

## Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study

Gabrielle Pétron,<sup>1,2</sup> Gregory Frost,<sup>1,2</sup> Benjamin R. Miller,<sup>1,2</sup> Adam I. Hirsch,<sup>1,3</sup> Stephen A. Montzka,<sup>2</sup> Anna Karion,<sup>1,2</sup> Michael Trainer,<sup>2</sup> Colm Sweeney,<sup>1,2</sup> Arlyn E. Andrews,<sup>2</sup> Lloyd Miller,<sup>4</sup> Jonathan Kofler,<sup>1,2</sup> Amnon Bar-Ilan,<sup>5</sup> Ed J. Dlugokencky,<sup>2</sup> Laura Patrick,<sup>1,2</sup> Charles T. Moore Jr.,<sup>6</sup> Thomas B. Ryerson,<sup>2</sup> Carolina Siso,<sup>1,2</sup> William Kolodzey,<sup>7</sup> Patricia M. Lang,<sup>2</sup> Thomas Conway,<sup>2</sup> Paul Novelli,<sup>2</sup> Kenneth Masarie,<sup>2</sup> Bradley Hall,<sup>2</sup> Douglas Guenther,<sup>1,2</sup> Duane Kitzis,<sup>1,2</sup> John Miller,<sup>1,2</sup> David Welsh,<sup>2</sup> Dan Wolfe,<sup>2</sup> William Neff,<sup>2</sup> and Pieter Tans<sup>2</sup>

Received 3 June 2011; revised 19 December 2011; accepted 20 December 2011; published 21 February 2012.

[1] The multispecies analysis of daily air samples collected at the NOAA Boulder Atmospheric Observatory (BAO) in Weld County in northeastern Colorado since 2007 shows highly correlated alkane enhancements caused by a regionally distributed mix of sources in the Denver-Julesburg Basin. To further characterize the emissions of methane and non-methane hydrocarbons (propane, n-butane, i-pentane, n-pentane and benzene) around BAO, a pilot study involving automobile-based surveys was carried out during the summer of 2008. A mix of venting emissions (leaks) of raw natural gas and flashing emissions from condensate storage tanks can explain the alkane ratios we observe in air masses impacted by oil and gas operations in northeastern Colorado. Using the WRAP Phase III inventory of total volatile organic compound (VOC) emissions from oil and gas exploration, production and processing, together with flashing and venting emission speciation profiles provided by State agencies or the oil and gas industry, we derive a range of bottom-up speciated emissions for Weld County in 2008. We use the observed ambient molar ratios and flashing and venting emissions data to calculate top-down scenarios for the amount of natural gas leaked to the atmosphere and the associated methane and non-methane emissions. Our analysis suggests that the emissions of the species we measured are most likely underestimated in current inventories and that the uncertainties attached to these estimates can be as high as a factor of two.

**Citation:** 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.

### 1. Introduction

[2] Since 2004, the National Oceanic and Atmospheric Administration Earth System Research Laboratory (NOAA ESRL) has increased its measurement network density over North America, with continuous carbon dioxide (CO<sub>2</sub>) and

carbon monoxide (CO) measurements and daily collection of discrete air samples at a network of tall towers (A. E. Andrews et al., manuscript in preparation, 2012) and bi-weekly discrete air sampling along vertical aircraft profiles (C. Sweeney et al., manuscript in preparation, 2012). Close to 60 chemical species or isotopes are measured in the discrete air samples, including long-lived greenhouse gases (GHGs) such as CO<sub>2</sub>, methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and sulfur hexafluoride (SF<sub>6</sub>), tropospheric ozone precursors such as CO and several volatile organic compounds (VOCs), and stratospheric-ozone-depleting substances. The NOAA multispecies regional data set provides unique information on how important atmospheric trace gases vary in space and time over the continent, and it can be used to quantify how different processes contribute to GHG burdens and/or affect regional air quality.

[3] In this study we focus our analysis on a very strong alkane atmospheric signature observed downwind of the Denver-Julesburg Fossil Fuel Basin (DJB) in the Colorado Northern Front Range (Figure 1 and auxiliary material

<sup>1</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Boulder, Colorado, USA.

<sup>2</sup>Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA.

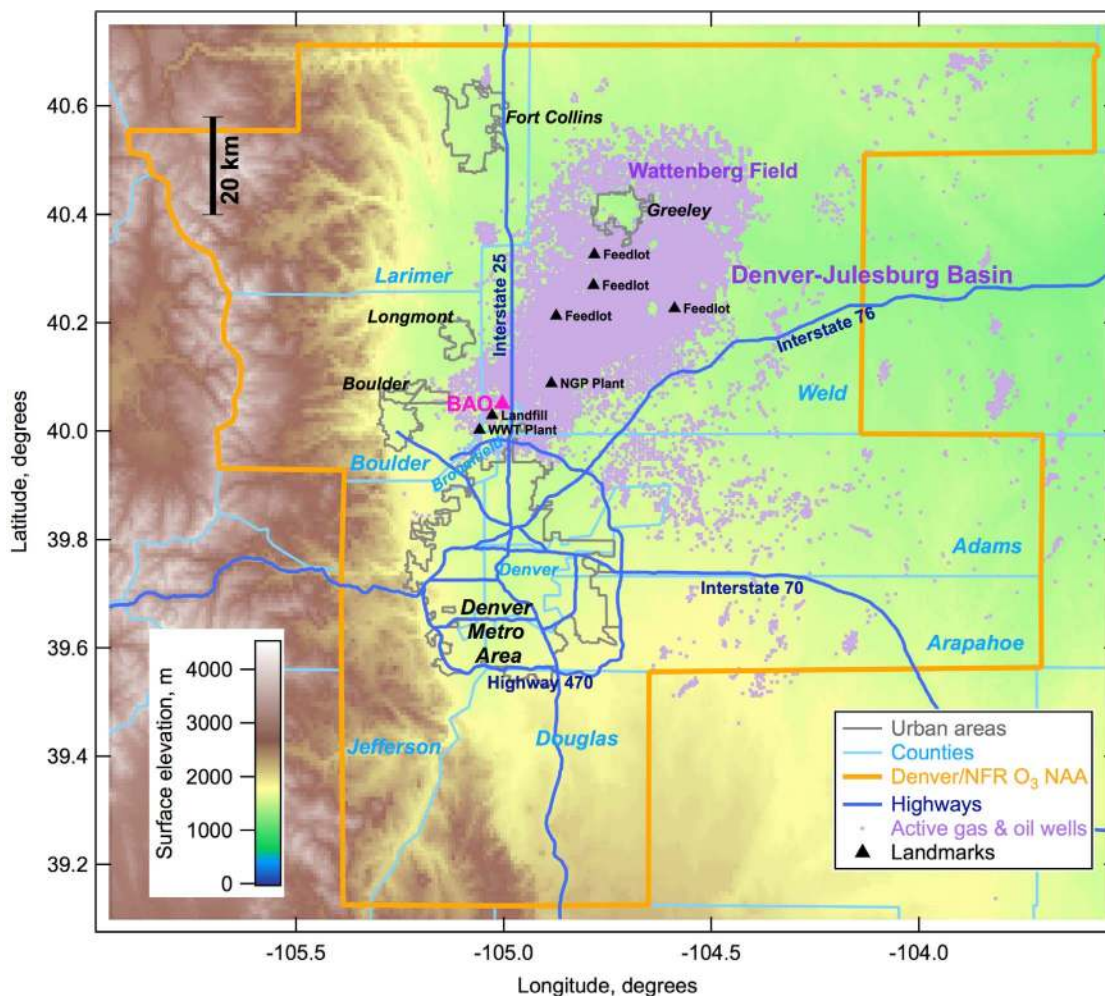
<sup>3</sup>Now at the National Renewable Energy Laboratory, Golden, Colorado, USA.

<sup>4</sup>Formerly at Science and Technology Corporation, Boulder, Colorado, USA.

<sup>5</sup>ENVIRON International Corporation, Novato, California, USA.

<sup>6</sup>Western Regional Air Partnership, Western Governors' Association, Fort Collins, Colorado, USA.

<sup>7</sup>Holcombe Department of Electrical and Computer Engineering, Clemson University, Clemson, South Carolina, USA.



**Figure 1.** Map of the study area centered on the Boulder Atmospheric Observatory (BAO), located 25 km east-northeast of Boulder. Overlaid on this map are the locations of active oil and gas wells (light purple dots) as of April 2008 (data courtesy of SkyTruth, <http://blog.skytruth.org/2008/06/colorado-all-natural-gas-and-oil-wells.html>, based on COGCC well data). Also shown are the locations of landmarks used in the study, including selected point sources (NGP Plant = natural gas processing plant, WWT Plant = Lafayette wastewater treatment plant).

Figure S1).<sup>1</sup> In 2008, the DJB was home to over 20,000 active natural gas and condensate wells. Over 90% of the production in 2008 came from tight gas formations.

[4] A few recent studies have looked at the impact of oil and gas operations on air composition at the local and regional scales in North America. *Katzenstein et al.* [2003] reported results of two intensive surface air discrete sampling efforts over the Anadarko Fossil Fuel Basin in the southwestern United States in 2002. Their analysis revealed substantial regional atmospheric CH<sub>4</sub> and non-methane hydrocarbon (NMHC) pollution over parts of Texas, Oklahoma, and Kansas, which they attributed to emissions from the oil and gas industry operations. More recently, *Schnell et al.* [2009] observed very high wintertime ozone levels in the vicinity of the Jonah-Pinedale Anticline natural gas field in western Wyoming. *Ryerson et al.* [2003], *Wert et al.*

[2003], *de Gouw et al.* [2009] and *Mellqvist et al.* [2010] reported elevated emissions of alkenes from petrochemical plants and refineries in the Houston area and studied their contribution to ozone formation. *Simpson et al.* [2010] present an extensive analysis of atmospheric mixing ratios for a long list of trace gases over oil sands mining operations in Alberta during one flight of the 2008 Arctic Research of the Composition of the Troposphere from Aircraft and Satellites campaign. Our study distinguishes itself from previous ones by the fact that it relies substantially on the analysis of daily air samples collected at a single tall-tower monitoring site between August 2007 and April 2010.

[5] Colorado has a long history of fossil fuel extraction [*Scamehorn*, 2002]. Colorado natural gas production has been increasing since the 1980s, and its share of national production jumped from 3% in 2000 to 5.4% in 2008. 1.3% of the nationally produced oil in 2008 also came from Colorado, primarily from the DJB in northeastern Colorado and from the Piceance Basin in western Colorado. As of

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011JD016360.

2004, Colorado also contained 43 natural gas processing plants, representing 3.5% of the conterminous U.S. processing capacity [U.S. Energy Information Administration (EIA), 2006], and two oil refineries, located in Commerce City, in Adams County just north of Denver.

[6] Emissions management requirements for both air quality and climate-relevant gases have led the state of Colorado to build detailed baseline emissions inventories for ozone precursors, including volatile organic compounds (VOCs), and for GHGs. Since 2004, a large fraction of the Colorado Northern Front Range, including Weld County and the Denver metropolitan area, has been in violation of the 8-h ozone national ambient air quality standard [Colorado Department of Public Health and Environment (CDPHE), 2008]. In December 2007, the Denver and Colorado Northern Front Range (DNFR) region was officially designated as a Federal Non-Attainment Area (NAA) for repeated violation in the summertime of the ozone National Ambient Air Quality Standard (see area encompassed by golden boundary in Figure 1). At the end of 2007, Colorado also adopted a Climate Action Plan, which sets greenhouse gas emissions reduction targets for the state [Ritter, 2007].

[7] Methane, a strong greenhouse gas with a global warming potential (GWP) of 25 over a 100 yr time horizon [Intergovernmental Panel on Climate Change, 2007], accounts for a significant fraction of Colorado GHG emissions, estimated at 14% in 2005 (Strait *et al.* [2007] and auxiliary material Table S1; note that in this report, the oil and gas industry CH<sub>4</sub> emission estimates were calculated with the EPA State Greenhouse Gas Inventory Tool). The natural gas industry (including exploration, production, processing, transmission and distribution) is the single largest source of CH<sub>4</sub> in the state of Colorado (estimated at 238 Gg/yr or ktonnes/yr), followed closely by coal mining (233 Gg/yr); note that all operating surface and underground coal mines are now in western Colorado. Emission estimates for oil production operations in the state were much lower, at 9.5 Gg/yr, than those from gas production. In 2005, Weld County represented 16.5% of the state's natural gas production and 51% of the state crude oil/natural gas condensate production (auxiliary material Table S2). Scaling the state's total CH<sub>4</sub> emission estimates from Strait *et al.* [2007], rough estimates for the 2005 CH<sub>4</sub> source from natural gas production and processing operations and from natural gas condensate/oil production in Weld County are 19.6 Gg and 4.8 Gg, respectively. It is important to stress here that there are large uncertainties associated with these inventory-derived estimates.

[8] Other important sources of CH<sub>4</sub> in the state include large open-air cattle feedlots, landfills, wastewater treatment facilities, forest fires, and agriculture waste burning, which are all difficult to quantify. 2005 state total CH<sub>4</sub> emissions from enteric fermentation and manure management were estimated at 143 and 48 Gg/yr, respectively [Strait *et al.*, 2007]; this combined source is of comparable magnitude to the estimate from natural gas systems. On-road transportation is not a substantial source of methane [Nam *et al.*, 2004].

[9] In 2006, forty percent of the DNFR NAA's total anthropogenic VOC emissions were estimated to be due to oil and gas operations [CDPHE, 2008]. Over the past few years, the State of Colorado has adopted more stringent VOC

emission controls for oil and gas exploration and processing activities. In 2007, the Independent Petroleum Association of Mountain States (IPAMS, now Western Energy Alliance), in conjunction with the Western Regional Air Partnership (WRAP), funded a working group to build a state-of-the-knowledge process-based inventory of total VOC and NO<sub>x</sub> sources involved in oil and gas exploration, production and gathering activities for the western United State's fossil fuel basins, hereafter referred to as the WRAP Phase III effort (<http://www.wrapair.org/forums/ogwg/index.html>). Most of the oil and gas production in the DJB is concentrated in Weld County. Large and small condensate storage tanks in the County are estimated to be the largest VOC fossil fuel production source category (59% and 9% respectively), followed by pneumatic devices (valve controllers) and unpermitted fugitives emissions (13% and 9% respectively). A detailed breakdown of the WRAP oil and gas source contributions is shown in auxiliary material Figure S2 for 2006 emissions and projected 2010 emissions [Bar-Ilan *et al.*, 2008a, 2008b]. The EPA NEI 2005 for Weld County, used until recently by most air quality modelers, did not include VOC sources from oil and natural gas operations (auxiliary material Table S3).

[10] Benzene (C<sub>6</sub>H<sub>6</sub>) is a known human carcinogen and it is one of the 188 hazardous air pollutants (HAPs) tracked by the EPA National Air Toxics Assessment (NATA). Benzene, like VOCs and CH<sub>4</sub>, can be released at many different stages of oil and gas production and processing. Natural gas itself can contain varying amounts of aromatic hydrocarbons, including C<sub>6</sub>H<sub>6</sub> [U. S. Environmental Protection Agency (EPA), 1998]. Natural gas associated with oil production (such sources are located in several places around the DJB) usually has higher C<sub>6</sub>H<sub>6</sub> levels [Burns, 1999] than non-associated natural gas. Glycol dehydrators used at wells and processing facilities to remove water from pumped natural gas can vent large amounts of C<sub>6</sub>H<sub>6</sub> to the atmosphere when the glycol undergoes regeneration [EPA, 1998]. Condensate tanks, venting and flaring at the wellheads, compressors, processing plants, and engine exhaust are also known sources of C<sub>6</sub>H<sub>6</sub> [EPA, 1998]. C<sub>6</sub>H<sub>6</sub> can also be present in the liquids used for fracturing wells [EPA, 2004].

