ± 64 kg/h.

Inventory estimates for nonoil and gas CH_4 sources in the region suggest that 7.1 ± 1.7 t/h on 29 May and 6.3 ± 1.0 t/h on 31 May were emitted by nonoil and natural gas sources. On average, we estimate that 75% (19.3 ± 6.9 t/h) of the total CH_4 emissions we detected are attributable to O&G operations in the study region.

Overall, our top-down emission estimates for CH_4 and NMHCs from oil and natural gas sources are at least twice as large as available bottom-up emission estimates. Accurate estimates of emissions from oil and natural gas operations at the regional and national levels are still needed to quantify (and minimize) their impacts on climate forcing and air quality. Research studies like this one, relying on recent technical developments in atmospheric measurements, are a necessary component for the evaluation of emissions inventories and emissions reduction programs. Further efforts are underway to overcome some of the limitations of the regional mass-balance approach. Specifically, the use of a dense network of CH_4, $\delta^{13}CH_4$, and hydrocarbon observations to attribute the total CH_4 emissions between different sources is under investigation. Longer-term monitoring observations ingested into inverse models (such as *Miller et al*. [2013]) can also provide a valuable approach to extend the temporal coverage of top-down emission estimates. More top-down studies are needed to evaluate (1) hydrocarbons emission inventories for dry gas/wet gas/oil production regions and (2) the actual impacts of emission mitigation regulations and best management practices including Leak Detection and Repair programs. Future research should also include the investigation of the apparent gap between bottom-up and top-down hydrocarbon emission estimates at the regional and national scales to track down which sources are either missing or underestimated and to quantify the contribution of anomalously large emitters, as suggested by *Brandt et al*. [2014].

Acknowledgments
The Environment Defense Fund (EDF) provided funding to conduct the aircraft measurements in May 2012. NOAA, EDF, Climate Program Office's Atmospheric Chemistry, Carbon Cycle and Climate (AC4) program, and NSF AirWaterGas Sustainability Research Network supported the data analysis and interpretation. The NOAA Climate Program Office's Atmospheric Chemistry, Carbon Cycle and Climate (AC4) program partly supported operations and data analysis. We thank the following NOAA Earth Systems Research Lab and University of Colorado CIRES colleagues: Danlei Chao, Andrew Crotwell, Molly Crotwell, Jack Higgs, Duane Kitzis, Ken Masarie, John Miller, Lloyd Miller, Eric Moglia, Carolina Siso, Kelly Sours, Jonathan Williams, Bill Dube, and Jeff Peischl for their many and varied technical contributions. We thank NOAA ESRL Chemical Sciences Division and Physical Sciences Division for supporting the deployment of the HRDL instrument at the NOAA Platteville site (CSD) and the wind profiler at the CHILL site near Greeley, Colorado (PSD). Surface flux measurements at the BAO are supported by an NSF Early Career award (AGS-0955841). We also thank NOAA ESRL Physical Sciences Division for providing high-quality meteorological measurements and supporting multiple long-term and intensive science operations at the NOAA Boulder Atmospheric Observatory near Erie, Colorado. We thank Dale Wells and the Colorado Department of Public Health and the Environment for providing emission inventory data and detailed information on how the state inventory is built. Finally, we gratefully acknowledge the constructive comments from two anonymous reviewers. The GMD data are available at http://www.esrl.noaa.gov/gmd/dv/data/.

References

Allen, D. T., et al. (2013), Measurements of methane emissions at natural gas production sites in the United States, *Proc. Natl. Acad. Sci. U. S. A.*, doi:10.1073/pnas.1304880110.

API/ANGA (2012), Characterizing pivotal sources of methane emissions from natural gas production, 57 pp.

Bar-Ilan, A., and R. Morris (2012), 2008 O&G emissions for Colorado Basins (Denver-Julesburg, Piceance, and North San Juan), final emissions technical memorandum 4a.

Bar-Ilan, A., et al. (2008), Development of baseline 2006 emissions from oil and gas activity in the Denver-Julesburg Basin, WRAP Phase III report, 34 pp., Western Reg. Air Partnership, Fort Collins, Colo. [Available at http://www.wrapair.org/forums/ogwg/documents/2008-04_06_Baseline_Emissions_D-J_Basin_Technical_Memo_(04-30).]

