

**Hydrocarbon Emissions Characterization in the Colorado Front Range – A Pilot Study**

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## **Abstract**

The multi-species 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.

## 1) Introduction

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 [Andrews et al., in preparation] and bi-weekly discrete air sampling along vertical aircraft profiles [Sweeney et al., in preparation]. 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 multi-species 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.

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 (Figures 1 and 1S). 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.

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. [2009] 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.

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

90 Emissions management requirements for both air quality and climate-relevant  
91 gases have led the state of Colorado to build detailed baseline emissions inventories for  
92 ozone precursors, including volatile organic compounds (VOCs), and for GHGs. Since  
93 2004, a large fraction of the Colorado Northern Front Range, including Weld County and  
94 the Denver metropolitan area, has been in violation of the 8-hour ozone national ambient  
95 air quality standard [CDPHE, 2008a]. In December 2007, the Denver and Colorado  
96 Northern Front Range (DNFR) region was officially designated as a Federal Non-  
97 Attainment Area (NAA) for repeated violation in the summertime of the ozone National  
98 Ambient Air Quality Standard (see area encompassed by golden boundary in Figure 1).  
99 At the end of 2007, Colorado also adopted a Climate Action Plan, which sets greenhouse  
100 gas emissions reduction targets for the state [Ritter, 2007].

101 Methane, a strong greenhouse gas with a global warming potential (GWP) of 25  
102 over a 100 yr time horizon [IPCC, 2007], accounts for a significant fraction of Colorado  
103 GHG emissions, estimated at 14% in 2005 ([Strait et al., 2007] and Table 1S; note that in  
104 this report, the oil and gas industry CH<sub>4</sub> emission estimates were calculated with the EPA  
105 State Greenhouse Gas Inventory Tool). The natural gas industry (including exploration,  
106 production, processing, transmission and distribution) is the single largest source of CH<sub>4</sub>  
107 in the state of Colorado (estimated at 238 Gg/yr or ktonnes/yr), followed closely by coal  
108 mining (233 Gg/yr); note that all operating surface and underground coal mines are now  
109 in western Colorado. Emission estimates for oil production operations in the state were  
110 much lower, at 9.5 Gg/yr, than those from gas production. In 2005, Weld County  
111 represented 16.5% of the state's natural gas production and 51% of the state crude oil/  
112 natural gas condensate production (Table 2S). 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.

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].

In 2006, forty percent of the DNFR NAA's total anthropogenic VOC emissions were estimated to be due to oil and gas operations [CDPHE, 2008b]. 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 Figure 2S for 2006 emissions and projected 2010 emissions [Bar-Ilan et al., 2008a,b]). 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 (Table 3S).

Benzene ( $C_6H_6$ ) 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  $CH_4$ , 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  $C_6H_6$  [EPA, 1998]. Natural gas associated with oil production (such sources are located in several places around the DJB) usually has higher  $C_6H_6$  levels [Burns et al., 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  $C_6H_6$  to the atmosphere when the glycol undergoes regeneration [EPA, 1998]. Condensate tanks, venting and flaring at the well-heads, compressors, processing plants, and engine exhaust are also known sources of  $C_6H_6$  [EPA, 1998].  $C_6H_6$  can also be present in the liquids used for fracturing wells [EPA, 2004].

In this paper, we focus on describing and interpreting the measured variability in  $CH_4$  and  $C_{3-5}$  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  $CH_4$  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.

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 multi-species analysis in the discrete air samples, we were able to identify two major sources of  $C_6H_6$  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 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 ( $C_3H_8$ ) estimates with the observed ambient alkane ratios to calculate top-down emission estimates for n-butane ( $n-C_4H_{10}$ ), i- and n-pentane ( $i-C_5H_{12}$ ,  $n-C_5H_{12}$ ), 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**

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.

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**

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., in preparation]. Two continuous ozone UV-

absorption instruments have also been deployed to monitor ozone at the surface and at the 300-m level.

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 ( $\text{CH}_4$ , also referred to as  $\text{C}_1$ ), CO, propane ( $\text{C}_3\text{H}_8$ , also referred to as  $\text{C}_3$ ), n-butane ( $\text{n-C}_4\text{H}_{10}$ ,  $\text{nC}_4$ ), isopentane ( $\text{i-C}_5\text{H}_{12}$ ,  $\text{iC}_5$ ), n-pentane ( $\text{n-C}_5\text{H}_{12}$ ,  $\text{nC}_5$ ), acetylene ( $\text{C}_2\text{H}_2$ ), benzene, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Ethane and i-butane were not measured.

In this study, we use the results from the NOAA GMD multi-species analysis of air samples collected midday at the 300-m level together with 30-second wind speed and direction measured at 300-m. 30-minute 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.

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 US 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 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 3050m), 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., in preparation; <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, 2008] 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**

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.

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-second 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., in preparation]. 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.

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.

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**

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, 0.7L, glass flasks of flow-through design, fitted with Teflon O-ring on both 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  $\sim 5 \text{ L min}^{-1}$  for about 1 min and  $10 \text{ L min}^{-1}$  for about 3 minutes respectively, before the flasks were pressurized to 2.7 atm. Upon returning to the NOAA lab, the PFP manifold was leak-checked and meta-data 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.

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 ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{n-C}_4\text{H}_{10}$ ,  $\text{i-C}_5\text{H}_{12}$ ,  $\text{n-C}_5\text{H}_{12}$ ) 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 & 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.

$\text{CH}_4$  was measured by gas chromatography (GC) with flame ionization detection ( $\pm 1.2 \text{ ppb}$  = 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:  $\text{ppm} = \mu\text{mol mol}^{-1}$ ,  $\text{ppb} = \text{nmol mol}^{-1}$ , and  $\text{ppt} = \text{pmol mol}^{-1}$ .  $\text{CO}$  was measured directly by resonance fluorescence at  $\sim 150 \text{ nm}$  ( $\pm 0.2 \text{ ppb}$ ) [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>).

Gas chromatography/mass spectrometric (GC/MS) measurements were also performed on ~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 ~110°C were then separated by a temperature-programmed GC column (combination 25 m x 0.25 mm DB5 and 30 m x 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 CH<sub>4</sub>) 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-C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>2</sub>, 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.

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 C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> 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>.

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 US**

Air samples collected at BAO tower have a distinct chemical signature (Figure 2), showing enhanced levels of most alkanes ( $C_3H_8$ ,  $nC_4H_{10}$ ,  $iC_5H_{12}$  and  $nC_5H_{12}$ ) in comparison to results from other NOAA cooperative tall towers (see summary of site locations in Table 1 and data time series in Figure 1S). The midday summer time median mixing ratios for  $C_3H_8$  and  $nC_4H_{10}$  at BAO were at least 6 times higher than those observed at most other tall tower sites. For  $iC_5H_{12}$  and  $nC_5H_{12}$ , the summertime median mixing ratios at BAO were at least 3 times higher than at the other tall towers.



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.

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 vs. 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 US, 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 US total methane emission estimate for year 2005 reported in the latest EPA US GHG Inventory [EPA, 2011a].

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***

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-minute 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°).

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.

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>.

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 & Figure 4).

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***

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 column) shows correlation plots of some of these BAO species for summer data in the NE wind sector.

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.

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**

The median winter C<sub>6</sub>H<sub>6</sub> 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<sub>6</sub>H<sub>6</sub>-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<sub>6</sub>H<sub>6</sub>-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 that is not a significant source of CO. The C<sub>6</sub>H<sub>6</sub>-to-C<sub>2</sub>H<sub>2</sub> correlation slope is slightly higher for the NE wind sector data compared to the other two wind sectors. C<sub>6</sub>H<sub>6</sub> in the BAO data from the NE wind sector correlates more strongly with C<sub>3</sub>H<sub>8</sub> than with CO. The C<sub>6</sub>H<sub>6</sub>-to-C<sub>3</sub>H<sub>8</sub> summer correlation slope for the NE wind sector is  $10.1 \pm 1.2$  ppt/ppb ( $r^2=0.67$ ).

For the S and W wind sectors BAO data, the C<sub>6</sub>H<sub>6</sub>-to-C<sub>2</sub>H<sub>2</sub> (0.27 - 0.32 ppt/ppt) and C<sub>6</sub>H<sub>6</sub>-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<sub>6</sub>H<sub>6</sub>-to-C<sub>2</sub>H<sub>2</sub> ratio and 0.617 ppt/ppb for C<sub>6</sub>H<sub>6</sub>-to-CO ratio [Warneke et al., 2007]. Baker et al. [2008] report an atmospheric molar C<sub>6</sub>H<sub>6</sub>-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.

The analysis of the BAO C<sub>6</sub>H<sub>6</sub> data suggests the existence of at least two distinct C<sub>6</sub>H<sub>6</sub> sources in the vicinity of BAO: an urban source related mainly to mobile emissions,

and a common source of alkanes and C<sub>6</sub>H<sub>6</sub> concentrated in northeastern Colorado. We discuss C<sub>6</sub>H<sub>6</sub> correlations and sources in more detail in section 4.4.

### **3.2. On-road surveys: tracking point and area source chemical signatures**

Road surveys with flask sampling and the Mobile Lab with the fast-response CH<sub>4</sub> 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<sub>4</sub> analyzer allowed us to detect large-scale plumes with long-lasting enhancements of CH<sub>4</sub> mixing ratios as well as small-scale plumes associated with local CH<sub>4</sub> point sources. In the last two Mobile Lab surveys (surveys 8 and 9), we combined the monitoring of the continuous CH<sub>4</sub> analyzer with targeted flask sampling, using the CH<sub>4</sub> data to decide when to collect flask samples in and out of plumes.