[11] In this paper, we focus on describing and interpreting the measured variability in CH<sub>4</sub> and C<sub>3-5</sub> alkanes observed in the Colorado Northern Front Range. We use data from daily air samples collected at a NOAA tall tower located in Weld County as well as continuous CH<sub>4</sub> observations and discrete targeted samples from an intensive mobile sampling campaign in the Colorado Northern Front Range. These atmospheric measurements are then used together with other emissions data sets to provide an independent view of methane and non-methane hydrocarbon emissions inventory results.

[12] The paper is organized as follows. Section 2 describes the study design and sampling methods. Section 3 presents results from the tall tower and the Mobile Lab surveys, in particular the strong correlation among the various alkanes measured. Based on the multispecies analysis in the discrete air samples, we were able to identify two major sources of C<sub>6</sub>H<sub>6</sub> in Weld County. In section 4.1 we discuss the results and in section 4.2 we compare the observed ambient molar ratios with other relevant data sets, including raw natural gas composition data from 77 gas wells in the DJB. The last discussion section 4.3, is an attempt to shed new light on

**Table 1.** Locations of a Subset of the NOAA ESRL Towers and Aircraft Profile Sites Used in This Study<sup>a</sup>

Site Code	City	State	Latitude (°N)	Longitude (°E)	Elevation (Meters Above Sea Level)	Sampling Height (Meters Above Ground)
BAO	Erie	Colorado	40.05	105.01	1584	300
LEF	Park Falls	Wisconsin	45.93	90.27	472	396
NWF	Niwot Ridge	Colorado	40.03	105.55	3050	23
STR	San Francisco	California	37.755	122.45	254	232
WGC	Walnut Grove	California	38.26	121.49	0	91
WKT	Moody	Texas	31.32	97.33	251	457
SGP <sup>b</sup>	Southern Great Plains	Oklahoma	36.80	97.50	314	<650

<sup>a</sup>STR and WGC in Northern California are collaborations with Department of Energy Environmental Energy Technologies Division at Lawrence Berkeley National Laboratory (PI: Marc Fischer). The last column gives the altitudes of the quasi-daily flask air samples used in this study. We use midday data for all sites, but at Niwot Ridge Forest we used nighttime data to capture background air from summertime downslope flow. We also show the location information of SGP, a NOAA ESRL aircraft site in north central Oklahoma, for which we used samples taken below 650 m altitude.

<sup>b</sup>Aircraft discrete air samples.

methane and VOC emission estimates from oil and gas operations in Weld County. We first describe how we derived speciated bottom-up emission estimates based on the WRAP Phase III total VOC emission inventories for counties in the DJB. We then used (1) an average ambient propane-to-methane molar ratio, (2) a set of bottom-up estimates of propane and methane flashing emissions in Weld County and (3) three different estimates of the propane-to-methane molar ratio for the raw gas leaks to build top-down methane and propane emission scenarios for venting sources in the county. We also scaled the top-down propane (C<sub>3</sub>H<sub>8</sub>) estimates with the observed ambient alkane ratios to calculate top-down emission estimates for n-butane (n-C<sub>4</sub>H<sub>10</sub>), i- and n-pentane (i-C<sub>5</sub>H<sub>12</sub>, n-C<sub>5</sub>H<sub>12</sub>), and benzene. We summarize our main conclusions in section 5.

## 2. The Front Range Emissions Study: Sampling Strategy, Instrumentation, and Sample Analysis

### 2.1. Overall Experimental Design

[13] The Colorado Northern Front Range study was a pilot project to design and test a new measurement strategy to characterize GHG emissions at the regional level. The anchor of the study was a 300-m tall tower located in Weld County, 25 km east-northeast of Boulder and 35 km north of Denver, called the Boulder Atmospheric Observatory (BAO) [40.05°N, 105.01°W; base of tower at 1584 m above sea level] (Figure 1). The BAO is situated on the southwestern edge of the DJB. A large landfill and a wastewater treatment plant are located a few kilometers southwest of BAO. Interstate 25, a major highway going through Denver, runs in a north-south direction 2 km east of the site. Both continuous and discrete air sampling have been conducted at BAO since 2007.

[14] To put the BAO air samples into a larger regional context and to better understand the sources that impacted the discrete air samples, we made automobile-based on-road air sampling surveys around the Colorado Northern Front Range in June and July 2008 with an instrumented “Mobile Lab” and the same discrete sampling apparatus used at all the NOAA towers and aircraft sampling sites.

### 2.2. BAO and Other NOAA Cooperative Tall Towers

[15] The BAO tall tower has been used as a research facility of boundary layer dynamics since the 1970s [Kaimal and Gaynor, 1983]. The BAO tower was instrumented by

the NOAA ESRL Global Monitoring Division (GMD) in Boulder in April 2007, with sampling by a quasi-continuous CO<sub>2</sub> non-dispersive infrared sensor and a CO Gas Filter Correlation instrument, both oscillating between three intake levels (22, 100 and 300 m above ground level) (Andrews et al., manuscript in preparation, 2012). Two continuous ozone UV-absorption instruments have also been deployed to monitor ozone at the surface and at the 300-m level.

[16] The tower is equipped to collect discrete air samples from the 300-m level using a programmable compressor package (PCP) and a programmable flasks package (PFP) described later in section 2.4. Since August 2007 one or two air samples have been taken approximately daily in glass flasks using PFPs and a PCP. The air samples are brought back to GMD for analysis on three different systems to measure a series of compounds, including methane (CH<sub>4</sub>, also referred to as C<sub>1</sub>), CO, propane (C<sub>3</sub>H<sub>8</sub>, also referred to as C<sub>3</sub>), n-butane (n-C<sub>4</sub>H<sub>10</sub>, nC<sub>4</sub>), isopentane (i-C<sub>5</sub>H<sub>12</sub>, iC<sub>5</sub>), n-pentane (n-C<sub>5</sub>H<sub>12</sub>, nC<sub>5</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), benzene, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Ethane and i-butane were not measured.

[17] In this study, we use the results from the NOAA GMD multispecies analysis of air samples collected midday at the 300-m level together with 30-second wind speed and direction measured at 300-m. 30-min averages of the wind speed and direction prior to the collection time of each flask are used to separate samples of air masses coming from three different geographic sectors: the North and East (NE sector), where the majority of the DJB oil and gas wells are located; the South (S sector), mostly influenced by the Denver metropolitan area; and the West (W sector), with relatively cleaner air.

[18] In 2008, NOAA and its collaborators were operating a regional air sampling network of eight towers and 18 aircraft profiling sites located across the continental U.S. employing in situ measurements (most towers) and flask sampling protocols (towers and aircraft sites) that were similar to those used at BAO. Median mixing ratios for several alkanes, benzene, acetylene, and carbon monoxide from BAO and a subset of five other NOAA towers and from one aircraft site are presented in the Results (section 3). Table 1 provides the three letter codes used for each sampling site, their locations and sampling heights. STR is located in San Francisco. WGC is located 34 km south of downtown Sacramento in California’s Central Valley where

**Table 2.** List of the Front Range Mobile Lab Measurement and Flasks Sampling Surveys<sup>a</sup>

Road Survey Number	Road Survey Date	Geographical Area/Target Sources	Measurements/Sampling Technique
1	June 4	Boulder	12 flasks
2	June 11	Boulder + Foothills	12 flasks
3	June 19	NOAA-Longmont-Fort Collins- Greeley (Oil and Gas Drilling, Feedlots)	24 flasks
4	July 1	NOAA - Denver	12 flasks
5	July 9	Around Denver	Picarro
6	July 14	NOAA - Greeley	12 flasks
7	July 15	NOAA-Greeley	Picarro
8	July 25	BAO surroundings - Natural Gas Processing Plant - Feedlot	Picarro + 8 flasks
9	July 31	“Regional” CH <sub>4</sub> enhancements, Landfill, Corn field	Picarro + 12 flasks

<sup>a</sup>Some trips (1, 2, 3, 4, 6) sampled air using the flask only. Surveys 5 and 7 used only the continuous analyzers on the Mobile Lab with no discrete flask collection. The last two trips targeted flask sampling close to known point or area sources based on the continuous methane measurement display in the Mobile Lab.

agriculture is the main economic sector. Irrigated crop fields and feedlots contribute to the higher CH<sub>4</sub> observed at WGC. The LEF tower in northern Wisconsin is in the middle of the Chequamegon National Forest which is a mix of temperate/boreal forest and lowlands/wetlands [Werner *et al.*, 2003]. Air samples from NWF (surface elevation 3050 m), in the Colorado Rocky Mountains, mostly reflect relatively unpolluted air from the free troposphere. The 457m tall Texas tower (WKT) is located between Dallas/Fort Worth and Austin. It often samples air masses from the surrounding metropolitan areas. In summer especially, it also detects air masses with cleaner background levels arriving from the Gulf of Mexico. The SGP NOAA aircraft sampling site (Sweeney *et al.*, manuscript in preparation, 2012; <http://www.esrl.noaa.gov/gmd/ccgg/aircraft/>) in northern Oklahoma is also used in the comparison study. At each aircraft site, twelve discrete air samples are collected at specified altitudes on a weekly or biweekly basis. Oklahoma is the fourth largest state for natural gas production in the USA (EIA, Natural gas navigator, 2008, [http://tonto.eia.doe.gov/dnav/ng/ng\\_prod\\_sum\\_a\\_EPG0\\_FGW\\_mmcf\\_a.htm](http://tonto.eia.doe.gov/dnav/ng/ng_prod_sum_a_EPG0_FGW_mmcf_a.htm)) and one would expect to observe signatures of oil and gas drilling operations at both SGP and BAO. Additional information on the tower and aircraft programs is available at <http://www.esrl.noaa.gov/gmd/ccgg/>. Median summer mixing ratios for several alkanes, C<sub>2</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub> and CO are presented in the Results section.

### 2.3. Mobile Sampling

[19] Two mobile sampling strategies were employed during this study. The first, the Mobile Lab, consisted of a fast response CO<sub>2</sub> and CH<sub>4</sub> analyzer (Picarro, Inc.), a CO gas-filter correlation instrument from Thermo Environmental, Inc., an O<sub>3</sub> UV-absorption analyzer from 2B Technologies and a Global Positioning System (GPS) unit. All were installed onboard a vehicle. A set of 3 parallel inlets attached to a rack on top of the vehicle brought in outside air from a few meters above the ground to the instruments. Another simpler sampling strategy was to drive around and collect flask samples at predetermined locations in the Front Range region. A summary of the on-road surveys is given in Table 2.

[20] The Mobile Lab’s Picarro EnviroSense CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>O analyzer (model G1301, unit CFADS09) employs Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS), a time-based measurement utilizing a near-infrared laser to measure a spectral signature of the molecule. CO<sub>2</sub>, CH<sub>4</sub>, and water vapor were measured at a 5-s sampling rate (0.2 Hz),

with a standard deviation of 0.09 ppm in CO<sub>2</sub> and 0.7 ppb for CH<sub>4</sub>. The sample was not dried prior to analysis, and the CO<sub>2</sub> and CH<sub>4</sub> mole fractions were corrected for water vapor after the experiment based on laboratory tests. For water mole fractions between 1% and 2.5%, the relative magnitude of the CH<sub>4</sub> correction was quasi-linear, with values between 1 and 2.6%. CO<sub>2</sub> and CH<sub>4</sub> mole fractions were assigned against a reference gas tied to the relevant World Meteorological Organization (WMO) calibration scale. Total measurement uncertainties were 0.1 ppm for CO<sub>2</sub> and 2 ppb for CH<sub>4</sub> (Sweeney *et al.*, manuscript in preparation, 2012). The CO and ozone data from the Mobile Lab are not discussed here. GPS data were also collected in the Mobile Lab at 1 Hz, to allow data from the continuous analyzers to be merged with the location of the vehicle.

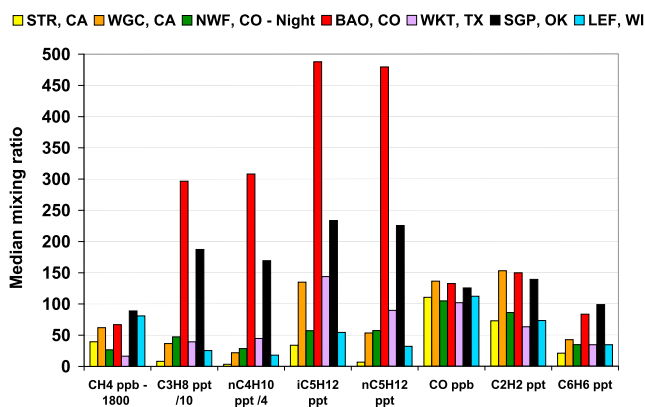
[21] The excursions with the flask sampler (PFP) focused on characterizing the concentrations of trace gases in Boulder (June 4 and 11, 2008), the northeastern Front Range (June 19), Denver (July 1) and around oil and gas wells and feedlots in Weld County south of Greeley (July 14) (see Table 2). Up to 24 sampling locations away from direct vehicle emissions were chosen before each drive.

[22] Each Mobile Lab drive lasted from four to six hours, after a ~30 min warm-up on the NOAA campus for the continuous analyzer before switching to battery mode. The first two Mobile Lab drives, which did not include discrete air sampling, were surveys around Denver (July 9) and between Boulder and Greeley (July 15). The last two drives with the Mobile Lab (July 25 and 31) combined in situ measurements with discrete flask sampling to target emissions from specific sources: the quasi-real-time display of the data from the continuous CO<sub>2</sub>/CH<sub>4</sub> analyzer was used to collect targeted flask samples at strong CH<sub>4</sub> point sources in the vicinity of BAO. Discrete air samples were always collected upwind of the surveying vehicle and when possible away from major road traffic.

### 2.4. Chemical Analyses of Flask Samples

[23] Discrete air samples were collected at BAO and during the road surveys with a two-component collection apparatus. One (PCP) includes pumps and batteries, along with an onboard microprocessor to control air sampling. Air was drawn through Teflon tubing attached to an expandable 3-m long fishing pole. The second package (PFP) contained a sampling manifold and twelve cylindrical, 0.7 L, glass flasks of flow-through design, fitted with Teflon O-ring on both





**Figure 2.** Observed median mixing ratios for several species measured in air samples taken at various sites at midday during June–August (2007–2010). The sites are described in Table 1. Only nighttime samples are shown for NWF to capture background air with predominantly downslope winds. Notice the different units with all columns and the different scaling applied to methane, propane and n-butane.

stopcocks. Before deployment, manifold and flasks were leak-checked then flushed and pressurized to  $\sim 1.4$  atm with synthetic dry zero-air containing approximately 330 ppm of  $\text{CO}_2$  and no detectable  $\text{CH}_4$ . During sampling, the manifold and flasks were flushed sequentially, at  $\sim 5$  L  $\text{min}^{-1}$  for about 1 min and 10 L  $\text{min}^{-1}$  for about 3 min respectively, before the flasks were pressurized to 2.7 atm. Upon returning to the NOAA lab, the PFP manifold was leak-checked and metadata recorded by the PFP during the flushing and sampling procedures were read to verify the integrity of each air sample collected. In case of detected inadequate flushing or filling, the affected air sample is not analyzed.

[24] Samples collected in flasks were analyzed for close to 60 compounds by NOAA GMD (<http://www.esrl.noaa.gov/gmd/ccgg/aircraft/analysis.html>). In this paper, we focus on eight species: 5 alkanes ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_5\text{H}_{12}$ ) as well as  $\text{CO}$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_6\text{H}_6$ .  $\text{CH}_4$  and  $\text{CO}$  in each flask were first quantified on one of two nearly identical automated analytical systems (MAGICC 1 and 2). These systems consist of a custom-made gas inlet system, gas-specific analyzers, and system-control software. Our gas inlet systems use a series of stream selection valves to select an air sample or standard gas, pass it through a trap for drying maintained at  $\sim -80^\circ\text{C}$ , and then to an analyzer.