Bogner, J., K. Spokas, and J. Chanton (2011), Seasonal greenhouse gas emissions (methane, carbon dioxide, nitrous oxide) from engineered landfills: Daily, intermediate, and final California landfill cover soils, *J. Environ. Qual.*, *40*, 1010–1020.

Brandt, A. R., et al. (2014), Methane leaks from North American natural gas systems, *Science*, *343*(6172), 733–735, doi:10.1126/science.1247045.

Colorado Department of Public Health and the Environment (CDPHE) (2002), Colorado greenhouse gas emissions inventory & forecast: 1990 to 2015, 74 pp.

Colorado Department of Public Health and the Environment (CDPHE) (2008), Denver metropolitan area and north Front Range 8-hour ozone state implementation plan, Technical Support Document For Proposed Pneumatic Controller Regulation. [Available at http://www.colorado.gov/airquality/documents/deno308/Pneumatic_Controller_TSD_DRAFT.pdf.]

Colorado Department of Natural Resources (2011), Colorado new oil boom: The Niobrara, Rock Talk, vol 13(1). [Available at http://geosurvey.state.co.us/pubs/Documents/rtv13n1%204-15-11%20B.pdf.]

Colorado Oil and Gas Conservation Commission (COGCC) (2014), County level production data available in the "DataBase" section. [Available at http://cogcc.state.co.us/.]

Czepiel, P. M., B. Mosher, R. C. Harriss, J. H. Shorter, J. B. McManus, C. E. Kolb, E. Allwine, and B. K. Lamb (1996), Landfill methane emissions measured by enclosure and atmospheric tracer methods, *J. Geophys. Res.*, *101*(D11), 16,711–16,719, doi:10.1029/96JD00864.

Czepiel, P. M., J. H. Shorter, B. Mosher, E. Allwine, J. B. McManus, R. C. Harriss, C. E. Kolb, and B. K. Lamb (2003), The influence of atmospheric pressure on landfill methane emissions, *Waste Manage.*, *23*(7), 593–598.

Dlugokencky, E. J., K. A. Masarie, P. P. Tans, T. J. Conway, and X. Xiong (1997), Is the amplitude of the methane seasonal cycle changing?, *Atmos. Environ.*, *31*(1), 21–26, doi:10.1016/s1352-2310(96)00174-4.

Eisele, A., M. Hannigan, J. Milford, D. Helmig, and P. Milmoe (2009), Understanding air toxics and carbonyl pollutant sources in Boulder County, Colorado, prepared for Environmental Protection Agency Region 8, 145 pp. [Available at http://www.epa.gov/ttnamti1/files/20052006csatam/BCPHAirToxicsReportEPA.pdf.]

Fishman, N. S., et al. (2005), *Energy Resource Studies, Northern Front Range, Colorado*, *U. S. Geol. Surv. Prof. Pap., 1698*. [Available at http://pubs.usgs.gov/pp/2005/1698/pdf/P1698.pdf.]

Gilman, J. B., B. M. Lerner, W. C. Kuster, and J. de Gouw (2013), Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado, *Environ. Sci. Technol.*, doi:10.1021/es304119a.

Goldan, P. D., M. Trainer, W. C. Kuster, D. D. Parrish, J. Carpenter, J. M. Roberts, J. E. Yee, and F. C. Fehsenfeld (1995), Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide, and nitrogen oxides in an urban basin in Colorado: Implications for emission inventories, *J. Geophys. Res.*, *100*(D11), 22,771–22,783, doi:10.1029/95JD01369.

Grund, C. J., et al. (2001), High-resolution Doppler lidar for boundary layer and cloud research, *J. Atmos. Oceanic Technol.*, *18*(3), 376–393.

Higley, D., and D. Cox (2007), Oil and gas exploration and development along the front range in the Denver Basin of Colorado, Nebraska, and Wyoming, in Higley, D.K., compiler, Petroleum systems and assessment of undiscovered oil and gas in the Denver Basin Province, Colorado, Kansas, Nebraska, South Dakota, and Wyoming—USGS Province 39: U.S. Geo. Surv. Digital Data Ser. DDS–69–P, ch. 2, 41 pp.