The regional background CH<sub>4</sub> mixing ratio at the surface (interpreted here as the lowest methane level sustained for ~10 minutes or more) was between 1800 ppb and 1840 ppb for most surveys. Some of the highest “instantaneous” CH<sub>4</sub> 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).

The analysis of the summer 2008 intensive data suggests that regional scale mixing ratio enhancements of CH<sub>4</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> did not exhibit any correlation. Unlike CO<sub>2</sub>, the CH<sub>4</sub> enhancements were not related to on-road emissions. Below we present two examples of regional enhancements of CH<sub>4</sub> observed during the Front Range Mobile Lab surveys.

### **3.2.1. Survey 9: C<sub>3-5</sub> alkane levels follow large-scale changes in methane**

Figure 5 shows a time series of the continuous CH<sub>4</sub> 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 am and measured increasing CH<sub>4</sub> levels going east towards the BAO tower (Figure 6). An air sample was collected close to the peak of the CH<sub>4</sub> broad enhancement centered around 11:55 am. The CH<sub>4</sub> mixing ratio then decreased over the next 25 minutes and reached a local minimum close to 1875 ppb. The CH<sub>4</sub> level stayed around 1875 ppb for over one hour and then decreased again, more slowly this time, to ~ 1830 ppb over the next two hours.

Flasks # 1 to 3 were collected before, at the peak, and immediately after the broad CH<sub>4</sub> feature between 11:40 and 12:15. Flasks # 4 & 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<sub>4</sub> was still elevated above background as these samples were collected. After a 90-minute 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<sub>4</sub> levels. The last flask sample was collected on the NOAA campus just before 17:00 MDT, about 5.5 hours after the first flask sample was collected. The flask samples were always collected upwind of the Mobile Lab car exhaust.

Sharp spikes in the continuous CH<sub>4</sub> data reflect local point sources (wastewater treatment plant, landfill). The highly variable signals in both the continuous and discrete CH<sub>4</sub> close to these sources are driven by the spatial heterogeneity of the CH<sub>4</sub> emissions and variations in wind speed and direction. Broader enhancements in the continuous CH<sub>4</sub> data reflect larger (regional) plumes. The last flask (#12) sampled at NOAA has much higher levels of combustion tracers (CO, C<sub>2</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>) than the other samples.

Figure 7 shows correlation plots for C<sub>3</sub>H<sub>8</sub> versus CH<sub>4</sub> and n-C<sub>4</sub>H<sub>10</sub> versus C<sub>3</sub>H<sub>8</sub> 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<sub>3</sub>H<sub>8</sub>-to-CH<sub>4</sub> (C<sub>3</sub>/C<sub>1</sub>) 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 waste water treatment plant and the landfill (flasks # 4-5 and 8) are off the C<sub>3</sub>H<sub>8</sub>-to-CH<sub>4</sub> correlation line and have higher CH<sub>4</sub> than air samples collected nearby but not under the influence of these local CH<sub>4</sub> 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.

The C<sub>3</sub>-C<sub>5</sub> 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<sub>4</sub>/C<sub>3</sub> 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<sub>5</sub>/C<sub>3</sub> and nC<sub>5</sub>/C<sub>3</sub> 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**

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 Figure 3S in Supplementary Material). Figure 8A shows a correlation plot of C<sub>3</sub>H<sub>8</sub> versus CH<sub>4</sub> mixing ratios in these air samples. Flasks collected NE of BAO and not near feedlots (# 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<sub>3</sub>H<sub>8</sub>-to-CH<sub>4</sub> correlation slope (0.083 ppb/ppb,  $r^2=0.93$ ). The  $r^2$  for the C<sub>3</sub>H<sub>8</sub>-to-CH<sub>4</sub> correlation using all the flasks is 0.91.

The n-C<sub>4</sub>H<sub>10</sub> versus C<sub>3</sub>H<sub>8</sub> correlation plot and its slope, along with the n-C<sub>4</sub>H<sub>10</sub>-to-C<sub>3</sub>H<sub>8</sub> and C<sub>5</sub>H<sub>12</sub>-to-C<sub>3</sub>H<sub>8</sub> correlation slopes for air samples not collected downwind of feedlots are shown in Figure 8B. The  $r^2$  for the n-C<sub>4</sub>H<sub>10</sub>-to-C<sub>3</sub>H<sub>8</sub> correlation using all the flasks is 0.98, which is slightly higher than the  $r^2$  for the C<sub>3</sub>H<sub>8</sub>-to-CH<sub>4</sub> correlation using all flasks (0.91). The  $r^2$  for the i-C<sub>5</sub>H<sub>12</sub>-to-n-C<sub>4</sub>H<sub>10</sub> and n-C<sub>5</sub>H<sub>12</sub>-to-n-C<sub>4</sub>H<sub>10</sub> 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<sub>4</sub>H<sub>10</sub> and the C<sub>5</sub>H<sub>12</sub> levels.

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<sub>3</sub>H<sub>8</sub> enhancements seen near the feedlots are due to leaks of propane fuel used for farm operations [Ronald Klusman, personal communication]. 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<sub>4</sub> enhancements (1946 and 2335 ppb), but no enhancement in C<sub>3</sub>H<sub>8</sub> (~ 1ppb), n-C<sub>4</sub>H<sub>10</sub> (<300ppt), the C<sub>5</sub>H<sub>12</sub> (< 130ppt) or C<sub>6</sub>H<sub>6</sub> (< 30ppt).

For survey #6, the n-C<sub>4</sub>H<sub>10</sub>-to-C<sub>3</sub>H<sub>8</sub> 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<sub>5</sub>H<sub>12</sub>-to-C<sub>3</sub>H<sub>8</sub> and n-C<sub>5</sub>H<sub>12</sub>-to-C<sub>3</sub>H<sub>8</sub> 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

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°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].

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/ppt,  $r^2=0.75$ ) 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.

The second subset of 46 samples corresponds to flasks with a  $C_3H_8$  mixing ratio larger than 3ppb. 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<sub>3</sub>H<sub>8</sub> 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**

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°N [Finlayson-Pitts and Pitts, 2000; Spivakovsky et al., 2000] respectively, 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 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.

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.

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.

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.

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<sub>4</sub> was not measured during that study. The correlation coefficient ( $r^2$ ) between 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 was around 0.86, with a clear minimum slope for the abundance ratios (see Figure 4 in Goldan et al. [1995]). The authors proposed that the C<sub>4</sub>-C<sub>6</sub> alkanes shared one common source with propane (called the “C<sub>3</sub> source” in the next section and in Figure 9), with additional emissions contributing to some C<sub>4</sub>-C<sub>6</sub> 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**

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<sub>x</sub> 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<sub>3</sub>H<sub>8</sub>, i,n-C<sub>4</sub>H<sub>10</sub>, i,n-C<sub>5</sub>H<sub>12</sub> and higher alkanes, C<sub>6</sub>H<sub>6</sub>, toluene, ethylbenzene, xylenes and 224-trimethylpentane. The WRAP Phase III inventories for 2006 and 2010 were only provided as total VOC and NO<sub>x</sub> 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. Supplementary Figure 2S and Bar-Ilan et al. [2008a,b] present more details on how the inventory emission estimates are derived.

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,b] (see Figure 2S). 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 supplementary Figure 2S and Bar-Ilan et al. [2008a] for more details on how the estimates are derived).

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. well head, 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 ([Bar-Ilan et al., 2008a,b], Figure 2S).

The molar compositions of venting and flashing emissions are quite different (see supplementary Figure 4S). Emissions from flash losses are enriched in C<sub>2+</sub> 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:

- Bar-Ilan et al. [2008a]: mean venting profile used for the 2006 DJB inventory, also called the "Venting-WRAP" profile;
- 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<sub>6</sub>H<sub>6</sub> was not reported in this data set;
- Colorado Department of Public Health and the Environment (CDPHE, personal communication): flashing emissions profiles based on condensate composition data from 16 different storage tanks in the DJB and EPA TANK2.0 (flashing emissions model) runs.



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 (cf. Table 4S 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.

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<sub>4</sub> [Gas Research Institute, 1992]. Since Goldan et al. [1995] did not measure CH<sub>4</sub> in their 1991 study, they could not determine if the atmospheric C<sub>3+</sub>/C<sub>1</sub> alkane ratios were higher than expected in processed natural gas.

#### **4.3. Estimation of the alkane source in Weld County**

##### ***Bottom-up speciated emission estimates***

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., 2008ab] 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., 2008] 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.

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 Figure 2S (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 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.

Next we describe the calculations, summarized in Figure 5S, 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 supplementary Figure 6S). From the total annual vented VOC source and the average vented emission profile provided by Bar-Ilan et al. [2008a] (Table 2S), 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. inventory data and assumptions [2008a], 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 mole 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).

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.

#### ***Top-Down emissions scenarios***

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> ( $y_m$ ,  $y_p$ )<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.

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.:

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

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) 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:

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

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

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

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

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.

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 CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>. This number is much higher than the 30% uncertainty reported by the EPA for the 2009 national CH<sub>4</sub> source estimate from natural gas systems [EPA, 2011c].

The scenario 1 mean top-down vented CH<sub>4</sub> 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 CH<sub>4</sub>, an average estimate of 118.4 Gg/yr of CH<sub>4</sub> 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 [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.