[25]  $\text{CH}_4$  was measured by gas chromatography (GC) with flame ionization detection ( $\pm 1.2$  ppb = average repeatability determined as 1 s.d. of  $\sim 20$  aliquots of natural air measured from a cylinder) [Dlugokencky *et al.*, 1994]. We use the following abbreviations for measured mole fractions: ppm =  $\mu\text{mol mol}^{-1}$ , ppb =  $\text{nmol mol}^{-1}$ , and ppt =  $\text{pmol mol}^{-1}$ .  $\text{CO}$  was measured directly by resonance fluorescence at  $\sim 150$  nm ( $\pm 0.2$  ppb) [Gerbig *et al.*, 1999; Novelli *et al.*, 1998]. All measurements are reported as dry air mole fractions relative to internally consistent calibration scales maintained at NOAA (<http://www.esrl.noaa.gov/gmd/ccl/scales.html>).

[26] Gas chromatography/mass spectrometric (GC/MS) measurements were also performed on  $\sim 200$  mL aliquots taken from the flask samples and pre-concentrated with a cryogenic trap at near liquid nitrogen temperatures [Montzka

*et al.*, 1993]. Analytes desorbed at  $\sim 110^\circ\text{C}$  were then separated by a temperature-programmed GC column (combination 25 m  $\times$  0.25 mm DB5 and 30 m  $\times$  0.25 mm Gaspro), followed by detection with mass spectrometry by monitoring compound-specific ion mass-to-charge ratios. Flask sample responses were calibrated versus whole air working reference gases which, in turn, are calibrated with respect to gravimetric primary standards (NOAA scales: benzene on NOAA-2006 and all other hydrocarbons (besides  $\text{CH}_4$ ) on NOAA-2008). We used a provisional calibration for n-butane based on a diluted Scott Specialty Gas standard. Total uncertainties for analyses from the GC/MS reported here are  $<5\%$  (accuracy) for all species except  $n\text{-C}_4\text{H}_{10}$  and  $\text{C}_2\text{H}_2$ , for which the total uncertainty at the time of this study was of the order of 15–20%. Measurement precision as repeatability is generally less than 2% for compounds present at mixing ratios above 10 ppt.

[27] To access the storage stability of the compounds of interest in the PFPs, we conducted storage tests of typically 30 days duration, which is greater than the actual storage time of the samples used in this study. Results for  $\text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_8$  show no statistically significant enhancement or degradation with respect to our “control” (the original test gas tank results) within our analytical uncertainty. For the remaining species, enhancements or losses average less than 3% for the 30 day tests. More information on the quality control of the flask analysis data is available at <http://www.esrl.noaa.gov/gmd/ccgg/aircraft/qc.html>.

[28] The flask samples were first sent to the GC/MS instrument for hydrocarbons, CFCs, and HFCs before being analyzed for major GHGs. This first step was meant to screen highly polluted samples that could potentially damage the greenhouse gas MAGICC analysis line with concentrations well above “background” levels. The time interval between flask collection and flask analysis spanned between 1 to 11 days for the GC/MS analysis and 3 to 12 days for MAGICC analysis.

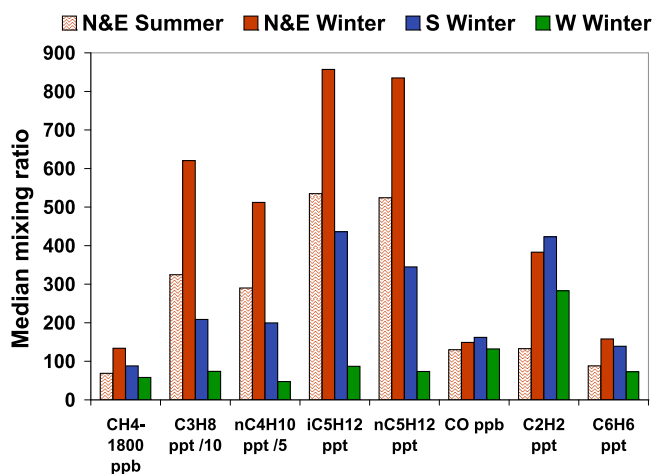
## 3. Results

### 3.1. BAO Tall Tower: Long-Term Sampling Platform for Regional Emissions

#### 3.1.1. Comparing BAO With Other Sampling Sites in the U.S.

[29] Air samples collected at BAO have a distinct chemical signature (Figure 2), showing enhanced levels of most alkanes ( $\text{C}_3\text{H}_8$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_5\text{H}_{12}$ ) in comparison to results from other NOAA cooperative tall towers (see summary of site locations in Table 1 and data time series in auxiliary material Figure S1). The midday summer time median mixing ratios for  $\text{C}_3\text{H}_8$  and  $n\text{-C}_4\text{H}_{10}$  at BAO were at least 6 times higher than those observed at most other tall tower sites. For  $i\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_5\text{H}_{12}$ , the summertime median mixing ratios at BAO were at least 3 times higher than at the other tall towers.

[30] In Figure 2, we show nighttime measurements at the Niwot Ridge Forest tower (NWF) located at a high elevation site on the eastern slopes of the Rocky Mountains, 50 km west of BAO. During the summer nighttime, downslope flow brings clean air to the tower [Roberts *et al.*, 1984]. The median summer mixing ratios at NWF for all the species shown in Figure 2 are much lower than at BAO, as would be expected given the site’s remote location.



**Figure 3.** Summertime and wintertime median mixing ratios of several species measured in air samples from the 300-m level at the BAO tower for three wind sectors: North and East (NE) where the density of gas drilling operations is highest, South (S) with Denver 35 km away, and West (W) with mostly clean air. The time span of the data is from August 2007 to April 2010. Summer includes data from June to August and winter includes data from November to April. Due to the small number of data points (<15), we do not show summer values for the S and W wind sectors. Data outside of the 11 am–3 pm local time window were not used. Notice the different scales used for methane, propane and n-butane. The minimum number of data points used for each wind sector is: NE summer 33, NE winter 89, S winter 65 and W winter 111.

[31] Similarly to BAO, the northern Oklahoma aircraft site, SGP, exhibits high alkane levels in the boundary layer and the highest methane summer median mixing ratio of all sites shown in Figure 2 (1889 ppb at SGP versus 1867 ppb at BAO). As for BAO, SGP is located in an oil- and gas-producing region. Oklahoma, the fourth largest state in terms of natural gas production in the U.S., has a much denser network of interstate and intrastate natural gas pipelines compared to Colorado. Katzenstein *et al.* [2003] documented the spatial extent of alkane plumes around the gas fields of the Anadarko Basin in Texas, Oklahoma, and Kansas during two sampling intensives. The authors estimated that methane emissions from the oil and gas industry in that entire region could be as high as 4–6 Tg CH<sub>4</sub>/yr, which is 13–20% of the U.S. total methane emission estimate for year 2005 reported in the latest EPA U.S. GHG Inventory (EPA, Inventory of U.S. Greenhouse Gas emissions and Sinks: 1990–2009, 2011, available at <http://www.epa.gov/climatechange/emissions>).

[32] Enhancements of CH<sub>4</sub> at BAO are not as striking in comparison to other sites. CH<sub>4</sub> is a long-lived gas destroyed predominantly by its reaction with OH radicals. CH<sub>4</sub> has a background level that varies depending on the location and season [Dlugokencky *et al.*, 1994], making it more difficult to interpret differences in median summer CH<sub>4</sub> mixing ratios at the suite of towers. Since we do not have continuous measurements of CH<sub>4</sub> at any of the towers except WGC, we cannot clearly separate CH<sub>4</sub> enhancements from background variability in samples with levels between

1800 and 1900 ppb if we only look at CH<sub>4</sub> mixing ratios by themselves (see more on this in the next section).

### 3.1.2. Influence of Different Sources at BAO

#### 3.1.2.1. Median Mixing Ratios in the Three Wind Sectors

[33] To better separate the various sources influencing air sampled at BAO, Figure 3 shows the observed median mixing ratios of several species as a function of prevailing wind direction. For this calculation, we only used samples for which the associated 30-min average wind speed (prior to collection time) was larger than 2.5 m/s. We separated the data into three wind sectors: NE, including winds from the north, northeast and east (wind directions between 345° and 120°); S, including south winds (120° to 240°); and W, including winds from the west (240° to 345°).

[34] For the NE sector, we can further separate summer (June to August) and winter (November to April) data. For the other two wind sectors, only the winter months have enough data points. The species shown in Figure 3 have different photochemical lifetimes [Parrish *et al.*, 1998], and all are shorter-lived in the summer season. This fact, combined with enhanced vertical mixing in the summer, leads to lower mixing ratios in summer than in winter.

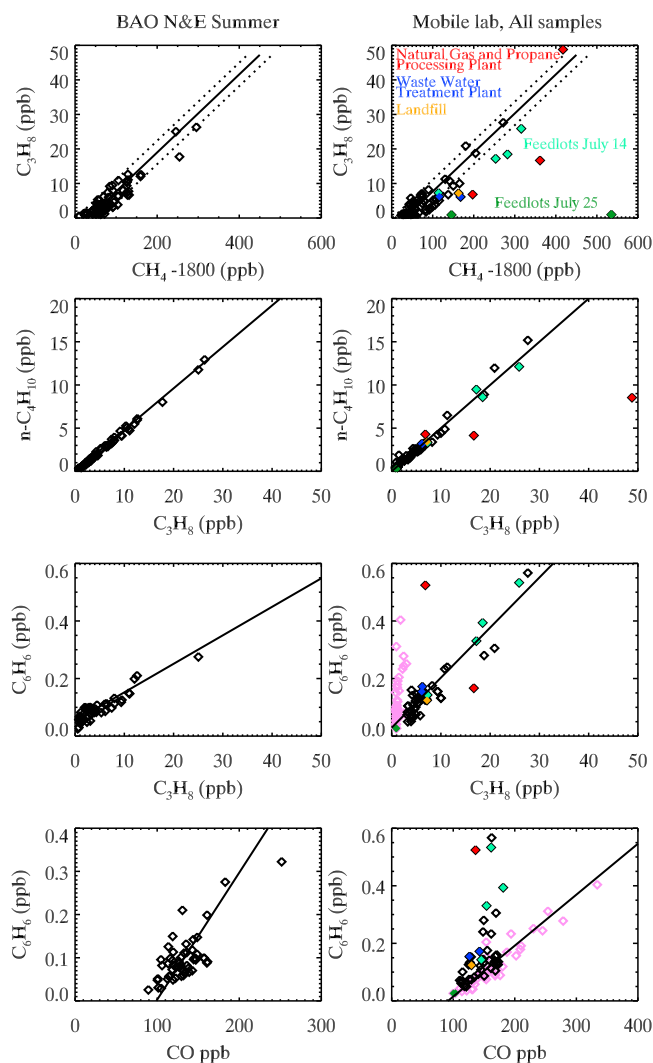
[35] Air masses from the NE sector pass over the oil and gas wells in the DJB and exhibit large alkane enhancements. In winter, median mole fractions of C<sub>3</sub>–C<sub>5</sub> alkanes are 8 to 11 times higher in air samples from the NE compared to the samples from the W sector, while the median CH<sub>4</sub> value is 76 ppb higher. The NE wind sector also shows the highest median values of C<sub>6</sub>H<sub>6</sub>, but not CO and C<sub>2</sub>H<sub>2</sub>.

[36] C<sub>3</sub>H<sub>8</sub>, n-C<sub>4</sub>H<sub>10</sub> and the C<sub>5</sub>H<sub>12</sub> isomers in air samples from the NE wind sector are much higher than in air samples coming from the Denver metropolitan area in the South wind sector. Besides being influenced by Denver, southern air masses may pass over two operating landfills, the Commerce City oil refineries, and some oil and gas wells (Figure 1). The S sector BAO CO and C<sub>2</sub>H<sub>2</sub> mixing ratios are higher than for the other wind sectors, consistent with the higher density of vehicular emission sources [Harley *et al.*, 1992; Warneke *et al.*, 2007; Baker *et al.*, 2008] south of BAO. There are also occasional spikes in CFC-11 and CFC-12 mixing ratios in the S sector (not shown). These are most probably due to leaks from CFC-containing items in the landfills. Air parcels at BAO coming from the east pass over Interstate Highway 25, which could explain some of the high mole fractions observed for vehicle combustion tracers such as CO, C<sub>2</sub>H<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub> in the NE sector data (see more discussion on C<sub>6</sub>H<sub>6</sub> and CO in section 4.4 and Figure 4).

[37] The W wind sector has the lowest median mole fractions for all anthropogenic tracers, consistent with a lower density of emission sources west of BAO compared to the other wind sectors. However, the S and W wind sectors do have some data points with high alkane values, and these data will be discussed further below.

#### 3.1.2.2. Strong Alkane Source Signature

[38] To detect if the air sampled at BAO has specific chemical signatures from various sources, we looked at correlation plots for the species shown in Figure 3. Table 3 summarizes the statistics for various tracer correlations for the three different wind sectors. Figure 4 (left) shows correlation plots of some of these BAO species for summer data in the NE wind sector.



**Figure 4.** Correlation plots for various species measured in the (left) BAO summertime NE wind sector flask samples and (right) summer 2008 Mobile Lab samples. Data at BAO were filtered to keep only midday air samples collected between June and August over the time period spanning August 2007 to August 2009. See also Table 3.

[39] Even though BAO data from the NE winds show the largest alkane mixing ratios (Figure 3), all three sectors exhibit strong correlations between  $C_3H_8$ ,  $n-C_4H_{10}$  and the  $C_5H_{12}$  isomers (Table 3). The  $r^2$  values for the correlations between  $C_3H_8$  and  $n-C_4H_{10}$  or the  $C_5H_{12}$  isomers are over 0.9 for the NE and W sectors.  $CH_4$  is also well correlated with  $C_3H_8$  in the NE wind sector for both seasons. For the NE wind sector BAO summertime data, a min/max range for the  $C_3H_8/CH_4$  slope is 0.099 to 0.109 ppb/ppb.

[40] The tight correlations between the alkanes suggest a common source located in the vicinity of BAO. Since large alkane enhancements are more frequent in the NE wind sector, this common source probably has larger emissions north and east of the tower. This NE wind sector encompasses Interstate Highway 25 and most of the DJB oil and gas wells. The  $C_3$ - $C_5$  alkane mole fractions do not always correlate well with combustion tracers such as  $C_2H_2$  and CO for the BAO NE wind sector ( $C_{3-5}/CO$  and  $C_{3-5}/C_2H_2$ :  $r^2 < 0.3$  for 50 summer samples;  $C_{3-5}/CO$ :  $r^2 < 0.4$  and  $C_{3-5}/C_2H_2$ :  $r^2 \sim 0.6$  for 115 winter samples). These results indicate that the source responsible for the elevated alkanes at BAO is not the major source of CO or  $C_2H_2$ , which argues against vehicle combustion exhaust as being responsible. Northeastern Colorado is mostly rural with no big cities. The only operating oil refineries in Colorado are in the northern part of the Denver metropolitan area, south of BAO. The main industrial operations in the northeastern Front Range are oil and natural gas exploration and production and natural gas processing and transmission. We therefore hypothesize here that the oil and gas operations in the DJB, as noted earlier in section 2, are a potentially substantial source of alkanes in the region.