IPCC (2000), Background papers IPCC expert meetings on good practice guidance and uncertainty management in national greenhouse gas inventories, CH_4 and N_2O emissions from livestock manure, pp. 321–338. [Available at http://www.ipcc-nggip.iges.or.jp/public/gp/gpg-bgp.html.]

Johnson, K. A., and D. E. Johnson (1995), Methane emissions from cattle, *J. Anim. Sci.*, *73*(8), 2483–92.

Karion, A., et al. (2013), Methane emissions estimates from airborne measurements over a western United States natural gas field, *Geophys. Res. Lett.*, *40*, 4393–4397, doi:10.1002/grl.50811.

Kebreab, E., K. A. Johnson, S. L. Archibeque, D. Pape, and T. Wirth (2008), Model for estimating enteric methane emissions from United States dairy and feedlot cattle, *J. Anim. Sci.*, *86*, 2738–2748, doi:10.2527/jas.2008-0960.

Klusman, R., and M. Jakel (1998), Natural microseepage of methane to the atmosphere from the Denver-Julesburg basin, Colorado, *J. Geophys. Res.*, *103*(D21), 28,041–28,045, doi:10.1029/98JD02399.

LaFranchi, B. W., et al. (2013), Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}CO_2$, *Atmos. Chem. Phys.*, *13*, 11,101–11,120, doi:10.5194/acp-13-11101-2013.

Levi, M. A. (2012), Comment on “Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study” by Gabrielle Pétron et al., *J. Geophys. Res.*, *117*, D21203, doi:10.1029/2012JD017686.

Lodman, D. W., M. E. Branine, B. R. Carmean, P. Zimmerman, G. M. Ward, and D. E. Johnson (1993), Estimates of methane emissions from manure of U.S. cattle, *Chemosphere*, *26*(1–4), 189–199.

Miller, S. M., et al. (2013), Anthropogenic emissions of methane in the United States, *Proc. Natl. Acad. Sci. U.S.A.*, doi:10.1073/pnas.1314392110.

Montzka, S. A., R. C. Myers, J. H. Butler, J. W. Elkins, and S. O. Cummings (1993), Global tropospheric distribution and calibration scale of HCFC-22, *Geophys. Res. Lett.*, *20*(8), 703–706, doi:10.1029/93GL00573.

Mosher, B. W., P. Czepiel, R. Harriss, J. Shorter, C. Kolb, J. B. McManus, E. Allwine, and B. Lamb (1999), CH_4 emissions at nine landfill sites in the northeastern United States, *Environ. Sci. Technol.*, *33*, 2088–2094.

NASS (2014), Colorado agricultural statistics 2013. [Available at http://www.nass.usda.gov/Statistics_by_State/Colorado/Publications/Annual_Statistical_Bulletin/Final%202013.pdf.]

Novelli, P. C., et al. (1998), An internally consistent set of globally distributed atmospheric carbon monoxide mixing ratios developed using results from an intercomparison of measurements, *J. Geophys. Res.*, *103*, 19,285–19,293, doi:10.1029/97JD00031.

Peischl, J., et al. (2013), Quantifying sources of methane using light alkanes in the Los Angeles basin, California, *J. Geophys. Res. Atmos.*, *118*, 4974–4990, doi:10.1002/jgrd.50413.

Pétron, G., et al. (2012), Hydrocarbon emissions characterization in the Colorado Front Range—A pilot study, *J. Geophys. Res.*, *117*, D04304, doi:10.1029/2011JD016360.

Pétron, G., G. J. Frost, M. K. Trainer, B. R. Miller, E. J. Dlugokencky, and P. Tans (2013), Reply to comment on “Hydrocarbon emissions characterization in the Colorado Front Range—A pilot study” by Michael A. Levi, *J. Geophys. Res. Atmos.*, *118*, 236–242, doi:10.1029/2012JD018487.

Roberts, S. B., J. L. Hynes, and C. L. Woodward (2001), Map showing the extent of mining, locations of mine shafts, adits, air shafts, and bedrock faults, and thickness of overburden above abandoned coal mines in the Boulder-Weld Coal Field, Boulder, Weld, and Adams Counties, Colorado. [Available at: http://pubs.usgs.gov/imap/i-2735/.]