Emissions for the other alkanes measured are all derived from the C<sub>3</sub>H<sub>8</sub> 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).

The main result of this exercise is that for each of the three top-down total emissions scenarios, the mean estimates for CH<sub>4</sub>, n-C<sub>4</sub>H<sub>10</sub> and the C<sub>5</sub>H<sub>12</sub> 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 C<sub>3</sub>H<sub>8</sub>) or higher than (for CH<sub>4</sub>, n-C<sub>4</sub>H<sub>10</sub>, i-C<sub>5</sub>H<sub>12</sub>, n-C<sub>5</sub>H<sub>12</sub>) the bottom-up mean estimates.

To put the top-down CH<sub>4</sub> source estimate from oil and gas exploration, production and processing operations in perspective, we compare it with an estimate of the passive “geological” CH<sub>4</sub> flux over the entire DJB. Klusman and Jakel [1998] reported an average flux of 0.57 mg CH<sub>4</sub>/m<sup>2</sup>/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 CH<sub>4</sub> /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**

On-road vehicles are estimated to be the largest source of C<sub>6</sub>H<sub>6</sub> in the US [EPA, 2009a]. 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<sub>6</sub>H<sub>6</sub> correlates well with CO and C<sub>2</sub>H<sub>2</sub>.

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<sub>6</sub>H<sub>6</sub>

source [EPA, 2009a].  $C_6H_6$  and  $C_3H_8$  have similar photochemical lifetimes (~ 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, 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.

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).

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 US EPA for the Toxics Release Inventory amounted to a total of 3.9 tonnes in 2008 [EPA, 2009b] and on-road emissions in Weld



County were estimated at 95.4 tonnes/yr in 2008 [CDPHE, personal communication]. Based on our analysis, oil and gas operations in the DJB could be the largest source of C<sub>6</sub>H<sub>6</sub> in Weld County.

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<sub>6</sub>H<sub>6</sub> 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<sub>6</sub>H<sub>6</sub> emission estimates for condensate tanks in Weld County (21.5 Mg/yr versus 1120 Mg/yr, respectively; see also Table 3S). Estimates in the 2008 NEI are much closer to estimates provided by CDPHE (personal communication) 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<sub>6</sub>H<sub>6</sub> 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

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

931 by a Mobile Lab equipped with a continuous methane analyzer and discrete canister  
932 sampling (June-July 2008). The analysis of the tower data filtered by wind sector reveals  
933 a strong alkane and benzene signature in air masses coming from northeastern Colorado,  
934 where the main activity producing these compounds is related to oil and gas operations  
935 over the Denver–Julesburg Fossil Fuel Basin. Using the Mobile Lab platform, we  
936 sampled air directly downwind of different methane sources (oil and gas wells, a landfill,  
937 feedlots, and a waste water treatment plant) and collected targeted air samples in and out  
938 of plumes. The tall tower and Mobile Lab data both revealed a common source for air  
939 masses with enhanced alkanes. In the data from both platforms, the alkane mixing ratios  
940 were strongly correlated, with slight variations in the correlation slopes depending on the  
941 location and day of sampling. The alkanes did not correlate with combustion tracers such  
942 as carbon monoxide and acetylene. We hypothesize that the observed alkanes were  
943 emitted by the same source located over the Denver-Julesburg Basin, "the DJB source".

944 The second part of the study brings in information on VOC emissions from oil  
945 and gas activities in the DJB from the detailed bottom-up WRAP Phase III inventory [Bar  
946 Ilan et al., 2008a,b]. We have used the total VOC emission inventory and associated  
947 emissions data for DJB condensate and gas production and processing operations to  
948 calculate annual emission estimates for  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{n-C}_4\text{H}_{10}$ ,  $\text{i-C}_5\text{H}_{12}$ ,  $\text{n-C}_5\text{H}_{12}$  and  $\text{C}_6\text{H}_6$   
949 in Weld County. The main findings are summarized below:

- 950 • The emissions profiles for flashing and venting losses are in good agreement with  
951 the atmospheric alkane enhancement ratios observed during this study and by  
952 Goldan et al. [1995] in Boulder in 1991. This is consistent with the hypothesis

953 that the observed alkane atmospheric signature is due to oil and gas operations in  
954 the DJB.

- 955 • The three top-down emission scenarios for oil and gas operations in Weld County  
956 in 2008 give a rather large range of potential emissions for CH<sub>4</sub> (71.6-251.9  
957 Gg/yr) and the higher alkanes. Except for propane, the lowest top-down alkanes  
958 emission estimates are always larger than the inventory-based mean estimate we  
959 derived based on the WRAP Phase III inventory data and the COGCC GWA raw  
960 gas composition data set.
- 961 • There are notable inconsistencies between our results and state and national  
962 regulatory inventories. In 2008 gas wells in Weld County represented 15% of the  
963 state's production. Based on our top-down analysis, Weld County methane  
964 emissions from oil and gas production and processing represent at least 30% of  
965 the state total methane source from natural gas systems derived by Strait et al.  
966 [2007] using the EPA State Inventory Tool. The methane source from natural gas  
967 systems in Colorado is most likely underestimated by at least a factor of two. Oil  
968 and gas operations are the largest source of alkanes in Weld County. They were  
969 included as a source of "total VOC" in the 2008 EPA NEI for Weld County but  
970 not in the 2005 NEI.
- 971 • There are at least two main sources of C<sub>6</sub>H<sub>6</sub> in the region: one related to  
972 combustion processes, which also emit CO and C<sub>2</sub>H<sub>2</sub> (engines and mobile  
973 vehicles), and one related to the DJB alkane source. The C<sub>6</sub>H<sub>6</sub> source we derived  
974 based on flashing and venting VOC emissions in the WRAP inventory (143  
975 Mg/yr) most likely underestimates the actual total source of C<sub>6</sub>H<sub>6</sub> from oil and gas

976 operations. Our top-down source estimates for C<sub>6</sub>H<sub>6</sub> from oil and gas operations  
977 in Weld County cover a large range: 385-2056 Mg/yr. Again, the lowest figure is  
978 much higher than reported in the 2008 CDPHE inventory for Weld County oil and  
979 gas total point sources (61.8 Mg/yr).

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

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

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994    **Acknowledgements**

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996    The authors thank John Grant (ENVIRON) and Kathleen Sgamma (Western Energy  
997    Alliance) for their expertise and support in interpreting the WRAP Phase III inventory  
998    public data. Special thanks are extended to the NOAA personnel and collaborators  
999    responsible for flask preparation, sample collection and sample analysis, data quality  
1000   control and database management.

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1186 List of Figures

1187

1188 Figure 1: Map of the study area centered on the Boulder Atmospheric Observatory  
1189 (BAO), located 25 km east-northeast of Boulder. Overlaid on this map are the locations  
1190 of active oil and gas wells (light purple dots) as of April 2008 (data courtesy of SkyTruth,  
1191 <http://blog.skytruth.org/2008/06/colorado-all-natural-gas-and-oil-wells.html>, based on  
1192 COGCC well data). Also shown are the locations of landmarks used in the study,  
1193 including selected point sources (NGP Plant = natural gas processing plant, WWT Plant  
1194 = Lafayette wastewater treatment plant).

1195 Figure 2: Observed median mixing ratios for several species measured in air samples  
1196 taken at various sites at midday during June-August (2007-2010). The sites are described  
1197 in Table 1. Only nighttime samples are shown for NWF to capture background air with  
1198 predominantly down-slope winds. Notice the different units with all columns and the  
1199 different scaling applied to methane, propane and n-butane.

1200 Figure 3: Summertime and wintertime median mixing ratios of several species measured  
1201 in air samples from the 300-meter level at the BAO tower for three wind sectors: North  
1202 and East (NE) where the density of gas drilling operations is highest, South (S) with  
1203 Denver 35 km away, and West (W) with mostly clean air. The time span of the data is  
1204 from August 2007 to April 2010. Summer includes data from June to August and winter  
1205 includes data from November to April. Due to the small number of data points (<15), we  
1206 do not show summer values for the S and W wind sectors. Data outside of the 11am-3pm  
1207 local time window were not used. Notice the different scales used for methane, propane  
1208 and n-butane. The minimum number of data points used for each wind sector is: NE  
1209 summer 33, NE winter 89, S winter 65 and W winter 111.

1210

1211 Figure 4: Correlation plots for various species measured in the BAO summertime NE  
1212 wind sector flask samples (left column) and summer 2008 Mobile Lab (right column)  
1213 samples. Data at BAO were filtered to keep only midday air samples collected between  
1214 June and August over the time period spanning August 2007 to August 2009. See also  
1215 Table 3.

1216

1217 Figure 5: (Top panel) Time series of the continuous methane measurements from Mobile  
1218 Lab Survey # 9 on July 31, 2008. Also shown are the mixing ratio data for the 12 flask  
1219 samples collected during the road survey. The GC/MS had a faulty high energy dynode  
1220 cable when these samples were analyzed, resulting in more noisy data for the alkanes and  
1221 the CFCs ( $\sigma < 10\%$  instead of 5%). However, the amplitudes of the C<sub>3-5</sub> alkane signals  
1222 are much larger than the noise here. The methane mixing ratio scale is shown on the left  
1223 hand vertical axis. For all other alkanes, refer to the right hand vertical axis.  
1224 (Bottom panel) Time series of wind directions at the NCAR Foothills and Mesa  
1225 Laboratories in Boulder (see Figure 6 for locations) and from the 300-m level at the BAO  
1226 on July 31, 2008.