### 3.1.2.3. At Least Two Sources of Benzene in BAO Vicinity

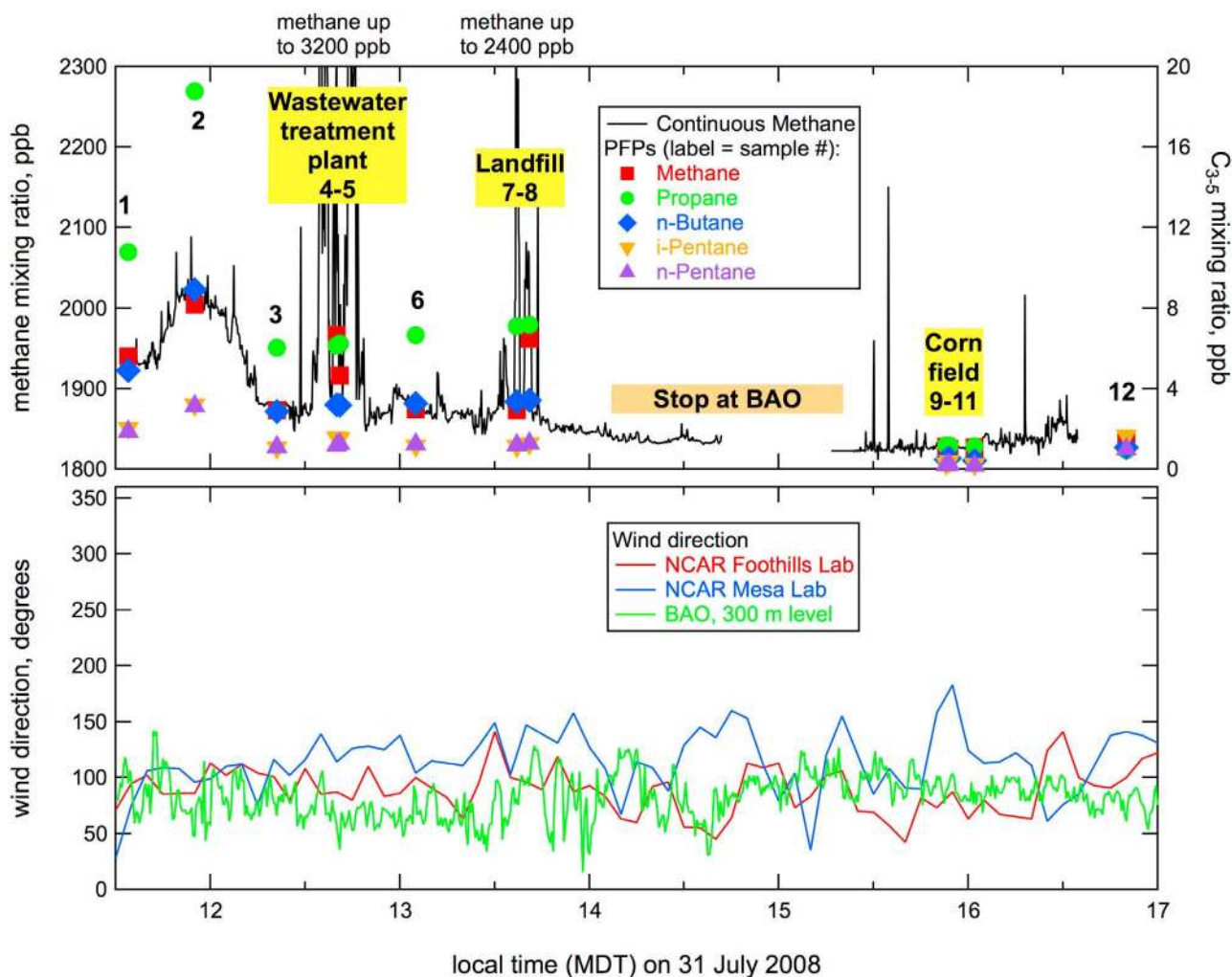
[41] The median winter  $C_6H_6$  mixing ratio at BAO is higher for the NE wind sector compared to the South wind sector, which comprises the Denver metropolitan area. The  $C_6H_6$ -to-CO winter correlation is highest for the S and W wind sectors BAO samples ( $r^2 = 0.85$  and  $0.83$  respectively) compared to the NE wind sector data ( $r^2 = 0.69$ ). The  $C_6H_6$ -to-CO correlation slope is substantially higher for the NE wind sector data compared to the other two wind sectors, suggesting that there may be a source of benzene in the NE

**Table 3.** Correlation Slopes and  $r^2$  for Various Species Measured in the BAO Tower Midday Air Flask Samples for Summer (June to August, When More Than 25 Samples Exist) and Winter (November to April) Over the Time Period Spanning August 2007 to April 2010<sup>a</sup>

Sector		BAO North and East														
Season		Summer			Winter			BAO South Winter			BAO West Winter			Mobile Lab Summer		
Molar Ratios y/x	Units	Slope	$r^2$	n	Slope	$r^2$	n	Slope	$r^2$	n	Slope	$r^2$	n	Slope	$r^2$	n
$C_3H_8/CH_4$	ppb/ppb	<b>0.104 ± 0.005</b>	0.85	81	<b>0.105 ± 0.004</b>	0.90	115	0.079 ± 0.008	0.53	130	<b>0.085 ± 0.005</b>	0.73	148	<b>0.095 ± 0.007</b>	0.76	77
$nC_4H_{10}/C_3H_8$	ppb/ppb	<b>0.447 ± 0.013</b>	1.00	81	<b>0.435 ± 0.005</b>	1.0	120	<b>0.449 ± 0.011</b>	0.98	131	<b>0.434 ± 0.006</b>	1.00	151	<b>0.490 ± 0.011</b>	1.00	85
$iC_5H_{12}/C_3H_8$	ppb/ppb	<b>0.14 ± 0.004</b>	1.00	81	<b>0.134 ± 0.004</b>	0.98	120	<b>0.142 ± 0.009</b>	0.81	121	<b>0.130 ± 0.004</b>	0.94	151	<b>0.185 ± 0.011</b>	0.81	85
$nC_5H_{12}/C_3H_8$	ppb/ppb	<b>0.150 ± 0.003</b>	1.00	81	<b>0.136 ± 0.004</b>	0.98	120	<b>0.142 ± 0.006</b>	0.90	131	<b>0.133 ± 0.003</b>	0.91	151	<b>0.186 ± 0.008</b>	0.92	85
$C_6H_6/C_3H_8$	ppt/ppb	10.1 ± 1.2	0.67	49	<b>8.2 ± 0.5</b>	0.79	117	-	0.33	130	-	0.39	150	<b>17.9 ± 1.1</b>	0.95	46
$C_6H_6/CO$	ppt/ppb	2.89 ± 0.40	0.58	53	3.18 ± 0.24	0.69	112	<b>1.57 ± 0.08</b>	0.85	123	<b>1.81 ± 0.08</b>	0.83	148	<b>1.82 ± 0.12</b>	0.89	39
$C_2H_2/CO$	ppt/ppb	<b>3.15 ± 0.33</b>	0.85	81	<b>7.51 ± 0.39</b>	0.85	100	<b>5.03 ± 0.17</b>	0.92	110	<b>5.85 ± 0.25</b>	0.86	131	<b>4.32 ± 0.28</b>	0.89	39
$C_6H_6/C_2H_2$	ppt/ppt	0.51 ± 0.09	0.55	50	<b>0.34 ± 0.02</b>	0.90	103	<b>0.27 ± 0.02</b>	0.90	111	<b>0.32 ± 0.02</b>	0.96	132	<b>0.37 ± 0.04</b>	0.75	39

<sup>a</sup>The three wind sectors used in Figure 3 are also used here with a 30-min average wind speed threshold of 2.5 m/s. Also shown are the slopes derived from flask samples collected by the Mobile Lab in summer 2008. The slope is in bold when  $r^2$  is higher than 0.7 and the slope is not shown when  $r^2$  is less than 0.4. The number of data points (n) used for the slope and  $r^2$  calculations are provided. All slope units are ppb/ppb, except for  $C_6H_6/C_3H_8$ ,  $C_6H_6/CO$  and  $C_2H_2/CO$ , which are in ppt/ppb. We used the IDL routine linmix\_err.pro for the calculations with the following random measurement errors: 2ppb for  $CH_4$  and CO and 5% for  $C_3H_8$ ,  $n-C_4H_{10}$ ,  $i-C_5H_{12}$ ,  $n-C_5H_{12}$ ,  $C_2H_2$ , and  $C_6H_6$ .





**Figure 5.** (top) Time series of the continuous methane measurements from Mobile Lab Survey 9 on July 31, 2008. Also shown are the mixing ratio data for the 12 flask samples collected during the road survey. The GC/MS had a faulty high energy dynode cable when these samples were analyzed, resulting in more noisy data for the alkanes and the CFCs ( $\sigma < 10\%$  instead of 5%). However, the amplitudes of the  $C_{3-5}$  alkane signals are much larger than the noise here. The methane mixing ratio scale is shown on the left hand vertical axis. For all other alkanes, refer to the right hand vertical axis. (bottom) Time series of wind directions at the NCAR Foothills and Mesa Laboratories in Boulder (see Figure 6 for locations) and from the 300-m level at the BAO on July 31, 2008.

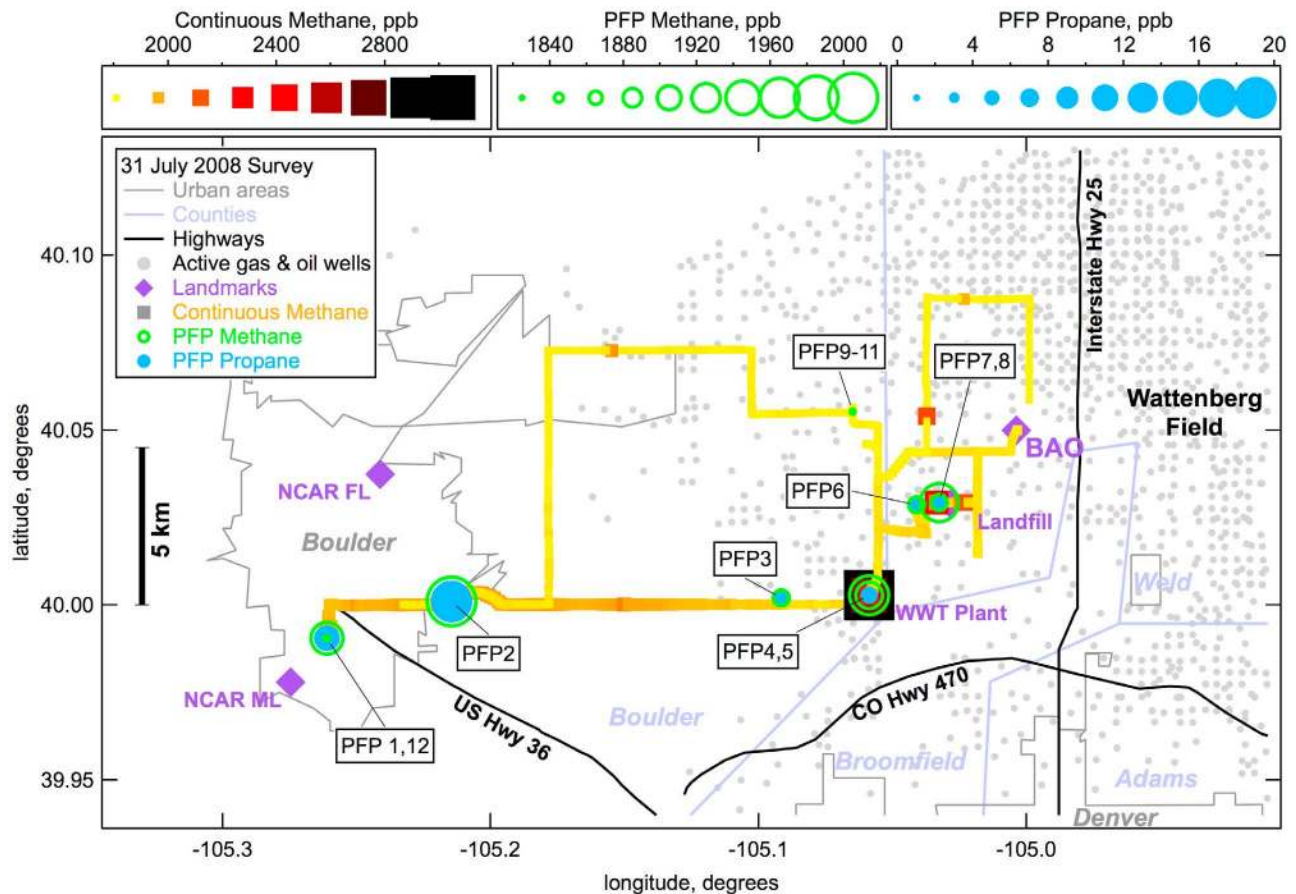
that is not a significant source of CO. The  $C_6H_6$ -to- $C_2H_2$  correlation slope is slightly higher for the NE wind sector data compared to the other two wind sectors.  $C_6H_6$  in the BAO data from the NE wind sector correlates more strongly with  $C_3H_8$  than with CO. The  $C_6H_6$ -to- $C_3H_8$  summer correlation slope for the NE wind sector is  $10.1 \pm 1.2$  ppt/ppb ( $r^2 = 0.67$ ).

[42] For the S and W wind sectors BAO data, the  $C_6H_6$ -to- $C_2H_2$  (0.27 - 0.32 ppt/ppt) and  $C_6H_6$ -to-CO (1.57 - 1.81 ppt/ppb) slopes are larger than observed emissions ratios for the Boston/New York City area in 2004: 0.171 ppt/ppt for  $C_6H_6$ -to- $C_2H_2$  ratio and 0.617 ppt/ppb for  $C_6H_6$ -to-CO ratio [Warneke *et al.*, 2007]. Baker *et al.* [2008] report an atmospheric molar  $C_6H_6$ -to-CO ratio of 0.9 ppt/ppb for Denver in summer 2004, which is in between the Boston/NYC emissions ratio value reported by Warneke *et al.* [2007] and the BAO S and W wind sectors correlation slopes.

[43] The analysis of the BAO  $C_6H_6$  data suggests the existence of at least two distinct  $C_6H_6$  sources in the vicinity of BAO: an urban source related mainly to mobile emissions, and a common source of alkanes and  $C_6H_6$  concentrated in northeastern Colorado. We discuss  $C_6H_6$  correlations and sources in more detail in section 4.4.

### 3.2. On-Road Surveys: Tracking Point and Area Source Chemical Signatures

[44] Road surveys with flask sampling and the Mobile Lab with the fast-response  $CH_4$  analyzer were carried out in June–July 2008 (Table 2). The extensive chemical analysis of air samples collected in the Front Range provides a snapshot of a broader chemical composition of the regional boundary layer during the time of the study. The Mobile Lab surveys around the Front Range using the in situ  $CH_4$  analyzer allowed us to detect large-scale plumes with long-



**Figure 6.** Continuous methane observations (colored squares) and flask (circles) samples collected during the July 31, 2008 Mobile Lab Survey 9 in Boulder and Weld County. The size of the symbols (and the symbol color for the continuous methane data) represents the mixing ratio of continuous/flask methane (squares, green circles) and flask propane (blue circles). The labels indicate the flask sample number (also shown in the time series in Figure 5). NCAR = National Center for Atmospheric Research, FL = NCAR Foothills Laboratory, ML = NCAR Mesa Laboratory, WWT Plant = Lafayette wastewater treatment plant.

lasting enhancements of  $\text{CH}_4$  mixing ratios as well as small-scale plumes associated with local  $\text{CH}_4$  point sources. In the last two Mobile Lab surveys (surveys 8 and 9), we combined the monitoring of the continuous  $\text{CH}_4$  analyzer with targeted flask sampling, using the  $\text{CH}_4$  data to decide when to collect flask samples in and out of plumes.