Scamehorn, L. (2002), High altitude energy: A history of fossil fuels in Colorado. Boulder: University Press of Colorado, 2002. xvi +232 pp. ISBN 0-87081-661-6.

Sharvelle, S., and L. Loetscher (2011), Anaerobic digestion of animal wastes in Colorado, Livestock Series - Management, Fact Sheet, 1.227, 3 pp. [Available at http://www.ext.colostate.edu/pubs/livestk/01227.pdf.]

Shorter, J. H., et al. (1997), Collection of leakage statistics in the natural gas system by tracer methods, *Environ. Sci. Technol.*, *31*, 2012–2019.

Sonnenberg, S. (2012), *The Niobrara Petroleum System, Rocky Mountain Region, Search and Discovery Article #80206*. [Available at: http://www.searchanddiscovery.com/documents/2012/80206sonnenberg/ndx_sonnenberg.pdf.]

Stackhouse, K. R., Y. Pan, Y. Zhao, and F. M. Mitloehner (2011), Greenhouse gas and alcohol emissions from feedlot steers and calves, *J. Environ. Qual.*, *40*, 899–906, doi:10.2134/jeq2010.0354.

Steed, J., Jr., and A. G. Hashimoto (1994), Methane emissions from typical manure management systems, *Bioresour. Technol.*, *50*(2), 123–130.

Strait, R., S. Roe, A. Bailie, H. Lindquist, and A. Jamison (2007), Colorado greenhouse gas inventory and reference case projections 1990–2020, report, 99 pp., CDPHE, Denver, Colo. [Available at http://www.cdphe. state.co.us/ap/studiesreports.html.]

Swarthout, R. F., R. S. Russo, Y. Zhou, A. H. Hart, and B. C. Sive (2013), Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources, *J. Geophys. Res. Atmos.*, *118*, 10,614–10,637, doi:10.1002/jgrd.50722.

USDA (2012), 2007 census of agriculture, County Level Data accessible via the USDA National Agricultural Statistical Services quick stat. [Available at http://quickstats.nass.usda.gov/.]

U.S. Environmental Protection Agency/Global Reporting Initiative (EPA/GRI) (1996), Methane emissions from the natural gas industry, Volume 2: *Tech. Rep.*, EPA-600/R-96-080b, 152pp.

U.S. Environmental Protection Agency (EPA) (1999), U.S. methane emissions 1990–2020: Inventories, projections, and opportunities for reductions, Appendix V: Livestock Manure Management, 26 pp. [Available at http://www.epa.gov/outreach/reports/05-manure.pdf.]

U.S. Environmental Protection Agency (EPA) (2004), Methane emissions from abandoned coal mines in the United States: Emission inventory methodology and 1990–2002 emissions estimates, 90 pp. [Available at http://www.epa.gov/cmop/docs/amm_final_report.pdf.]

U.S. Environmental Protection Agency (EPA) (2009), Technical support document for manure management systems: Proposed rule for mandatory reporting of greenhouse gases, 20 pp. [Available at: http://www.epa.gov/ghgreporting/documents/pdf/archived/tsd/TSD%20manure_020409.pdf.]

U.S. Environmental Protection Agency (EPA) (2013a), Inventory of U.S. greenhouse gas emissions and sinks: 1990–2011. [Available at http://www.epa.gov/climatechange/ghgemissions/usinventoryreport/archive.html.]

U.S. Environmental Protection Agency (EPA) (2013b), 2012 greenhouse gas emissions from large facilities. [Available at http://ghgdata.epa.gov/ghgp/main.do.]

U.S. Environmental Protection Agency (EPA) (2014), Draft inventory of U.S. greenhouse gas emissions and sinks: 1990–2012. [Available at http://www.epa.gov/climatechange/ghgemissions/usinventoryreport.html.]

Wells, D. (2012), Condensate tanks emissions, Extended abstract to EPA 2012 International Emission Inventory Conference "Emission Inventories - Meeting the Challenges Posed by Emerging Global, National, Regional and Local Air Quality Issues", 12 pp. [Available at http://www.epa.gov/ttnchie1/conference/ei20/.]

Westberg, H., B. Lamb, K. A. Johnson, and M. Huyler (2001), Inventory of methane emissions from U.S. cattle, *J. Geophys. Res.*, *106*, 12,633–12,642, doi:10.1029/2000JD900808.