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.

Figure 7: A) Propane versus methane mixing ratios for air samples collected during Survey #9 on July 31, 2008. B) n-butane versus propane mixing ratios in the same air samples. The black line in plot A 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 plot B 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).

Figure 8: A) Propane versus methane mixing ratios for air samples collected during Survey #6 on July 14, 2008. B) n-butane versus propane mixing ratios in the same air samples. The black line in plot A 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 plot B shows the correlation line for samples not impacted by local sources of propane.

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 (grey) 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<sub>4-5</sub> alkane ratios to propane (dark propane, 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)).

Figure 10: Bottom-up (inventory-derived) emission estimates and top-down emission scenarios for CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, n-C<sub>4</sub>H<sub>10</sub>, i-C<sub>5</sub>H<sub>12</sub>, n-C<sub>5</sub>H<sub>12</sub> and C<sub>6</sub>H<sub>6</sub> 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.

## Tables

Table 1: Locations of a subset of the NOAA ESRL Towers and Aircraft Profile Sites used in this study. 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 night time 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 meters altitude.

Site Code	City	State	Latitude °North	Longitude °East	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	37.7553	122.45	254	232
WGC	Walnut Grove	California	38.265	121.49	0	91
WKT	Moody	Texas	31.32	97.33	251	457
SGP*	Southern Great Plains	Oklahoma	36.80	97.50	314	< 650

\* aircraft discrete air samples

Table 2: List of the Front Range Mobile Lab measurement and flasks sampling surveys. 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.

Road Survey #	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 Dacono Natural Gas Compressor - Feedlot	Picarro + 8 flasks
9	July 31	“Regional” CH <sub>4</sub> enhancements, Landfill, Corn field	Picarro + 12 flasks

1293 Table 3: Correlation slopes and  $r^2$  for various species measured in the BAO tower midday air flask samples for summer (June to  
1294 August, when more than 25 samples exist) and winter (November to April) over the time period spanning August 2007 to April 2010.  
1295 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  
1296 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  
1297 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  
1298 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  
1299 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- $C_5H_{12}$ ,  
1300  $C_2H_2$ , and  $C_6H_6$ .

Sector		BAO North and East						BAO South			BAO West			Mobile Lab		
Season		summer			winter			winter			winter			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</b> $\pm 0.005$	0.85	81	<b>0.105</b> $\pm 0.004$	0.90	115	0.079 $\pm 0.008$	0.53	130	<b>0.085</b> $\pm 0.005$	0.73	148	<b>0.095</b> $\pm 0.007$	0.76	77
n- $C_4H_{10}/C_3H_8$	ppb/ppb	<b>0.447</b> $\pm 0.013$	1.00	81	<b>0.435</b> $\pm 0.005$	1.0	120	<b>0.449</b> $\pm 0.011$	0.98	131	<b>0.434</b> $\pm 0.006$	1.00	151	<b>0.490</b> $\pm 0.011$	1.00	85
i- $C_5H_{12}/C_3H_8$	ppb/ppb	<b>0.141</b> $\pm 0.004$	1.00	81	<b>0.134</b> $\pm 0.004$	0.98	120	<b>0.142</b> $\pm 0.009$	0.81	121	<b>0.130</b> $\pm 0.004$	0.94	151	<b>0.185</b> $\pm 0.011$	0.81	85
n- $C_5H_{12}/C_3H_8$	ppb/ppb	<b>0.150</b> $\pm 0.003$	1.00	81	<b>0.136</b> $\pm 0.004$	0.98	120	<b>0.142</b> $\pm 0.006$	0.90	131	<b>0.133</b> $\pm 0.003$	0.91	151	<b>0.186</b> $\pm 0.008$	0.92	85
$C_6H_6/C_3H_8$	ppt/ppb	10.1 $\pm 1.2$	0.67	49	<b>8.2</b> $\pm 0.5$	0.79	117	-	0.33	130	-	0.39	150	<b>17.9</b> $\pm 1.1$	0.95	46
$C_6H_6/CO$	ppt/ppb	2.89 $\pm 0.40$	0.58	53	3.18 $\pm 0.24$	0.69	112	<b>1.57</b> $\pm 0.08$	0.85	123	<b>1.81</b> $\pm 0.08$	0.83	148	<b>1.82</b> $\pm 0.12$	0.89	39
$C_2H_2/CO$	ppt/ppb	<b>3.15</b> $\pm 0.33$	0.85	81	<b>7.51</b> $\pm 0.39$	0.85	100	<b>5.03</b> $\pm 0.17$	0.92	110	<b>5.85</b> $\pm 0.25$	0.86	131	<b>4.32</b> $\pm 0.28$	0.89	39
$C_6H_6/C_2H_2$	ppt/ppt	0.51 $\pm 0.09$	0.55	50	<b>0.34</b> $\pm 0.02$	0.90	103	<b>0.27</b> $\pm 0.02$	0.90	111	<b>0.32</b> $\pm 0.02$	0.96	132	<b>0.37</b> $\pm 0.04$	0.75	39

1301 **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**  
1302 **County.**

	Bottom-Up Estimates				Top-Down Scenarios <sup>c</sup> : Venting			Top-Down Scenarios <sup>c</sup> : TOTAL Bottom-Up Flashing + Top-Down Venting			Top-Down Scenarios <sup>c</sup> : % of production vented <sup>f</sup>		
Gg/yr	Flashing <sup>b</sup>	Venting <sup>c</sup>	Flashing + venting	% of production vented <sup>d</sup>	1	2	3	1	2	3	1	2	3
<b>methane</b>	<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%
<b>min<sup>a</sup></b>	<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%
<b>max<sup>a</sup></b>	<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>
<b>propane</b>	<b>18.3</b>	7.8	26.1		17.4	10.2	28	<b>35.7</b>	28.5	46.3			
<b>min<sup>a</sup></b>	<b>14</b>	1	15		12.7	7.5	20.5	26.7	<b>21.5</b>	34.5			
<b>max<sup>a</sup></b>	<b>24</b>	28	52		25.3	14.9	40.8	49.3	38.9	<b>64.8</b>			

1303 <sup>a</sup> The minimum and maximum values reported here come from the ensemble of 16 condensate tank emissions speciation profiles  
1304 provided by CDPHE.

1305 <sup>b</sup> The bottom-up flashing emissions for methane and propane were calculated using the 2008 estimate of total VOC flash emissions  
1306 derived by averaging the WRAP estimate for 2006 and the projection for 2010 (Cf. section 4.3).

1307 <sup>c</sup> The bottom-up venting emissions for methane and propane were calculated using the WRAP Phase III inventory estimate for the  
1308 total volume of natural gas vented and the GWA 77 natural gas composition profiles.

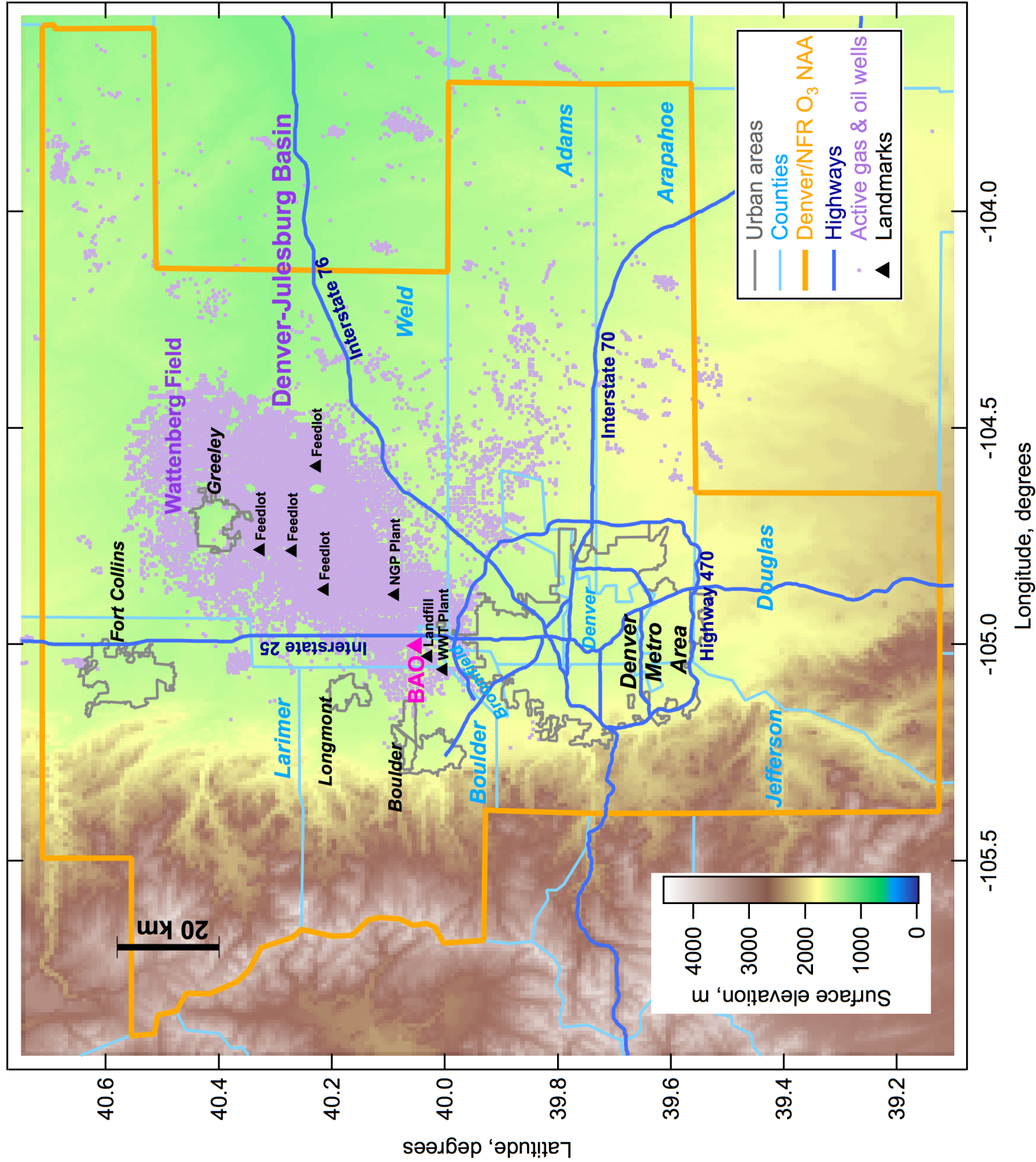
1309 <sup>d</sup> Using the WRAP Phase III inventory data set and assumptions, including a CH<sub>4</sub> mean molar ratio of 77.44% for the vented natural  
1310 gas and a molar volume for the gas of 22.4 L/mol.