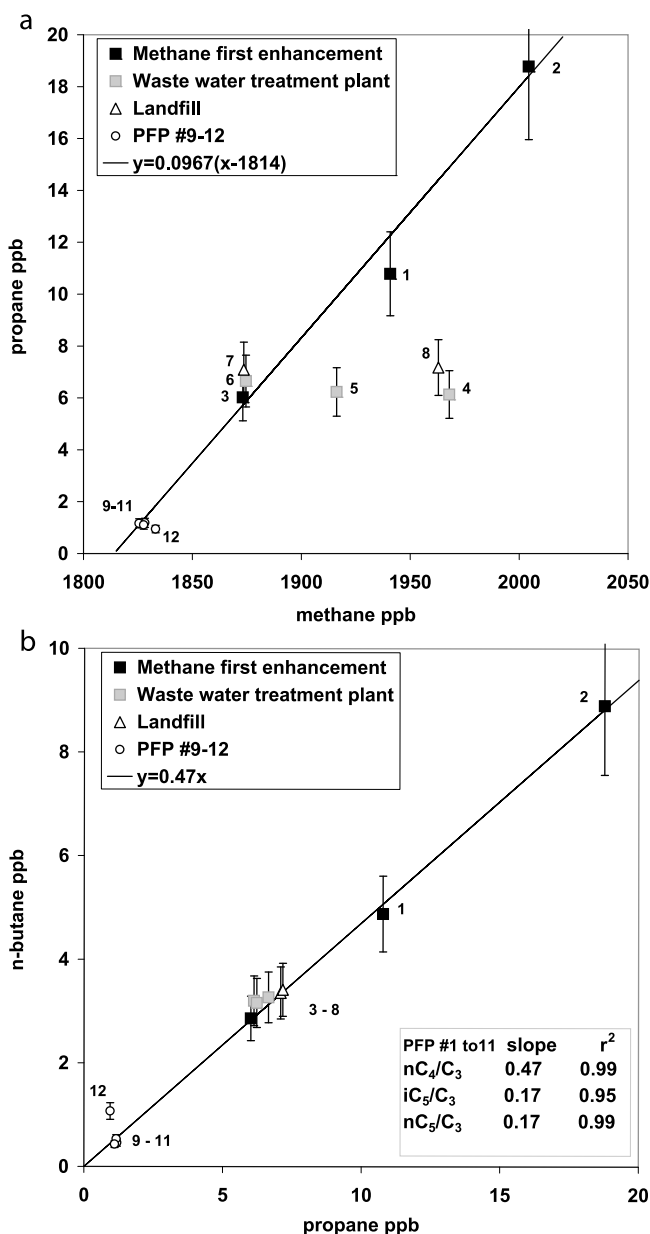
[45] The regional background  $\text{CH}_4$  mixing ratio at the surface (interpreted here as the lowest methane level sustained for  $\sim 10$  min or more) was between 1800 ppb and 1840 ppb for most surveys. Some of the highest “instantaneous”  $\text{CH}_4$  mixing ratios measured during the Mobile Lab surveys were: 3166 ppb at a wastewater treatment plant, 2329 ppb at a landfill, 2825 ppb at a feedlot near Dacono, over 7000 ppb close to a feedlot waste pond near Greeley, and 4709 ppb at a large natural gas processing and propane plant in Fort Lupton (Figure 1).

[46] The analysis of the summer 2008 intensive data suggests that regional scale mixing ratio enhancements of  $\text{CH}_4$  and other alkanes are not rare events in the Colorado Northern Front Range airshed. Their occurrence and extent depends on both emissions and surface wind conditions, which are quite variable and difficult to predict in this area. During the Mobile Lab road surveys, the high-frequency

measurements of  $\text{CO}_2$  and  $\text{CH}_4$  did not exhibit any correlation. Unlike  $\text{CO}_2$ , the  $\text{CH}_4$  enhancements were not related to on-road emissions. Below we present two examples of regional enhancements of  $\text{CH}_4$  observed during the Front Range Mobile Lab surveys.

### 3.2.1. Survey 9: $\text{C}_{3-5}$ Alkane Levels Follow Large-Scale Changes in Methane

[47] Figure 5 shows a time series of the continuous  $\text{CH}_4$  mixing ratio data and alkane mixing ratios measured in twelve flask samples collected during the Front Range Mobile Lab survey on 31 July 2008 (flasks 1 to 12, sampled sequentially as shown in Figure 6). The wind direction on that day was from the ENE or E at the NCAR Foothills Lab and BAO tower. The Mobile Lab left the NOAA campus in Boulder around 11:40 A.M. and measured increasing  $\text{CH}_4$  levels going east toward the BAO tower (Figure 6). An air sample was collected close to the peak of the  $\text{CH}_4$  broad enhancement centered around 11:55 A.M. The  $\text{CH}_4$  mixing ratio then decreased over the next 25 min and reached a local minimum close to 1875 ppb. The  $\text{CH}_4$  level stayed around 1875 ppb for over one hour and then decreased again, more slowly this time, to  $\sim 1830$  ppb over the next two hours.



**Figure 7.** (a) Propane versus methane mixing ratios for air samples collected during Survey 9 on July 31, 2008. (b) The n-butane versus propane mixing ratios in the same air samples. The black line in Figure 7a shows the correlation line for samples not impacted by local sources of methane (all flasks except 4, 5, 8, and 12). The black line in Figure 7b shows the correlation line for all samples except flask 12. The flask sample number is shown next to each data point. The twelve samples were filled sequentially (see Figure 6).

[48] Flasks 1 to 3 were collected before, at the peak, and immediately after the broad  $CH_4$  feature between 11:40 and 12:15. Flasks 4 and 5 were sampled close to a wastewater treatment plant and flasks 7 to 8 were sampled in a landfill. The in situ measurements showed that  $CH_4$  was still elevated above background as these samples were collected. After a 90-min stop at BAO to recharge the Mobile Lab UPS batteries, flasks 9 to 11 were collected in a corn field while the

in situ measurements showed lower  $CH_4$  levels. The last flask sample was collected on the NOAA campus just before 17:00 MDT, about 5.5 h after the first flask sample was collected. The flask samples were always collected upwind of the Mobile Lab car exhaust.

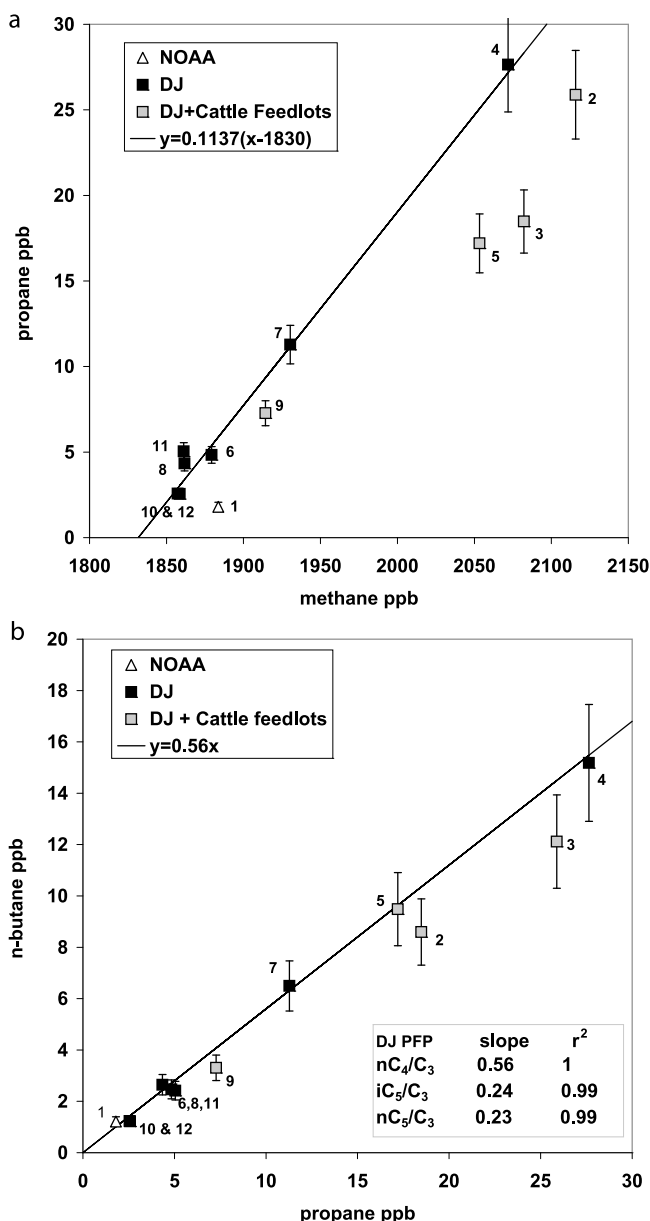
[49] Sharp spikes in the continuous  $CH_4$  data reflect local point sources (wastewater treatment plant, landfill). The highly variable signals in both the continuous and discrete  $CH_4$  close to these sources are driven by the spatial heterogeneity of the  $CH_4$  emissions and variations in wind speed and direction. Broader enhancements in the continuous  $CH_4$  data reflect larger (regional) plumes. The last flask (12) sampled at NOAA has much higher levels of combustion tracers ( $CO$ ,  $C_2H_2$ ,  $C_6H_6$ ) than the other samples.

[50] Figure 7 shows correlation plots for  $C_3H_8$  versus  $CH_4$  and  $n-C_4H_{10}$  versus  $C_3H_8$  in the 12 flasks taken on 31 July. Air samples not directly influenced by identified point sources (flasks 1–3, 6–7, 9–12) show a very strong correlation between the various measured alkanes. Using the data from the air samples not directly influenced by identified point sources (flasks 1–3, 6–7, 9–12), we derive a  $C_3H_8$ -to- $CH_4$  ( $C_3/C_1$ ) mixing ratio slope of  $0.097 \pm 0.005$  ppb/ppb (Figure 7a). This slope is very similar to the one observed for the summertime NE wind sector data at BAO ( $0.104 \pm 0.005$ ; Table 3). Three air samples collected downwind of the wastewater treatment plant and the landfill (flasks 4–5 and 8) are off the  $C_3H_8$ -to- $CH_4$  correlation line and have higher  $CH_4$  than air samples collected nearby but not under the influence of these local  $CH_4$  sources (flasks 3 and 6). Flask 8 also has elevated CFC-11 (310 ppt) compared to the other samples collected that day (<255 ppt), probably related to leaks from old appliances buried in the landfill.

[51] The  $C_3$ - $C_5$  alkane mixing ratios in samples collected on 31 July are tightly correlated for flasks 1 to 11 with  $r^2 > 0.95$  (Figure 7b). As concluded for the BAO alkane mixing ratio enhancements earlier, this tight correlation suggests that the non-methane alkanes measured during the surveys are coming from the same source types. The  $nC_4/C_3$  correlation slope on 31 July (0.47 ppb/ppb; flasks 1–11) is similar to the summer slope in the BAO NE samples (0.45 ppb/ppb), while the 31 July  $iC_5/C_3$  and  $nC_5/C_3$  slopes are slightly higher (0.17 and 0.17 ppb/ppb, respectively) than for BAO (0.14 and 0.15 ppb/ppb, respectively).

### 3.2.2. Survey 6: Alkane Enhancements in the Denver-Julesburg Oil and Gas Production Zone and Cattle Feedlot Contributions to Methane

[52] The flask-sampling-only mobile survey on 14 July 2008 focused on the agricultural and oil and gas drilling region south of Greeley. Eleven of the twelve air samples collected on 14 July were taken over the Denver-Julesburg Basin (flasks 2–12 in auxiliary material Figure S3). Figure 8a shows a correlation plot of  $C_3H_8$  versus  $CH_4$  mixing ratios in these air samples. Flasks collected NE of BAO and not near feedlots (flasks 4, 6–8, and 10–12) fall on a line:  $y = 0.114(x - 1830)$  ( $r^2 = 0.99$ ). This slope and the correlation slope calculated for the BAO NE wind sector data are indistinguishable (within the  $1-\sigma$  uncertainties in the slopes). Four samples collected in the vicinity of four different cattle feedlots (flasks 2, 3, 5, and 9) exhibit a lower  $C_3H_8$ -to- $CH_4$  correlation slope (0.083 ppb/ppb,  $r^2 = 0.93$ ). The  $r^2$  for the  $C_3H_8$ -to- $CH_4$  correlation using all the flasks is 0.91.



**Figure 8.** (a) Propane versus methane mixing ratios for air samples collected during Survey 6 on July 14, 2008. (b) The n-butane versus propane mixing ratios in the same air samples. The black line in Figure 8a shows the correlation line for samples not impacted by local sources of methane (all flasks except 1–3, 5, and 9). The black line in Figure 8b shows the correlation line for samples not impacted by local sources of propane.

[53] The  $n-C_4H_{10}$  versus  $C_3H_8$  correlation plot and its slope, along with the  $n-C_4H_{10}$ -to- $C_3H_8$  and  $C_5H_{12}$ -to- $C_3H_8$  correlation slopes for air samples not collected downwind of feedlots are shown in Figure 8b. The  $r^2$  for the  $n-C_4H_{10}$ -to- $C_3H_8$  correlation using all the flasks is 0.98, which is slightly higher than the  $r^2$  for the  $C_3H_8$ -to- $CH_4$  correlation using all flasks (0.91). The  $r^2$  for the  $i-C_5H_{12}$ -to- $n-C_4H_{10}$  and  $n-C_5H_{12}$ -to- $n-C_4H_{10}$  correlations using all the flasks are 0.96 ppb/ppb and 0.99 ppb/ppb, respectively. These results suggest that

cattle feedlots have no substantial impact on  $n-C_4H_{10}$  and the  $C_5H_{12}$  levels.

[54] The strong correlation observed between the various alkane mixing ratios for air samples not collected downwind of feedlots once again suggests that a common source contributes to most of the observed alkanes enhancements. It is possible that some of the  $C_3H_8$  enhancements seen near the feedlots are due to leaks of propane fuel used for farm operations (R. Klusman, personal communication, 2010). Two flask samples were collected downwind of a cattle feedlot near Dacono during Mobile Lab survey 8, on 25 July 2008. The analysis of these samples revealed large  $CH_4$  enhancements (1946 and 2335 ppb), but no enhancement in  $C_3H_8$  ( $\sim 1$  ppb),  $n-C_4H_{10}$  ( $< 300$  ppt), the  $C_5H_{12}$  ( $< 130$  ppt) or  $C_6H_6$  ( $< 30$  ppt).

[55] For survey 6, the  $n-C_4H_{10}$ -to- $C_3H_8$  correlation slope (0.56 ppb/ppb) is 16% higher than the summer slope observed at BAO for the NE wind sector data, while the 14 July  $i-C_5H_{12}$ -to- $C_3H_8$  and  $n-C_5H_{12}$ -to- $C_3H_8$  correlation slopes (0.24 and 0.23 ppb/ppb, respectively) are 76% and 53% higher, respectively, than the summer NE BAO data. These slopes are higher than for flasks from survey 9. The difference in the  $C_5/C_3$  slopes between the various Mobile Lab surveys data and the BAO NE summer data may reflect the spatial variability in the alkane source molar composition.

### 3.2.3. Benzene Source Signatures

[56] To look at the  $C_6H_6$  correlations with other tracers, the 88 Mobile Lab flask samples have been divided into two subsets, none of which includes the three samples collected downwind of the natural gas and propane processing plant near Dacono, CO. In the summer, the lifetimes of  $C_6H_6$  and  $C_3H_8$  at 800 mbar and  $40^\circ N$  are close to 3 or 4 days and the lifetime of CO is about 10 days [Finlayson-Pitts and Pitts, 2000; Spivakovsky et al., 2000].

[57] The first subset of 39 samples has  $C_3H_8$  mixing ratios smaller than 3 ppb and it includes flasks collected mostly during surveys 2, 3 and 4. For this subset influenced mostly by urban and mobile emissions,  $C_6H_6$  correlates well with CO (slope = 1.82 ppt/ppb,  $r^2 = 0.89$ ) and  $C_2H_2$  (slope = 0.37 ppt/ppb,  $r^2 = 0.75$ ) but not with  $C_3H_8$  ( $r^2 < 0.3$ ). The  $C_6H_6$ -to-CO correlation slope for this subset is similar to the correlation slopes for the BAO S and W wind sector winter samples.