1311 <sup>e</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  
1312 molar ratios in GWA data set) and 24.83 for scenario 3 (mean of molar ratios in GWA data set).

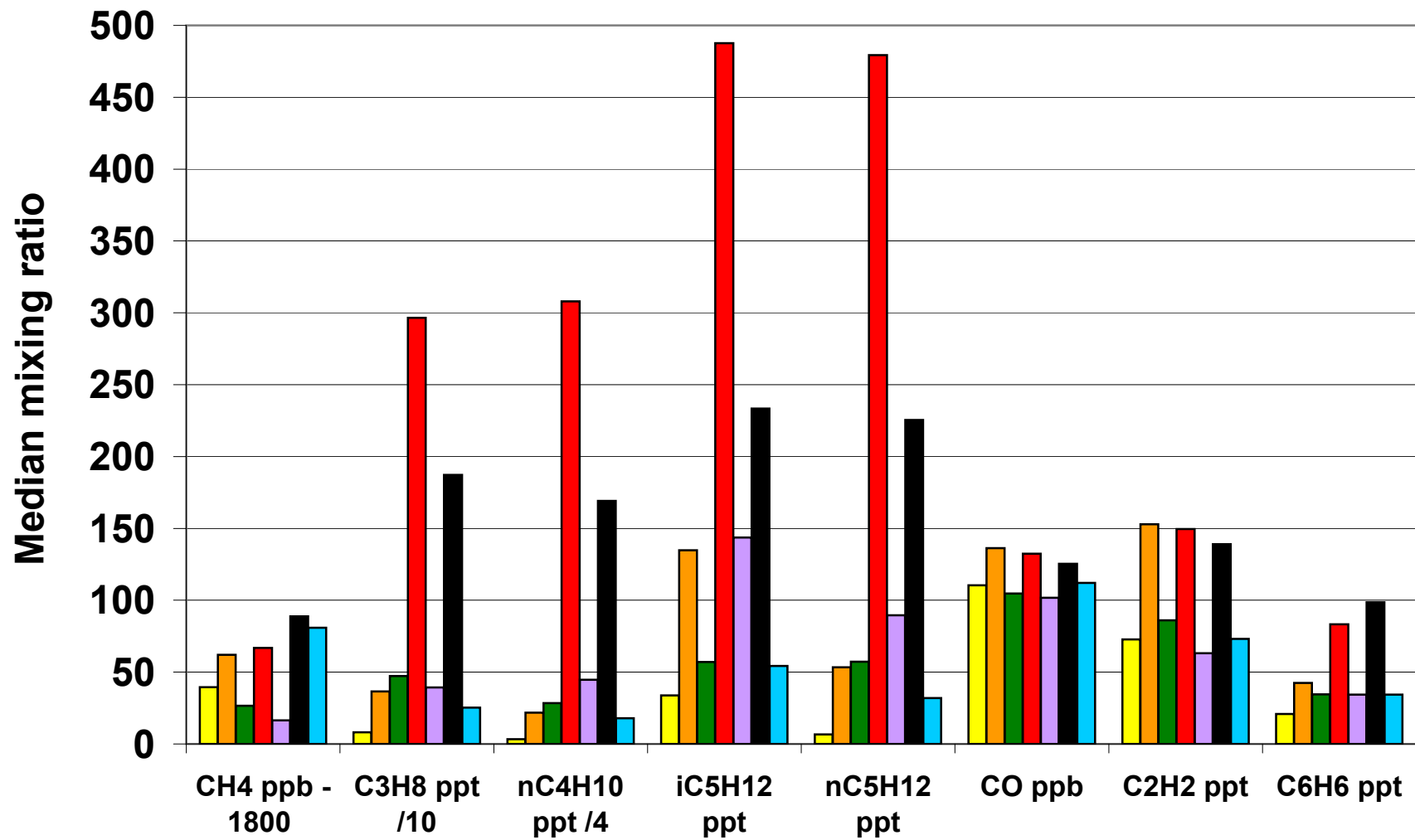
1313 <sup>f</sup> Using the assumptions of a CH<sub>4</sub> molar ratio of 77% for the vented natural gas and a molar volume for the gas of 23.6 L/mol  
1314 (Pressure= 14.73 pounds per square inch and Temperature= 60°F) as used by the EIA [EIA, 2004].  
1315

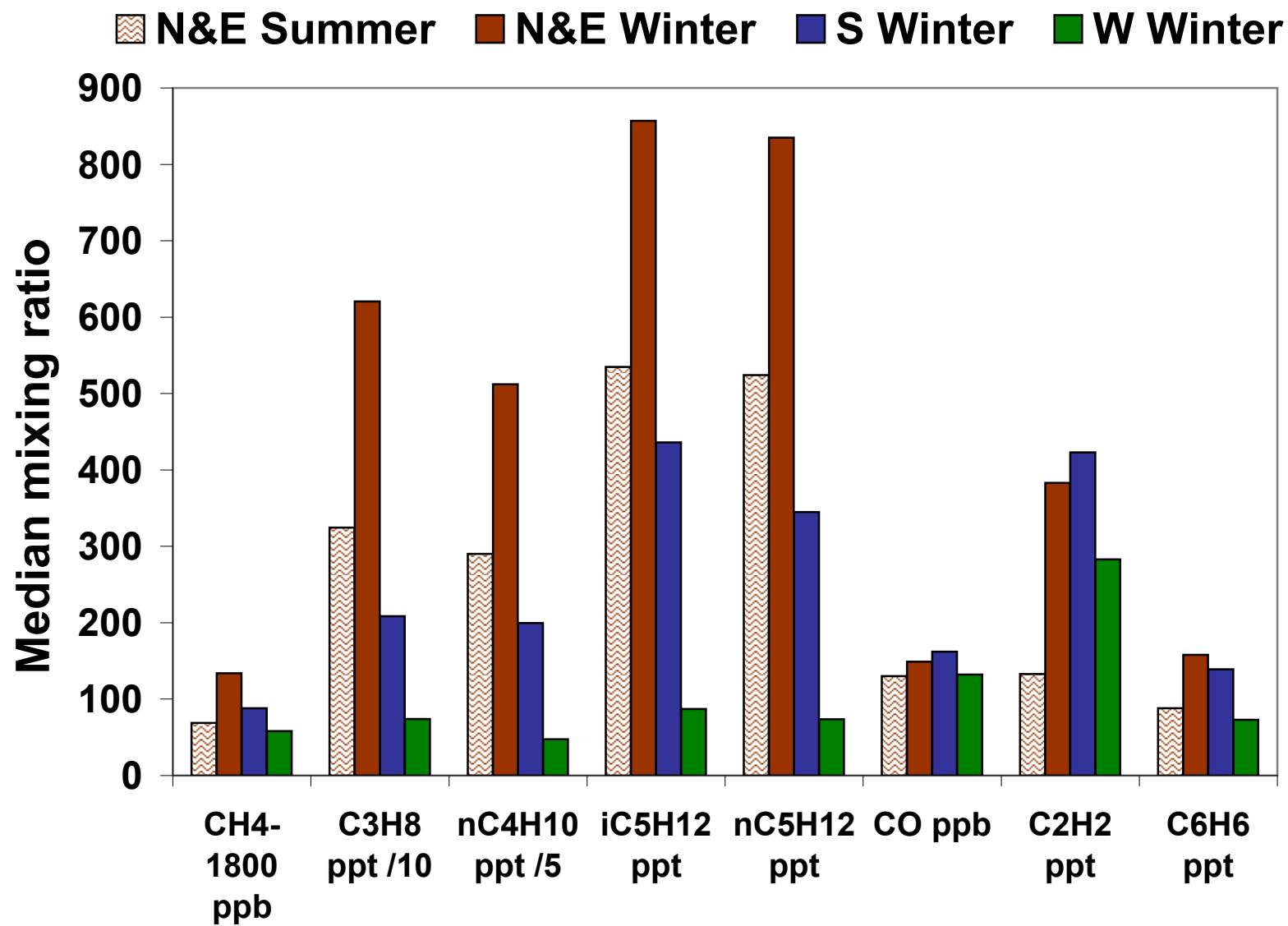




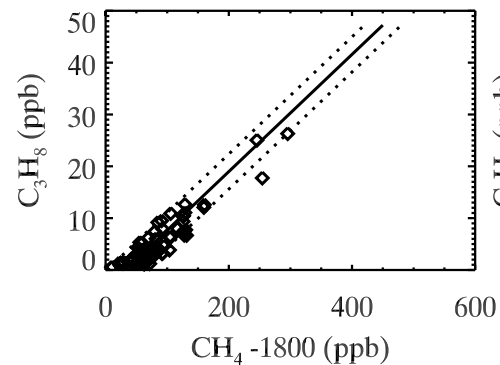


■ STR, CA 
 ■ WGC, CA 
 ■ NWF, CO - Night 
 ■ BAO, CO 
 ■ WKT, TX 
 ■ SGP, OK 
 ■ LEF, WI

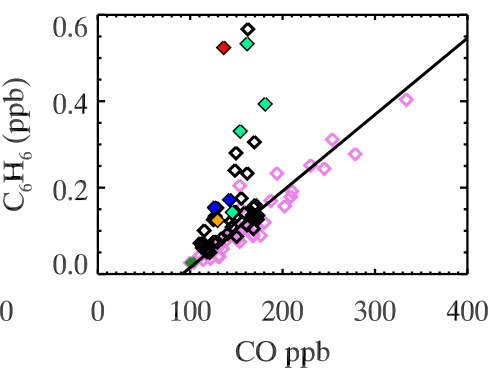
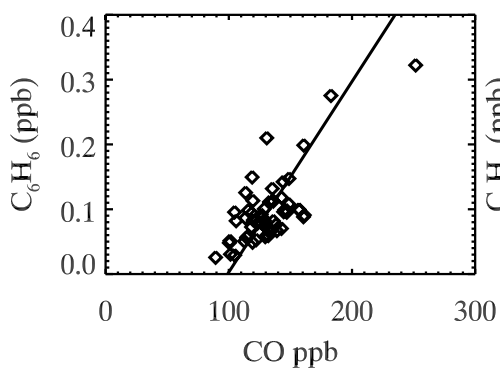
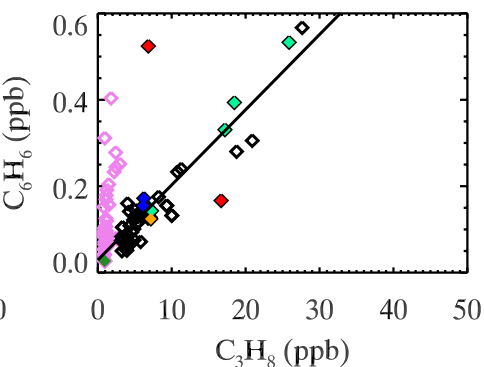
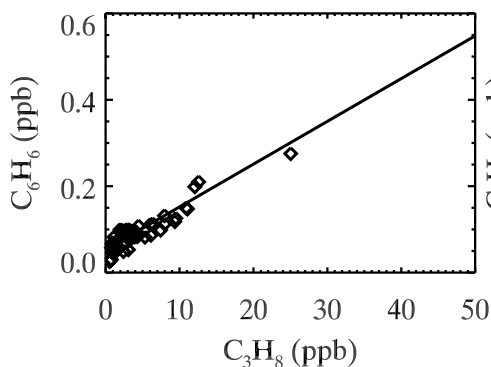
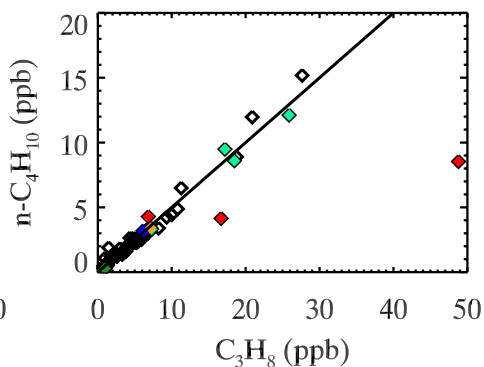
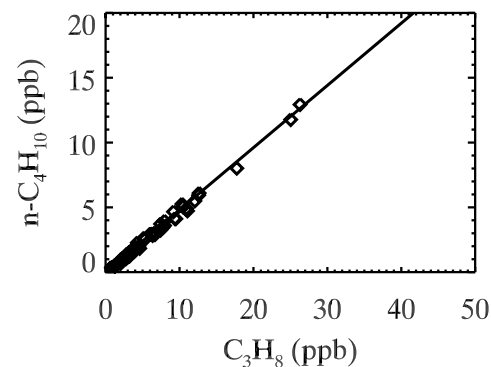
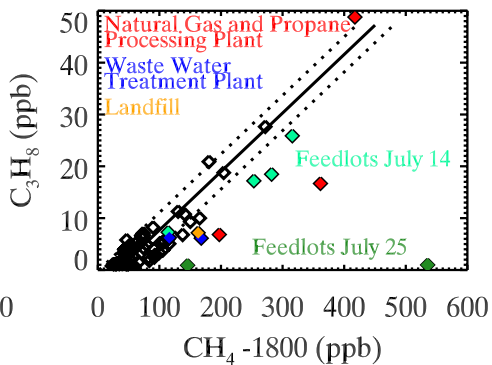