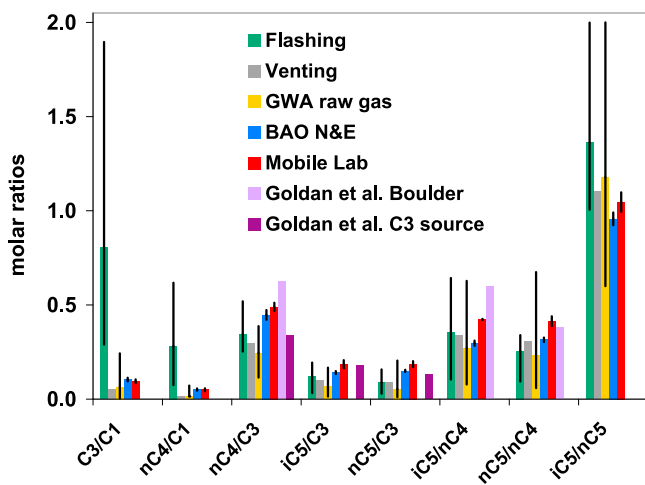
[58] The second subset of 46 samples corresponds to flasks with a  $C_3H_8$  mixing ratio larger than 3 ppb. These flasks were collected mostly during surveys 1, 6, 8 and 9. For this second subset influenced mostly by emissions from the DJB,  $C_6H_6$  correlates well with  $C_3H_8$  (slope = 17.9 ppt/ppb,  $r^2 = 0.95$ ) but not with CO or  $C_2H_2$  ( $r^2 < 0.3$ ). The  $C_6H_6$ -to- $C_3H_8$  slope for these samples is almost twice as big as the slope calculated for the BAO NE wind sector data (10.1 ppt/ppb) (Table 3).

## 4. Discussion

### 4.1. Comparing the Alkane Enhancements in the BAO and Mobile Lab Data Sets

[59] In the previous section we showed two examples of enhanced alkanes in northeast Colorado using mobile sampling (surveys 6 and 9 on 14 and 31 July 2008, respectively). With lifetimes against OH removal on the order of 3.5, 1.7 and 1.0 days in the summer at  $40^\circ N$  [Finlayson-Pitts and Pitts, 2000; Spivakovsky et al., 2000] respectively,  $C_3H_8$ ,





**Figure 9.** Alkane correlation slopes in air samples collected at BAO (NE wind sector, summer samples only, blue) and over the Denver-Julesburg Basin (red) during the Front Range Study (June–July 2008) are compared with VOC emissions molar ratios for flashing (green) and venting (gray) sources used by *Bar-Ilan et al.* [2008a] for the DJB WRAP Phase III emissions inventory. The error bars indicate the min and max values for the flashing emissions molar ratios. Also shown are the mean, min and max molar ratios derived from the composition analysis of gas samples collected in 2006 at 77 different gas wells in the Great Wattenberg Area (yellow) [Colorado Oil and Gas Conservation Commission, 2007]. *Goldan et al.* [1995] data are from a two week measurement campaign in the Foothills, west of Boulder, in February 1991 (light purple). *Goldan et al.* identified a “local” propane source (lower limit for correlation slope) with clear  $C_{4-5}$  alkane ratios to propane (dark purple, see also text). The error bars on the observed atmospheric molar ratios are the 2-sigma calculated for the ratios with `linmix_err.pro` ([http://idlastro.gsfc.nasa.gov/ftp/pro/math/linmix\\_err.pro](http://idlastro.gsfc.nasa.gov/ftp/pro/math/linmix_err.pro)).

$n-C_4H_{10}$  and the  $C_5H_{12}$  isomers do not accumulate over the continent. Instead their atmospheric mixing ratios and the slopes of correlations between different alkanes reflect mostly local or regional sources within a few days of atmospheric transport.

[60] The source responsible for the alkane enhancements observed at BAO and in multiple surveys during the Front Range Study appears to be located in the northeastern part of the Front Range region within the Denver-Julesburg Basin, so we call it the DJB source. The small differences in alkane correlation slopes for the BAO and Mobile Lab samples likely reflect differences in the emitted alkane molar ratios across this distributed source, as well as the mix of chemical ages for the air samples collected at a variety of locations and on different days.

[61] In Table 3 and Figure 4, we compare the alkane correlation slopes in the Mobile Lab flask data set with the correlation slopes in the BAO data set. To calculate the DJB source  $C_3H_8$ -to- $CH_4$  correlation slope from the Mobile Lab data set, we have removed air samples collected downwind of feedlots, the wastewater treatment plant, and the natural gas and propane processing plant (Figure 1). The Mobile

Lab flasks  $C_3H_8$ -to- $CH_4$  correlation slope is  $0.095 \pm 0.007$  ppb/ppb ( $R^2 = 0.76$ , 77 samples), similar to the slope calculated for the BAO NE wind sector data. Samples collected downwind of the natural gas processing plant exhibit variable chemical signatures, reflecting a complex mix of contributions from leaks of gas and combustion exhaust from flaring units and compressor engines.

[62] To calculate the DJB source  $n-C_4H_{10}$ -to- $C_3H_8$ ,  $i-C_5H_{12}$ -to- $C_3H_8$  and  $n-C_5H_{12}$ -to- $C_3H_8$  correlation slopes from the Mobile Lab data set, we have removed the three air samples collected downwind of the natural gas and propane processing plant (Figure 1). The  $C_4/C_3$ ,  $i-C_5/C_3$  and  $n-C_5/C_3$  correlation slopes in the Mobile Lab data are 0.49, 0.19 and 0.19 ppb/ppb, respectively ( $r^2 > 0.8$ , 85 samples). The  $i-C_5/C_3$  and  $n-C_5/C_3$  correlation slopes are 40% and 30% higher, respectively, than the BAO NE sector summer slopes. If we remove the 11 data points from survey 6 samples collected in the middle of the DJB, the  $C_5H_{12}$ -to- $C_3H_8$  ratios are only 15% higher than calculated for the NE sector at BAO.

[63] High correlations among various alkanes were reported in this region by *Goldan et al.* [1995]. In that study, hourly air samples were analyzed with an in situ gas chromatograph deployed on a mesa at the western edge of Boulder for two weeks in February 1991.  $CH_4$  was not measured during that study. The correlation coefficient ( $r^2$ ) between  $C_3H_8$ ,  $n-C_4H_{10}$ , and the  $C_5H_{12}$  isomers was around 0.86, with a clear minimum slope for the abundance ratios [see *Goldan et al.*, 1995, Figure 4]. The authors proposed that the  $C_4$ - $C_6$  alkanes shared one common source with propane (called the “ $C_3$  source” in the next section and in Figure 9), with additional emissions contributing to some  $C_4$ - $C_6$  alkane enhancements.

#### 4.2. Comparing the Front Range Observed Alkane Signatures With VOC Emissions Profiles for Oil And Gas Operations in the Denver-Julesburg Basin

[64] In this section we compare the alkane ratios calculated from the BAO NE wind sector and the Mobile Lab samples to emissions profiles from the DJB oil and gas exploration and production sector. Most of these profiles were provided by the WRAP Phase III inventory team, who developed total VOC and  $NO_x$  emission inventories for oil and gas production and processing operation in the DJB for 2006 [Bar-Ilan et al., 2008a]. Emissions and activity data were extrapolated by the WRAP Phase III inventory team to derive emission estimates for 2010 based on projected production numbers and on state and federal emissions control regulations put in place in early 2008 for oil and gas permitted activities in the DNFR NAA [Bar-Ilan et al., 2008b]. The VOCs included in the inventories are:  $C_3H_8$ ,  $i,n-C_4H_{10}$ ,  $i,n-C_5H_{12}$  and higher alkanes,  $C_6H_6$ , toluene, ethylbenzene, xylenes and 224-trimethylpentane. The WRAP Phase III inventories for 2006 and 2010 were only provided as total VOC and  $NO_x$  emitted at the county level for all the counties in the Colorado part of the DJB. The emission estimates are based on various activity data (including the number of new wells (spuds), the total number of wells, estimates of oil, condensate and gas production, and equipment counts) and measured/reported or estimated VOC speciation profiles for the different source categories. Auxiliary material Figure S2 and Bar-Ilan et al. [2008a, 2008b] present more details on how the inventory emission estimates are derived.

[65] We focus primarily on flashing and venting sources here, since the WRAP Phase III inventory indicates that these two sources are responsible for 95% of the total VOC emissions from oil and gas exploration and production operations in Weld County and in the NAA [Bar-Ilan *et al.*, 2008a, 2008b] (see auxiliary material Figure S2). In 2006, all the oil produced in the DJB was from condensate wells. Condensate tanks at well pads or processing plants store a mostly liquid mix of hydrocarbons and aromatics separated from the lighter gases in the raw natural gas. Flash losses or emissions happen for example when the liquid condensate is exposed to decreasing atmospheric pressure: gases dissolved in the liquid are released and some of the heavier compounds may be entrained with these gases. Flashing emissions from condensate storage tanks are the largest source of VOCs from oil and gas operations in the DJB. In the DNFR NAA, operators of large condensate tanks have to control and report emission estimates to the Colorado Department of Public Health and the Environment (CDPHE). In 2006 and 2010 flashing emissions represented 69% and 65% respectively of the total VOC source from oil and gas exploration, production and processing operations, for the nine counties in the NAA (see auxiliary material Figure S2 and Bar-Ilan *et al.* [2008a] for more details on how the estimates are derived).

[66] Venting emissions are related to loss of raw natural gas when a new oil or gas well is drilled or when an existing well is vented (blowdown), repaired or restimulated (recompletion). Equipment at active well sites (e.g., wellhead, glycol dehydrators and pumps) or in the midstream network of compressors and pipelines gathering the raw natural gas can also leak significant amounts of natural gas. In the WRAP Phase III inventory, venting emissions represented 27% and 21% respectively of the total VOC estimated source from the NAA oil and gas operations in 2006 and 2010 (see Bar-Ilan *et al.* [2008a, 2008b] and auxiliary material Figure S2).

[67] The molar compositions of venting and flashing emissions are quite different (see auxiliary material Figure S4). Emissions from flash losses are enriched in  $C_{2+}$  alkanes compared to the raw natural gas emissions. To convert the total VOC bottom-up source into speciated emission ratio estimates, we use molar ratio profiles for both flashing and venting emissions reported in three data sets: (1) Bar-Ilan *et al.* [2008a]: mean venting profile used for the 2006 DJB inventory, also called the “Venting-WRAP” profile; (2) Colorado Oil and Gas Conservation Commission (COGCC) [2007]: composition of 77 samples of raw natural gas collected at different wells in the Greater Wattenberg Area in December 2006, also called “Venting-GWA” profiles. Note that  $C_6H_6$  was not reported in this data set; and (3) Colorado Department of Public Health and the Environment (C. LaPlante, CDPHE, personal communication, 2011): flashing emissions profiles based on condensate composition data from 16 different storage tanks in the DJB and EPA TANK2.0 (flashing emissions model) runs.

[68] Figure 9 shows a comparison of the alkane molar ratios for the raw natural gas and flash emissions data sets with the correlation slopes derived for the Mobile Lab 2008 samples and for air samples collected at BAO in the summer months only (between August 2007 and April 2010) for the NE wind sector (see auxiliary material Table S4 to get the plotted values). The alkane correlation slopes observed at BAO and across the Northern Front Range with the Mobile

Lab are all within the range of ratios reported for flashing and/or venting emissions. The  $C_{3-5}$  alkane ratios for both flashing and venting emissions are too similar for their atmospheric ratios to be useful in distinguishing between the two source processes. The ambient  $C_3H_8$ -to- $CH_4$  and  $n-C_4H_{10}$ -to- $CH_4$  molar ratios are lower than what could be expected from condensate tank flashing emissions alone, indicating that most of the  $CH_4$  observed came from the venting of raw natural gas. In the next section, we will describe how we derive bottom-up emission estimates for  $CH_4$  and  $C_3H_8$  as well as three top-down emissions scenarios consistent with the observed atmospheric slopes.

[69] Figure 9 also shows the correlation slopes calculated by Goldan *et al.* [1995] for the 1991 Boulder study. These slopes compare very well with the BAO and Mobile Lab results and the oil and gas venting and flashing emissions ratios. Goldan *et al.* [1995] compared the measured  $C_4/C_3$  and  $C_5/C_3$  ratios for the Boulder  $C_3$  source (see definition in section 4.1) with the ratios reported in the locally distributed pipeline-quality natural gas for February 1991, and concluded that the common  $C_3H_8$  and higher alkane source was not linked with the local distribution system of processed natural gas. However, the composition of the raw natural gas at the extraction well is quite different from the purified pipeline-quality natural gas distributed to end-users. Processed pipeline-quality natural gas delivered throughout the USA is almost pure  $CH_4$  [Gas Research Institute, 1992]. Since Goldan *et al.* [1995] did not measure  $CH_4$  in their 1991 study, they could not determine if the atmospheric  $C_{3+}/C_1$  alkane ratios were higher than expected in processed natural gas.

### 4.3. Estimation of the Alkane Source in Weld County

#### 4.3.1. Bottom-Up Speciated Emission Estimates

[70] In this section, we derive bottom-up and top-down estimates of alkane emissions from the DJB source for Weld County. We have averaged the 2006 and 2010 WRAP Phase III total VOC emissions data [Bar-Ilan *et al.*, 2008a, 2008b] to get bottom-up estimates for the year 2008, resulting in 41.3 Gg/yr for flashing emissions and 16.8 Gg/yr for venting emissions. There are no uncertainty estimates provided in the WRAP Phase III inventory. 2006 total VOC flashing emission estimates in Weld County are based on reported emissions for controlled large condensate tanks (34.8 Gg/yr) and calculated emissions for uncontrolled small condensate tanks (5.4 Gg/yr) (see Bar-Ilan *et al.* [2008a] for more details). Uncertainties attached to these estimates may be due to inaccurate emissions factors (number of pounds of VOC flashed per tons of condensate produced) and/or inaccurate estimate of the effectiveness of emission control systems.

[71] The WRAP Phase III total VOC emission from venting sources for Weld County was calculated by averaging industry estimates of the volume of natural gas vented or leaked to the atmosphere by various processes shown in auxiliary material Figure S2 (well blowdown, well completion, pneumatic devices...). A basin-wide average of gas composition analyses provided by oil and gas producers was then used to compute a bottom-up estimate of the total mass of VOC vented to the atmosphere by oil and gas exploration, production and processing operations. Uncertainties attached to the venting source can be related to

**Table 4.** Bottom-Up (Inventory-Derived) Emission Estimates and Top-Down Emissions Scenarios for CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> in Weld County

	Bottom-Up Estimates				Top-Down Scenarios: Venting <sup>a</sup> (Gg/yr)			Top-Down Scenarios: Flashing + Top-Down Venting <sup>a</sup> (Gg/yr)			Top-Down Scenarios: Percent Of Production Vented <sup>a,b</sup>		
	Flashing <sup>c</sup> (Gg/yr)	Venting <sup>d</sup> (Gg/yr)	Flashing + Venting (Gg/yr)	Percent of Production Vented <sup>c</sup>	1	2	3	1	2	3	1	2	3
Methane	<b>11.2</b>	53.1	64.3	<b>1.68%</b>	118.4	92.5	157	<b>129.6</b>	103.7	168.2	<b>4.0%</b>	3.1%	5.3%
Min <sup>f</sup>	<b>4</b>	42	46		86.5	67.6	114.7	90.5	<b>71.6</b>	118.7	2.9%	<b>2.3%</b>	3.8%
Max <sup>f</sup>	<b>23</b>	63	86		172.6	134.9	228.9	195.6	157.9	<b>251.9</b>	5.8%	4.5%	<b>7.7%</b>
Propane	<b>18.3</b>	7.8	26.1		17.4	10.2	28	<b>35.7</b>	28.5	46.3			
Min <sup>f</sup>	<b>14</b>	1	15		12.7	7.5	20.5	26.7	<b>21.5</b>	34.5			
Max <sup>f</sup>	<b>24</b>	28	52		25.3	14.9	40.8	49.3	38.9	<b>64.8</b>			

<sup>a</sup>The CH<sub>4</sub>-to-C<sub>3</sub>H<sub>8</sub> molar ratio for vented natural gas is 18.75 (WRAP report estimate) for scenario 1, 15.43 for scenario 2 (median of molar ratios in GWA data set) and 24.83 for scenario 3 (mean of molar ratios in GWA data set).

<sup>b</sup>Using the assumptions of a CH<sub>4</sub> molar ratio of 77% for the vented natural gas and a molar volume for the gas of 23.6 L/mol (Pressure = 14.73 pounds per square inch and Temperature = 60°F) as used by the EIA [2004].

<sup>c</sup>The bottom-up flashing emissions for methane and propane were calculated using the 2008 estimate of total VOC flash emissions derived by averaging the WRAP estimate for 2006 and the projection for 2010 (Cf. section 4.3).

<sup>d</sup>The bottom-up venting emissions for methane and propane were calculated using the WRAP Phase III inventory estimate for the total volume of natural gas vented and the GWA 77 natural gas composition profiles.

<sup>e</sup>Using the WRAP Phase III inventory data set and assumptions, including a CH<sub>4</sub> mean molar ratio of 77.44% for the vented natural gas and a molar volume for the gas of 22.4 L/mol.

<sup>f</sup>The minimum and maximum values reported here come from the ensemble of 16 condensate tank emissions speciation profiles provided by CDPHE.

uncertainties in leak rates or intensity of out-gassing events, as well to the variability in the composition of raw natural gas, none of which were quantitatively taken into account in the WRAP Phase III inventory.

[72] Next we describe the calculations, summarized in auxiliary material Figure S5, to derive bottom-up estimates of venting and flashing emissions for the various trace gases we measured using information from the WRAP Phase III inventory and the COGCC GWA raw natural gas composition data set (Table 4 and auxiliary material Figure S6). From the total annual vented VOC source and the average vented emission profile provided by *Bar-Ilan et al.* [2008a] (auxiliary material Table S2), we derived an estimate of the volume of natural gas that we assumed is vented to the atmosphere by the oil and gas production and processing operations in Weld County. Following *Bar-Ilan et al.* [2008a] inventory data and assumptions, we used the weight fraction of total VOC in the vented gas (18.74%), the molar mass of the vented gas (21.5g/mol) and standard pressure and temperature with the ideal gas law to assume that 1 mol of raw natural gas occupies a volume 22.4 L (as was done in the WRAP Phase III inventory). The total volume of vented gas we calculate for Weld County in 2008 is 3.36 billion cubic feet (Bcf), or the equivalent of 1.68% of the total natural gas produced in the county in 2008 (202.1 Bcf). We then use the estimate of the volume of vented gas and the molar composition profiles for the 77 raw natural gas samples reported in the COGCC GWA study to compute average, minimum, and maximum emissions for CH<sub>4</sub>, each of the C<sub>3-5</sub> alkanes we measured, and C<sub>6</sub>H<sub>6</sub>. Using this procedure, 2008 Weld County average venting CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> bottom-up source estimates are 53.1 Gg/yr and 7.8 Gg/yr, respectively (Table 4).

[73] For flashing emissions, we distributed the WRAP 2008 total annual VOC source estimate (41.3 Gg/yr) using the modeled flash loss composition profiles for 16 different condensate tanks provided by the CDPHE. Average CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> emissions as well as the minimum and maximum estimates are reported in Table 4. The 2008 average flashing CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> bottom-up emission estimates are 11.2 Gg/yr

and 18.3 Gg/yr, respectively (Table 4). The total flashing + venting CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> bottom-up estimates range from 46 to 86 Gg/yr and from 15 to 52 Gg/yr, respectively.

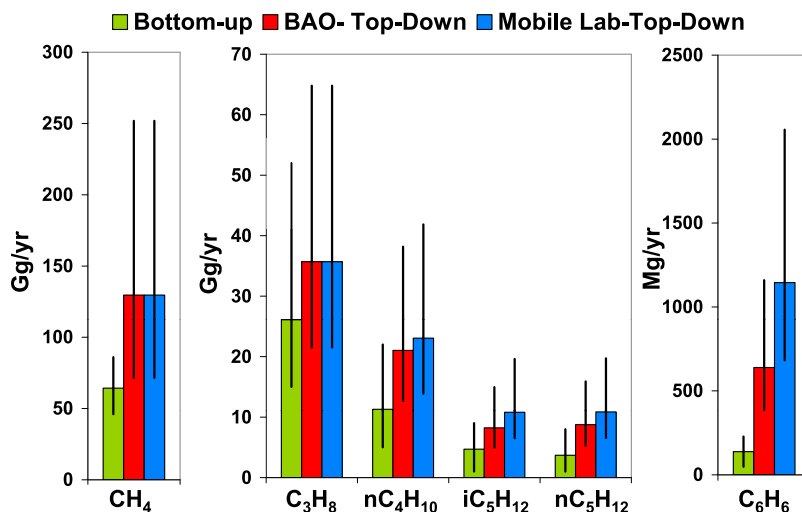
#### 4.3.2. Top-Down Emissions Scenarios

[74] Finally, we use our atmospheric measurements to bring new independent constraints for the estimation of venting and flashing emissions in Weld County in 2008. The exercise consists in calculating three top-down venting emission scenarios for CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> ( $x_m, x_p$ : mass of methane and propane vented respectively) consistent with a mean observed CH<sub>4</sub>-to-C<sub>3</sub>H<sub>8</sub> atmospheric molar ratio of 10 ppb/ppb (Table 4) in the DJB. We assume, as done earlier in the bottom-up calculations, that the observed C<sub>3</sub>H<sub>8</sub>-to-CH<sub>4</sub> ratio in the DJB results from a combination of flashing and venting emissions. The bottom-up information used here is (1) the set of speciated flashing emissions derived earlier for the 16 condensate tanks provided by CDPHE for CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> ( $v_m, y_p$ )<sub>tank=1,16</sub>, and (2) three scenarios for the basin-average raw (vented) natural gas CH<sub>4</sub>-to-C<sub>3</sub>H<sub>8</sub> molar ratio, denoted  $v_{m/p}$ . The three values used for basin-average vented gas CH<sub>4</sub>-to-C<sub>3</sub>H<sub>8</sub> molar ratio are: 18.75, which is the WRAP Phase III inventory assumption (scenario 1); 15.43, which is the median of the molar ratios for the COGCC GWA 77 gas samples (scenario 2); and 24.83, which is the mean of the molar ratios for the COGCC GWA 77 gas samples (scenario 3). For each vented gas profile scenario, we use the set of 16 flash emission estimates to calculate an ensemble of venting emission estimates for CH<sub>4</sub> ( $x_m$ ) and C<sub>3</sub>H<sub>8</sub> ( $x_p$ ) following the two equations below.

[75] The first equation formalizes the assumption for CH<sub>4</sub>-to-C<sub>3</sub>H<sub>8</sub> molar ratio of the vented raw natural gas, with  $M_m$  (16g/mol) and  $M_p$  (44g/mol) being the molar masses of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> respectively.:

$$v_{m/p} = \frac{M_p}{M_m} \times \frac{x_m}{x_p} \quad (1)$$

[76] In the second equation, the mean observed atmospheric CH<sub>4</sub>-to-C<sub>3</sub>H<sub>8</sub> molar ratio ( $a_{m/p} = 10$  ppb/ppb)



**Figure 10.** Bottom-up (inventory-derived) emission estimates and top-down emission scenarios for  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_5\text{H}_{12}$  and  $\text{C}_6\text{H}_6$  in Weld County. The vertical bars show scenario 1 average values and the error bars indicate the minimum and maximum values for the three scenarios described in Table 4.

constrains the overall ratio of methane versus propane emitted by both flashing and venting sources. Therefore, for each set of 16 bottom-up flashed emission estimates ( $y_m$ ,  $y_p$ ), we have:

$$\frac{M_p(x_m + y_m)}{M_m(x_p + y_p)} = a_{m/p} \quad (2)$$

[77] The analytical solutions to this set of equations are given by:

$$x_p = \frac{1}{(v_{m/p} - a_{m/p})} \times \left( a_{m/p} \times y_p - \frac{M_p}{M_m} y_m \right) \quad (3)$$

$$x_m = v_{m/p} \times \frac{M_m}{M_p} \times x_p$$

[78] The average, minimum and maximum venting emission estimates,  $x_m$  and  $x_p$ , are reported for the three vented gas profile scenarios in Table 4 and Figure 10.

[79] The first goal of this top-down estimation exercise is to highlight the many assumptions required to build the bottom-up and top-down emission estimates. The choices made for the WRAP Phase III inventory or our top-down calculations are all reasonable, and the uncertainty attached to the values chosen (if available) should be propagated to calculate total uncertainty estimates for the final emission products. When the error propagation is done conservatively, the emission uncertainty is close to a factor of 2 for both  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$ . This number is much higher than the 30% uncertainty reported by the EPA for the 2009 national  $\text{CH}_4$  source estimate from natural gas systems [EPA, 2011].

[80] The scenario 1 mean top-down vented  $\text{CH}_4$  source (118.4 Gg/yr) is twice as large as the bottom-up estimate of 53.1 Gg/yr (Table 4). If we assume that 77% (by volume) of the raw gas is  $\text{CH}_4$ , an average estimate of 118.4 Gg/yr of  $\text{CH}_4$  vented would mean that the equivalent of 4% of the 2008 natural gas gross production in Weld County was vented. It is important to note that the top-down scenarios cover a

large range (67–229 Gg/yr), corresponding to between 2.3% and 7.7% of the annual production being lost to the atmosphere through venting (Table 4). The lowest estimate is, however, larger than what we derived from the WRAP Phase III bottom-up inventory (1.68%). If instead of using the EIA [2004] convention for the molar volume of gas (23.6 L/mol), we used the standard molar volume used by WRAP (22.4 L/mol), our top-down calculations of the volume of gas vented would be 5% lower than reported in Table 4.

[81] Emissions for the other alkanes measured are all derived from the  $\text{C}_3\text{H}_8$  total sources scaled with the atmospheric molar ratios observed in the BAO NE summer samples and the Mobile Lab samples. Figure 10 shows a comparison of the bottom-up estimates and the top-down emission scenarios (mean of scenario 1 and overall minimum and maximum of the three scenarios).

[82] The main result of this exercise is that for each of the three top-down total emissions scenarios, the mean estimates for  $\text{CH}_4$ ,  $n\text{-C}_4\text{H}_{10}$  and the  $\text{C}_5\text{H}_{12}$  isomers are at least 60% higher than the bottom-up mean estimates. The minimum top-down emissions scenarios are lower than (in the case of  $\text{C}_3\text{H}_8$ ) or higher than (for  $\text{CH}_4$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_5\text{H}_{12}$ ) the bottom-up mean estimates.

[83] To put the top-down  $\text{CH}_4$  source estimate from oil and gas exploration, production and processing operations in perspective, we compare it with an estimate of the passive “geological”  $\text{CH}_4$  flux over the entire DJB. *Klusman and Jakel* [1998] reported an average flux of 0.57 mg  $\text{CH}_4/\text{m}^2/\text{day}$  in the DJB due to natural microseepage of light alkanes. Multiplied by a rough upper boundary estimate of the DJB surface area (Figure 1), the estimated annual natural flux is 0.66 Gg  $\text{CH}_4/\text{yr}$ , or less than 1% of the top-down venting source estimated for active exploration and production of natural gas in Weld County.

#### 4.4. Benzene Sources in the Northern Front Range

[84] On-road vehicles are estimated to be the largest source of  $\text{C}_6\text{H}_6$  in the U.S. (EPA, 2008 report on the environment,



2009, [www.epa.gov/roe](http://www.epa.gov/roe)). Emissions from on-road and off-road vehicles and from large point sources (including chemical plants and refineries) have been regulated by the EPA for over thirty years [Fortin *et al.*, 2005; Harley *et al.*, 2006]. When motor vehicle combustion dominates emissions, such as in the BAO S and W wind sectors,  $C_6H_6$  correlates well with CO and  $C_2H_2$ .

[85] Crude oil and natural gas production and processing emitted an estimated 8333 tonnes of benzene nationally in 2005, which represented 2% of the national total  $C_6H_6$  source (EPA, 2008 report on the environment, 2009, [www.epa.gov/roe](http://www.epa.gov/roe)).  $C_6H_6$  and  $C_3H_8$  have similar photochemical lifetimes ( $\sim 3$ – $4$  days in the summer), so the observed atmospheric ratios we report in Table 3 should be close to their emission ratio if they are emitted by a common source. The strong correlation between  $C_6H_6$  and  $C_3H_8$  (Figure 4 and Table 3) for the BAO NE wind sector and in the DJB Mobile Lab air samples suggests that oil and gas operations could also be a non-negligible source of  $C_6H_6$  in the Northern Colorado Front Range.

[86] The  $C_6H_6$ -to- $C_3H_8$  molar ratios in the flash losses from 16 condensate tanks simulated with the EPA TANK model are between 0.4 to 5.6 ppt/ppb. The  $C_6H_6$ -to- $C_3H_8$  molar ratio reported for vented emissions in the WRAP Phase III inventory is 5.3 ppt/ppb, based on regionally averaged raw gas speciation profiles provided by local companies [Bar-Ilan *et al.*, 2008a] (only an average profile was provided, other data is proprietary). These emission ratios are at least a factor of two lower than the atmospheric ratios measured in the Front Range air samples influenced by the DJB source (Table 3).

[87] If we use the mean  $C_3H_8$  emission estimate for scenario 1 described in section 4.3 (35.7 Gg/yr), together with the  $C_6H_6$ -to- $C_3H_8$  correlation slope for the summer BAO NE wind sector data and that from the Mobile Lab samples (10.1 ppt/ppb and 17.9 ppt/ppb respectively), we derive a  $C_6H_6$  emission estimate for the DJB source in Weld County in 2008 of 639 tonnes/yr (min/max range: 478/883 tonnes/yr) and 1145 tonnes/yr (min/max range: 847/1564 tonnes/yr), respectively. As expected, these numbers are much higher than what we derived for the bottom-up flashing and venting emissions (total of 139 tonnes/yr, min/max range of 49–229 tonnes/yr). For comparison,  $C_6H_6$  emissions from facilities in Colorado reporting to the U.S. EPA for the Toxics Release Inventory amounted to a total of 3.9 tonnes in 2008 (EPA, Toxics Release Inventory program, 2009, data available at <http://www.epa.gov/triexplorer/chemical.htm>) and on-road emissions in Weld County were estimated at 95.4 tonnes/yr in 2008 (C. LaPlante, CDPHE, personal communication, 2011). Based on our analysis, oil and gas operations in the DJB could be the largest source of  $C_6H_6$  in Weld County.

[88] More measurements are needed to further evaluate the various potential sources associated with oil and gas operations (for example, glycol dehydrators and condensate tank flash emissions). The past two iterations of the  $C_6H_6$  emissions inventory developed by the State of Colorado for the National Emissions Inventory and compiled by the EPA do not show much consistency from one year to another. The 2008 and 2005 NEI reported very different  $C_6H_6$  emission estimates for condensate tanks in Weld County (21.5 Mg/yr versus 1120 Mg/yr, respectively; see also auxiliary material

Table S3). Estimates in the 2008 NEI are much closer to estimates provided by CDPHE (C. LaPlante, personal communication, 2011) for 2008 (21.3 Mg/yr), suggesting the 2005 NEI estimate may be flawed, even though it is in the range of our top-down estimation. We conclude that the current level of understanding of emissions of  $C_6H_6$  from oil and gas operations cannot explain the top-down range of estimates we derive in our study, suggesting that, once again, more field measurements are needed to understand and quantify oil and gas operation sources.