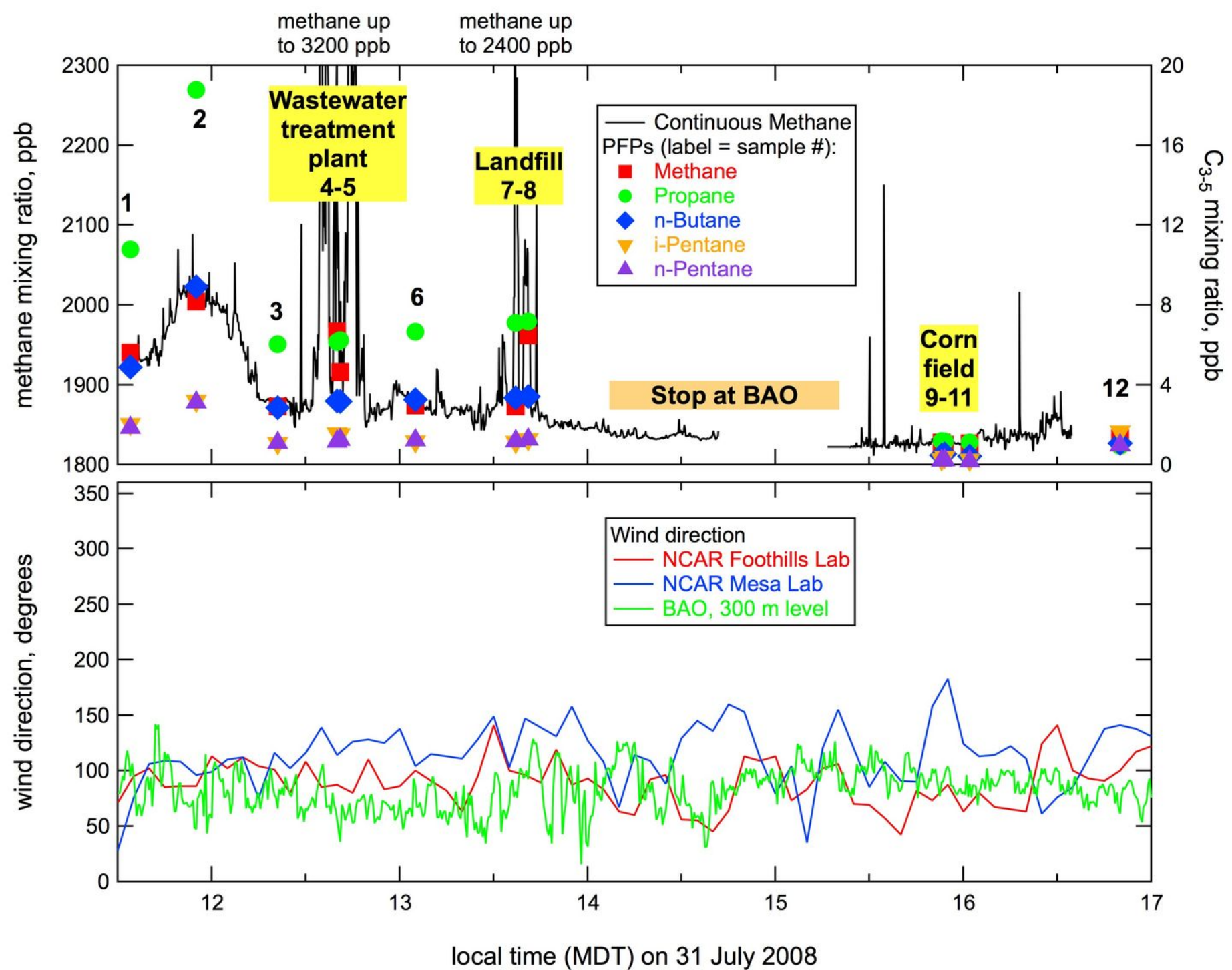


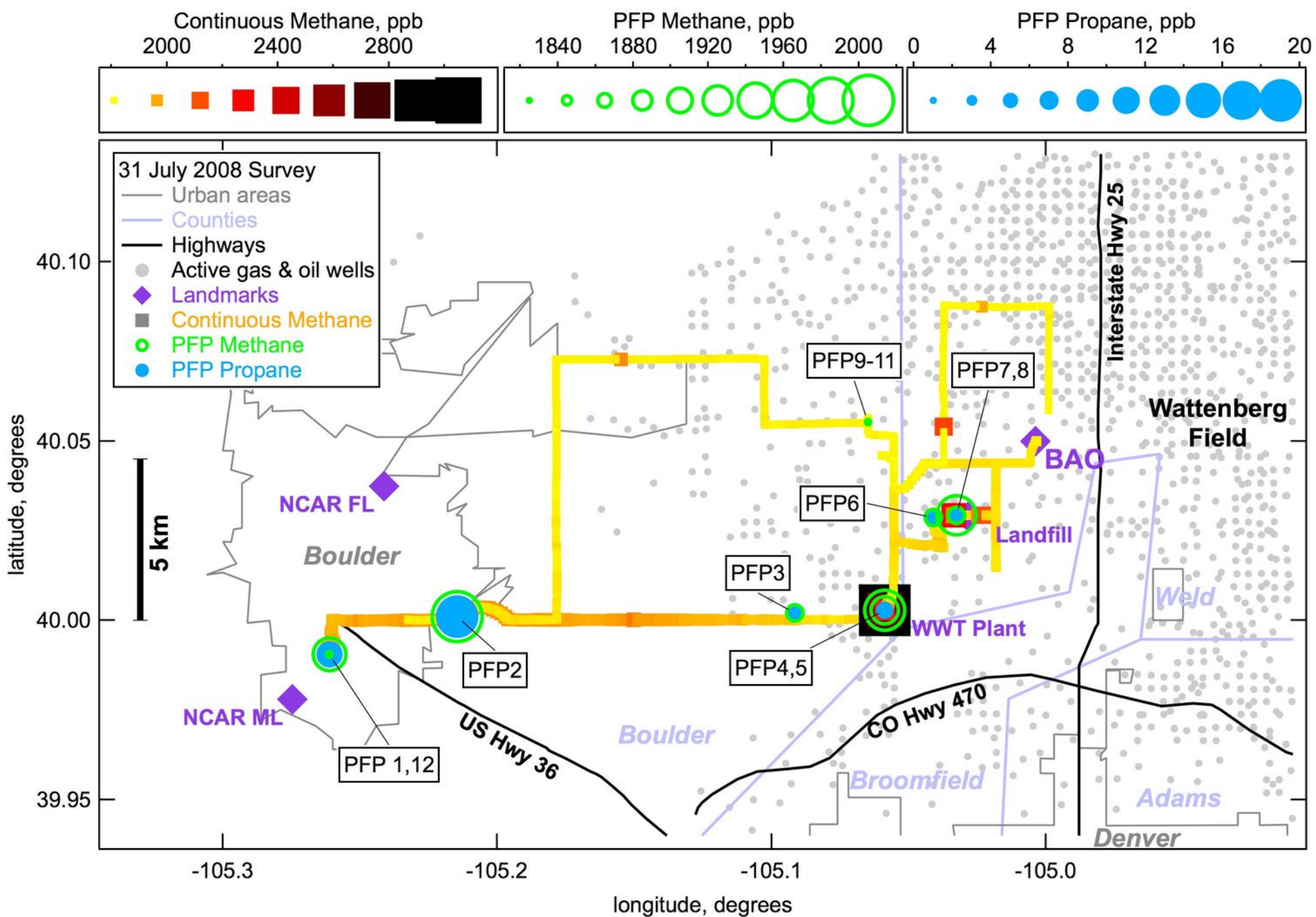
BAO N&amp;E Summer

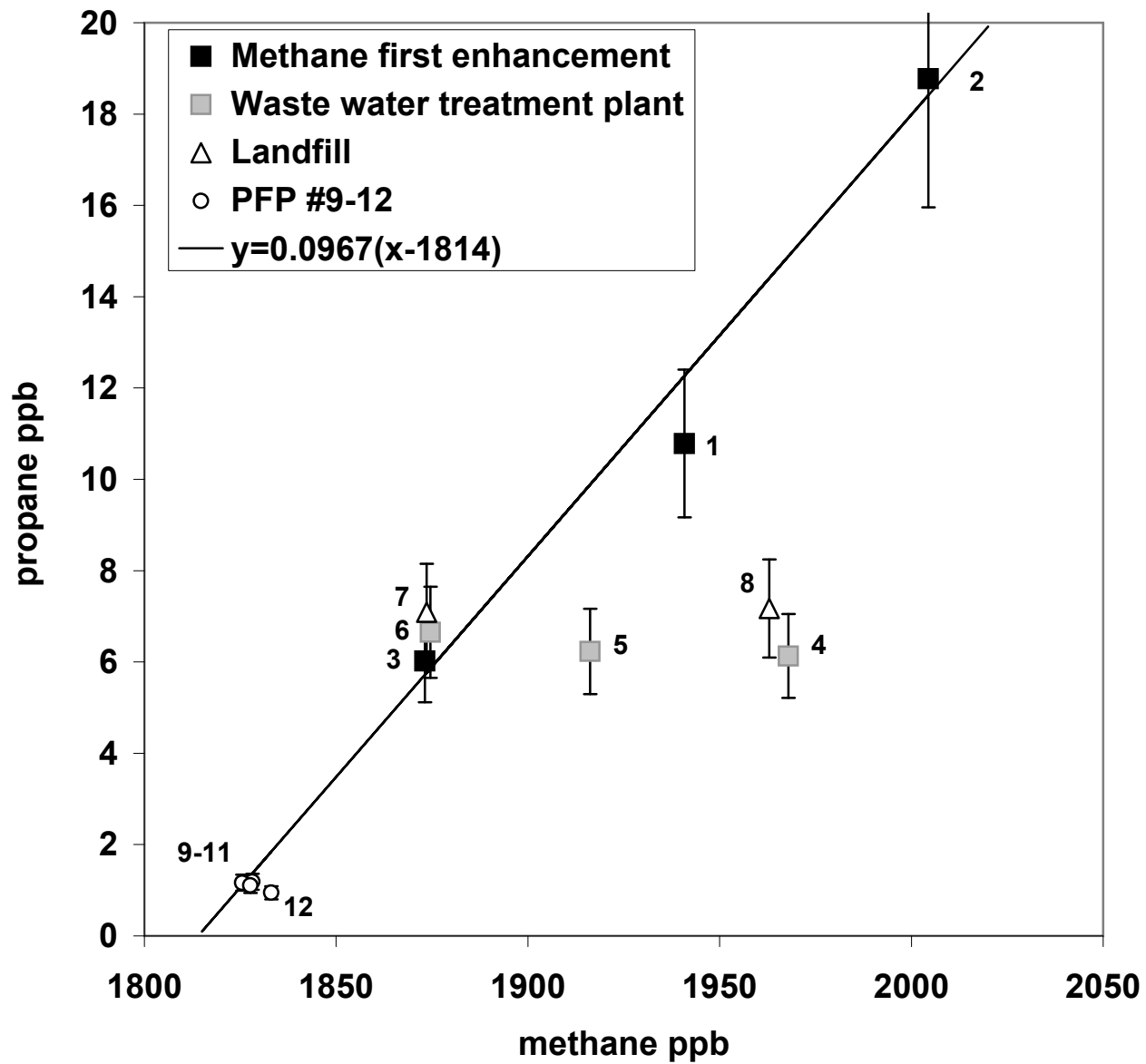