## 5. Conclusion

[89] This study provides a regional overview of the processes impacting ambient alkane and benzene levels in northeastern Colorado in the late 2000s. We report atmospheric observations collected by two sampling platforms: a 300-m tall tower located in the SW corner of Weld County (samples from 2007 to 2010), and road surveys by a Mobile Lab equipped with a continuous methane analyzer and discrete canister sampling (June–July 2008). The analysis of the tower data filtered by wind sector reveals a strong alkane and benzene signature in air masses coming from northeastern Colorado, where the main activity producing these compounds is related to oil and gas operations over the Denver–Julesburg Fossil Fuel Basin. Using the Mobile Lab platform, we sampled air directly downwind of different methane sources (oil and gas wells, a landfill, feedlots, and a wastewater treatment plant) and collected targeted air samples in and out of plumes. The tall tower and Mobile Lab data both revealed a common source for air masses with enhanced alkanes. In the data from both platforms, the alkane mixing ratios were strongly correlated, with slight variations in the correlation slopes depending on the location and day of sampling. The alkanes did not correlate with combustion tracers such as carbon monoxide and acetylene. We hypothesize that the observed alkanes were emitted by the same source located over the Denver–Julesburg Basin, “the DJB source.”

[90] The second part of the study brings in information on VOC emissions from oil and gas activities in the DJB from the detailed bottom-up WRAP Phase III inventory [Bar-Ilan *et al.*, 2008a, 2008b]. We have used the total VOC emission inventory and associated emissions data for DJB condensate and gas production and processing operations to calculate annual emission estimates for  $CH_4$ ,  $C_3H_8$ ,  $n-C_4H_{10}$ ,  $i-C_5H_{12}$ ,  $n-C_5H_{12}$  and  $C_6H_6$  in Weld County. The main findings are summarized below:

1. The emissions profiles for flashing and venting losses are in good agreement with the atmospheric alkane enhancement ratios observed during this study and by Goldan *et al.* [1995] in Boulder in 1991. This is consistent with the hypothesis that the observed alkane atmospheric signature is due to oil and gas operations in the DJB.

2. The three top-down emission scenarios for oil and gas operations in Weld County in 2008 give a rather large range of potential emissions for  $CH_4$  (71.6–251.9 Gg/yr) and the higher alkanes. Except for propane, the lowest top-down alkanes emission estimates are always larger than the inventory-based mean estimate we derived based on the WRAP Phase III inventory data and the COGCC GWA raw gas composition data set.

3. There are notable inconsistencies between our results and state and national regulatory inventories. In 2008 gas wells in Weld County represented 15% of the state's production. Based on our top-down analysis, Weld County methane emissions from oil and gas production and processing represent at least 30% of the state total methane source from natural gas systems derived by Strait *et al.* [2007] using the EPA State Inventory Tool. The methane source from natural gas systems in Colorado is most likely underestimated by at least a factor of two. Oil and gas operations are the largest source of alkanes in Weld County. They were included as a source of "total VOC" in the 2008 EPA NEI for Weld County but not in the 2005 NEI.

4. There are at least two main sources of C<sub>6</sub>H<sub>6</sub> in the region: one related to combustion processes, which also emit CO and C<sub>2</sub>H<sub>2</sub> (engines and mobile vehicles), and one related to the DJB alkane source. The C<sub>6</sub>H<sub>6</sub> source we derived based on flashing and venting VOC emissions in the WRAP inventory (143 Mg/yr) most likely underestimates the actual total source of C<sub>6</sub>H<sub>6</sub> from oil and gas operations. Our top-down source estimates for C<sub>6</sub>H<sub>6</sub> from oil and gas operations in Weld County cover a large range: 385–2056 Mg/yr. Again, the lowest figure is much higher than reported in the 2008 CDPHE inventory for Weld County oil and gas total point sources (61.8 Mg/yr).

5. Samples collected at the BAO tall tower or while driving around the Front Range reflect the emissions from a complex mix of sources distributed over a large area. Using a multispecies analysis including both climate and air quality relevant gases, we can start unraveling the contributions of different source types. Daily multispecies measurements from the NOAA collaborative network of tall towers in the U.S. provide a unique opportunity to understand source chemical signatures in different airsheds and how these emissions may change over time.

6. More targeted multispecies well-calibrated atmospheric measurements are needed to evaluate current and future bottom-up inventory emissions calculations for the fossil fuel energy sector and to reduce uncertainties on absolute flux estimates for climate and air quality relevant trace gases.

[91] **Acknowledgments.** The authors thank John Grant (ENVIRON) and Kathleen Sgamma (Western Energy Alliance) for their expertise and support in interpreting the WRAP Phase III inventory public data. Special thanks are extended to the NOAA personnel and collaborators responsible for flask preparation, sample collection and sample analysis, data quality control and database management.

## References

- Baker, A. K., A. J. Beyersdorf, L. A. Doezema, A. Katzenstein, S. Meinardi, I. Simpson, D. R. Blake, and F. S. Rowland (2008), Measurements of non-methane hydrocarbons in 28 United States cities, *Atmos. Environ.*, **42**, 170–182, doi:10.1016/j.atmosenv.2007.09.007.
- Bar-Ilan, A., et al. (2008a), 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\\_DJ\\_Basin\\_Technical\\_Memo\\_\(04-30\).pdf](http://www.wrapair.org/forums/ogwg/documents/2008-04_06_Baseline_Emissions_DJ_Basin_Technical_Memo_(04-30).pdf).]
- Bar-Ilan, A., et al. (2008b), Development of the 2010 oil and gas emissions projections for the Denver-Julesburg Basin, WRAP Phase III report, 26 pp., Western Reg. Air Partnership, Fort Collins, Colo. [Available at [http://www.wrapair.org/forums/ogwg/documents/2008-04\\_10\\_Projection\\_Emissions\\_DJ\\_Basin\\_Technical\\_Memo\(04-30\).pdf](http://www.wrapair.org/forums/ogwg/documents/2008-04_10_Projection_Emissions_DJ_Basin_Technical_Memo(04-30).pdf).]
- Burns, D. (1999), Minimizing benzene emissions from glycol dehydrators, presented at the Benzene Emissions Conference on January 27, 1999 in Calgary, Alberta, report, 4 pp., Gas Liquids Engineering Ltd., Calgary, Alberta, Canada. [Available at <http://www.gasliquids.com/papers/benzene99.pdf>.]
- Colorado Department of Public Health and Environment (CDPHE) (2008), Denver metropolitan area and North Front Range 8-hour ozone state implementation plan—Emissions inventory, report, 44 pp., Denver, Colo. [Available at [http://www.colorado.gov/airquality/documents/deno308/Emission\\_Inventory\\_TSD\\_DraftFinal.pdf](http://www.colorado.gov/airquality/documents/deno308/Emission_Inventory_TSD_DraftFinal.pdf).]
- Colorado Oil and Gas Conservation Commission (2007), Greater Wattenberg area baseline study, report, 156 pp., Denver, Colo. [Available at [http://cogcc.state.co.us/Library/DenverBasin/Greater\\_Wattenberg\\_Baseline\\_Study\\_Report\\_062007.pdf](http://cogcc.state.co.us/Library/DenverBasin/Greater_Wattenberg_Baseline_Study_Report_062007.pdf).]
- de Gouw, J. A., et al. (2009), Airborne measurements of ethene from industrial sources using laser photo-acoustic spectroscopy, *Environ. Sci. Technol.*, **43**, 2437–2442, doi:10.1021/es802701a.
- Drugokkeny, E., L. Steele, P. Lang, and K. Masarie (1994), The growth rate and distribution of atmospheric methane, *J. Geophys. Res.*, **99**(D8), 17,021–17,043, doi:10.1029/94JD01245.
- Finlayson-Pitts, B., and J. N. Pitts (2000), *Chemistry of the Upper and Lower Atmosphere*, 969 pp., Academic, San Diego, Calif.
- Fortin, T. J., B. J. Howard, D. D. Parrish, P. D. Goldan, W. C. Kuster, E. L. Atlas, and R. A. Harley (2005), Temporal changes in U.S. benzene emissions inferred from atmospheric measurements, *Environ. Sci. Technol.*, **39**, 1403–1408, doi:10.1021/es049316n.
- Gas Research Institute (1992), Variability of natural gas composition in select major metropolitan areas of the United States, *Rep. GRI-92/0123*, Univ. of Calif., Berkeley.
- Gerbig, C., S. Schmitgen, D. Kley, A. Volz-Thomas, K. Dewey, and D. Haaks (1999), An improved fast-response vacuum-UV resonance fluorescence CO instrument, *J. Geophys. Res.*, **104** (D1), 1699–1704, doi:10.1029/1998JD100031.
- 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.
- Harley, R. A., M. P. Hannigan, and G. R. Cass (1992), Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere, *Environ. Sci. Technol.*, **26**, 2395–2408.
- Harley, R. A., D. S. Hooper, A. J. Kean, T. W. Kirchstetter, J. M. Hesson, N. T. Balberan, E. D. Stevenson, and G. R. Kendall (2006), Effects of reformulated gasoline and motor vehicle fleet turnover on emissions and ambient concentrations of benzene, *Environ. Sci. Technol.*, **40**, 5084–5088, doi:10.1021/es0604820.
- Intergovernmental Panel on Climate Change (2007), *Climate Change 2007: Fourth Assessment Report: AR4 Synthesis Report*, Cambridge Univ. Press, Cambridge, U. K.
- Kaimal, J. C., and J. E. Gaynor (1983), The Boulder Atmospheric Observatory, *J. Clim. Appl. Meteorol.*, **22**, 863–880, doi:10.1175/1520-0450(1983)22<0863:TBAO>2.0.CO;2.
- Katzenstein, A. S., L. A. Doezema, I. J. Simpson, D. R. Blake, and F. S. Rowland (2003), Extensive regional atmospheric hydrocarbon pollution in the southwestern United States, *Proc. Natl. Acad. Sci. U. S. A.*, **100**(21), 11,975–11,979, doi:10.1073/pnas.1635258100.
- 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.
- Mellqvist, J., J. Samuelsson, J. Johansson, C. Rivera, B. Lefer, and S. Alvarez (2010), Measurements of industrial emissions of alkenes in Texas using the Solar Occultation Flux method, *J. Geophys. Res.*, **115**, D00F17, doi:10.1029/2008JD011682.
- Montzka, S., R. Myers, J. Butler, J. Elkins, and S. Cummings (1993), Global tropospheric distribution and calibration scale of HCFC-22, *Geophys. Res. Lett.*, **20**(8), 703–706, doi:10.1029/93GL00753.
- Nam, E. K., T. E. Jensen, and T. J. Wallington (2004), Methane emissions from vehicles, *Environ. Sci. Technol.*, **38**(7), 2005–2010, doi:10.1021/es034837g.
- 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**(D15), 19,285–19,293, doi:10.1029/97JD00031.
- Parrish, D. D., et al. (1998), Internal consistency tests for evaluation of measurements of anthropogenic hydrocarbons in the troposphere, *J. Geophys. Res.*, **103**(D17), 22,339–22,359, doi:10.1029/98JD01364.
- Ritter, B., Jr. (2007), Colorado Climate Action Plan: A strategy to address global warming, report, 35 pp., Gov. Off., Denver, Colo. [Available at: <http://www.pewclimate.org/docUploads/COClimatePlan.pdf>.]
- Roberts, J., et al. (1984), Measurements of aromatic hydrocarbon ratios and NO<sub>x</sub> concentrations in the rural troposphere: Observation of air mass

- photochemical aging and NO<sub>x</sub> removal, *Atmos. Environ.*, 18(11), 2421–2432, doi:10.1016/0004-6981(84)90012-X.
- Ryerson, T. B., et al. (2003), Effect of petrochemical industrial emissions of reactive alkenes and NO<sub>x</sub> on tropospheric ozone formation in Houston, Texas, *J. Geophys. Res.*, 108(D8), 4249, doi:10.1029/2002JD003070.
- Scamehorn, L. (2002), *High Altitude Energy: A History of Fossil Fuel in Colorado*, 244 pp., Univ. Press of Colo., Boulder.
- Schnell, R. C., S. J. Oltmans, R. R. Neely, M. S. Endres, J. V. Molenaar, and A. B. White (2009), Rapid photochemical production of ozone at high concentrations in a rural site during winter, *Nat. Geosci.*, 2, 120–122, doi:10.1038/ngeo415.
- Simpson, I. J., et al. (2010), Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C<sub>2</sub>–C<sub>10</sub> volatile organic compounds (VOCs), CO<sub>2</sub>, CH<sub>4</sub>, CO, NO, NO<sub>2</sub>, NO<sub>y</sub>, O<sub>3</sub> and SO<sub>2</sub>, *Atmos. Chem. Phys.*, 10, 11,931–11,954, doi:10.5194/acp-10-11931-2010.
- Spivakovsky, C. M., et al. (2000), Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, 105, 8931–8980, doi:10.1029/1999JD901006.
- 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>.]
- U.S. Energy Information Administration (EIA) (2004), How EIA estimates natural gas production, report, 50 pp., Washington, D. C. [Available at [ftp://ftp.eia.doe.gov/pub/oil\\_gas/natural\\_gas/analysis\\_publications/ngprod/ngprod.pdf](ftp://ftp.eia.doe.gov/pub/oil_gas/natural_gas/analysis_publications/ngprod/ngprod.pdf).]
- U.S. Energy Information Administration (EIA) (2006), Natural gas processing: The crucial link between natural gas production and its transportation to market, report, 11 pp., Off. of Oil and Gas, Washington, D. C. [Available at [http://www.eia.doe.gov/pub/oil\\_gas/natural\\_gas/feature\\_articles/2006/ngprocess/ngprocess.pdf](http://www.eia.doe.gov/pub/oil_gas/natural_gas/feature_articles/2006/ngprocess/ngprocess.pdf).]
- U. S. Environmental Protection Agency (EPA) (1998), Locating and estimating air toxic emissions from sources of benzene, *EPA-454/R-98-011*, 361 pp., Washington, D. C. [Available at <http://www.epa.gov/ttn/chiefl/e/>.]
- U. S. Environmental Protection Agency (EPA) (2004), Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs, *EPA 816-R-04-003*, 424 pp., Washington, D. C.
- U. S. Environmental Protection Agency (EPA) (2011), Inventory of U.S. greenhouse gas emissions and sinks: 1990–2009, Annex 7, report, 21 pp., Washington, D. C. [Available at <http://epa.gov/climatechange/emissions/downloads11/US-GHG-Inventory-2011-Annex-7.pdf>.]
- Warneke, C., et al. (2007), Determination of urban volatile organic compound emission ratios and comparison with an emissions database, *J. Geophys. Res.*, 112, D10S47, doi:10.1029/2006JD007930.
- Werner, C., K. Davis, P. Bakwin, C. Yi, D. Hursts, and L. Lock (2003), Regional-scale measurements of CH<sub>4</sub> exchange from a tall tower over a mixed temperate/boreal lowland and wetland forest, *Global Change Biol.*, 9, 1251–1261, doi:10.1046/j.1365-2486.2003.00670.x.
- Wert, B. P., et al. (2003), Signatures of terminal alkene oxidation in airborne formaldehyde measurements during TexAQ5 2000, *J. Geophys. Res.*, 108(D3), 4104, doi:10.1029/2002JD002502.
- 
- A. E. Andrews, T. Conway, E. J. Dlugokencky, G. Frost, D. Guenther, B. Hall, A. Karion, D. Kitzis, J. Kofler, P. M. Lang, K. Masarie, B. R. Miller, J. Miller, S. A. Montzka, W. Neff, P. Novelli, L. Patrick, G. Pétron, T. B. Ryerson, C. Siso, C. Sweeney, P. Tans, M. Trainer, D. Welsh, and D. Wolfe, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, R/GMD1 325 Broadway, Boulder, CO 80305, USA. (gabrielle.petron@noaa.gov)
- A. Bar-Ilan, ENVIRON International Corporation, 773 San Marin Dr., Ste. 2115, Novato, CA 94998, USA.
- A. I. Hirsch, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA.
- W. Kolodzey, Holcombe Department of Electrical and Computer Engineering, Clemson University, Clemson, SC 29634, USA.
- C. T. Moore Jr., Western Regional Air Partnership, Western Governors' Association, 1375 Campus Delivery, CIRA, Colorado State University, Fort Collins, CO 80523-1375, USA.