Mobile lab, All samples

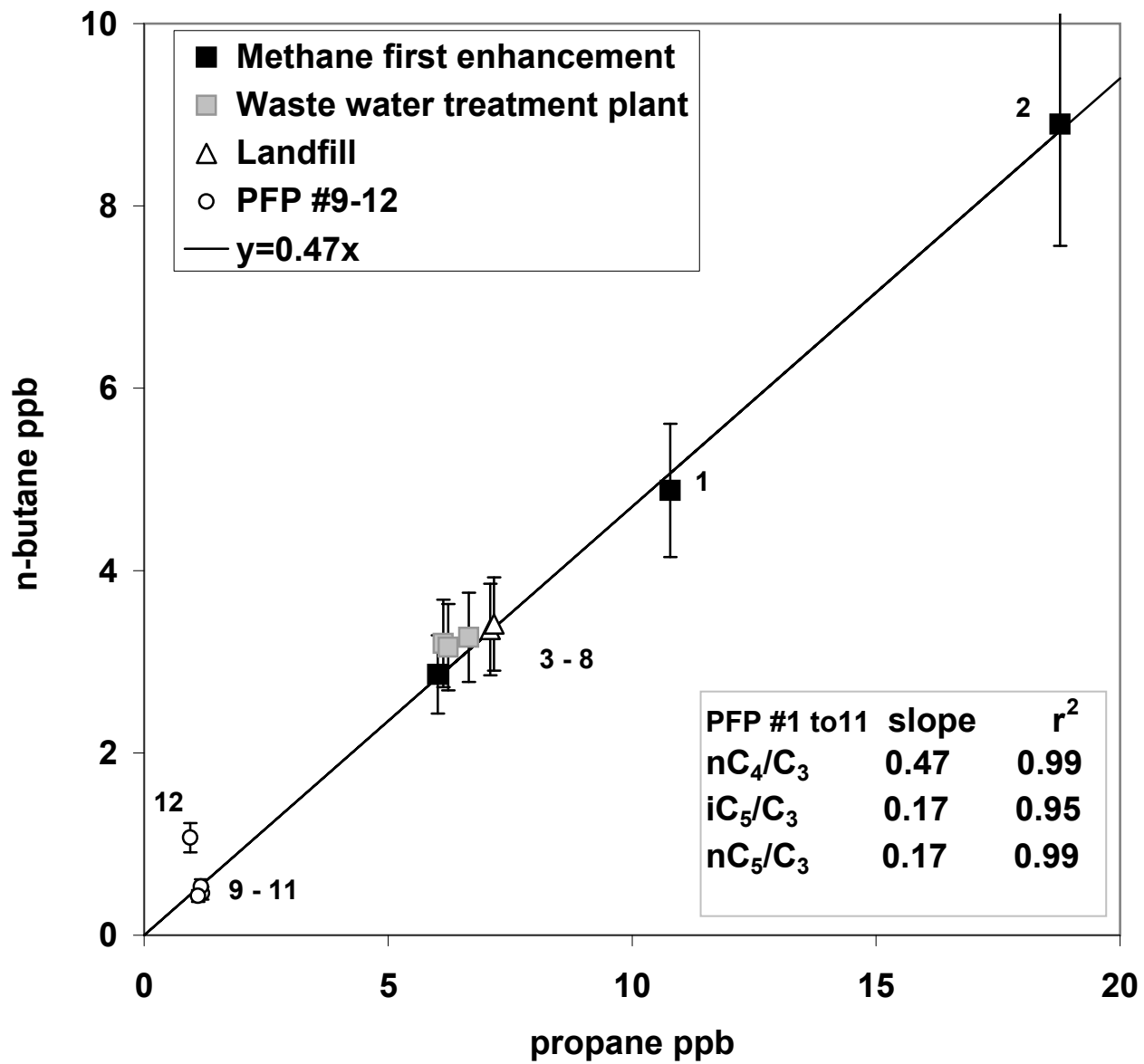


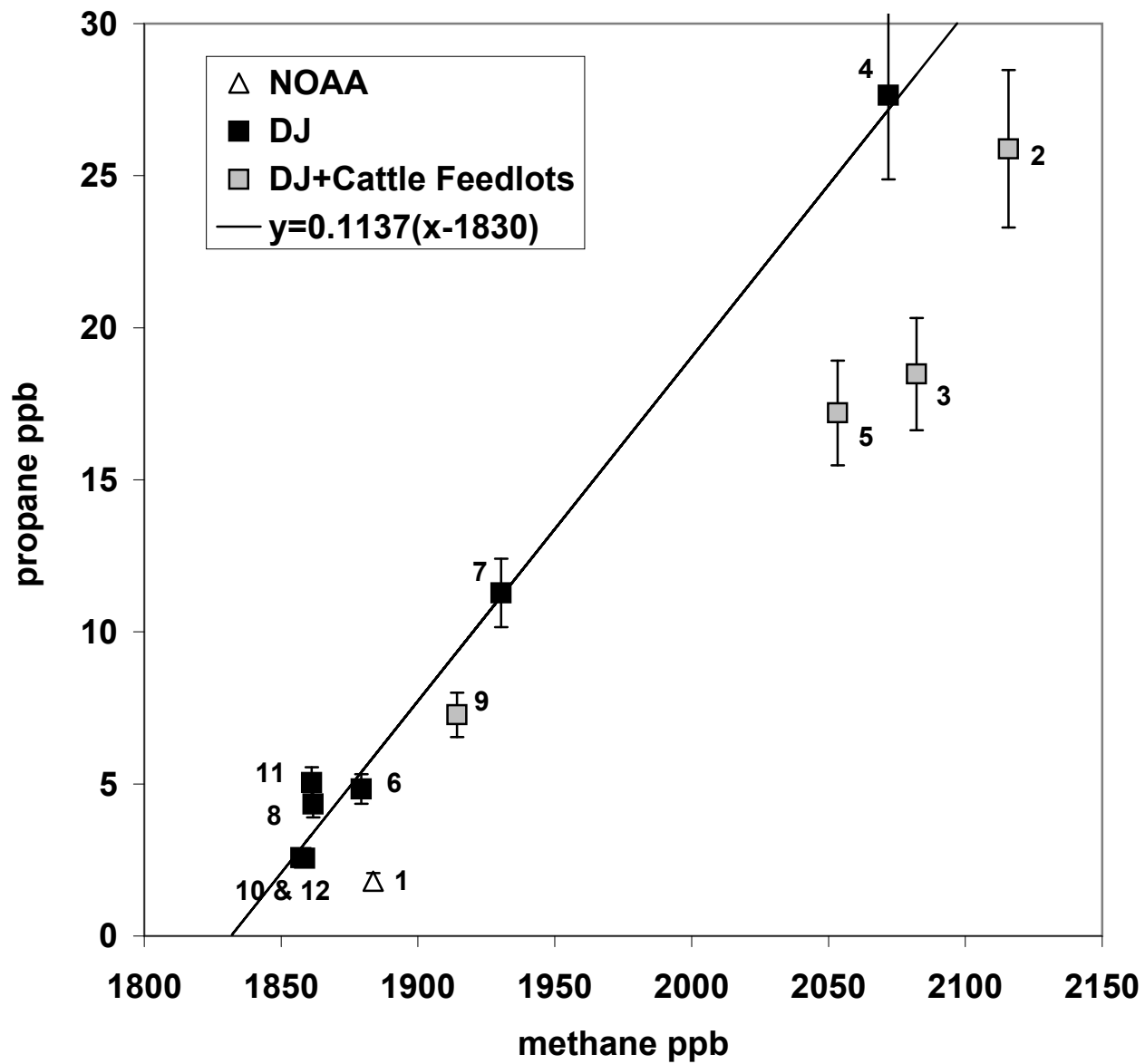


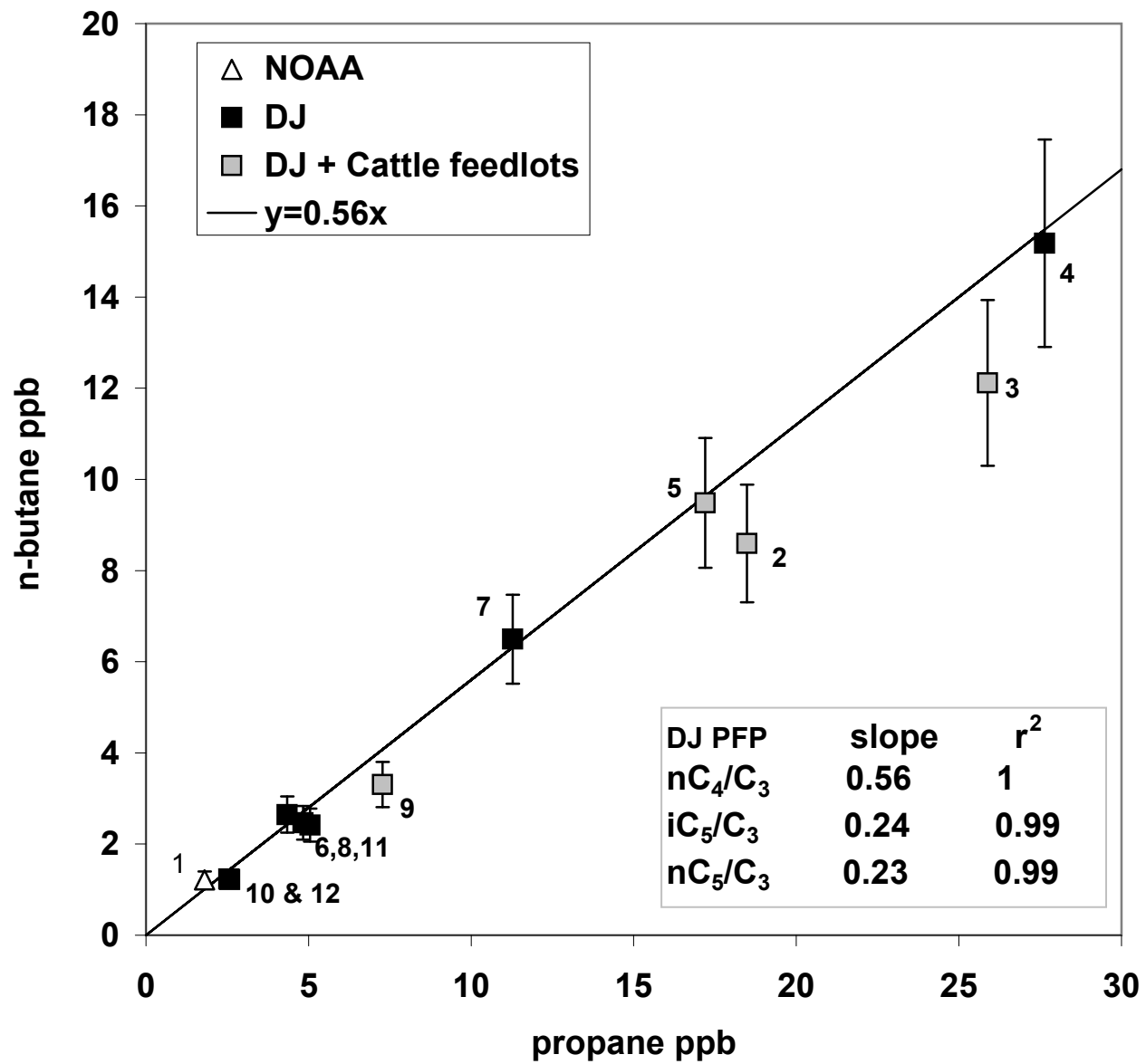


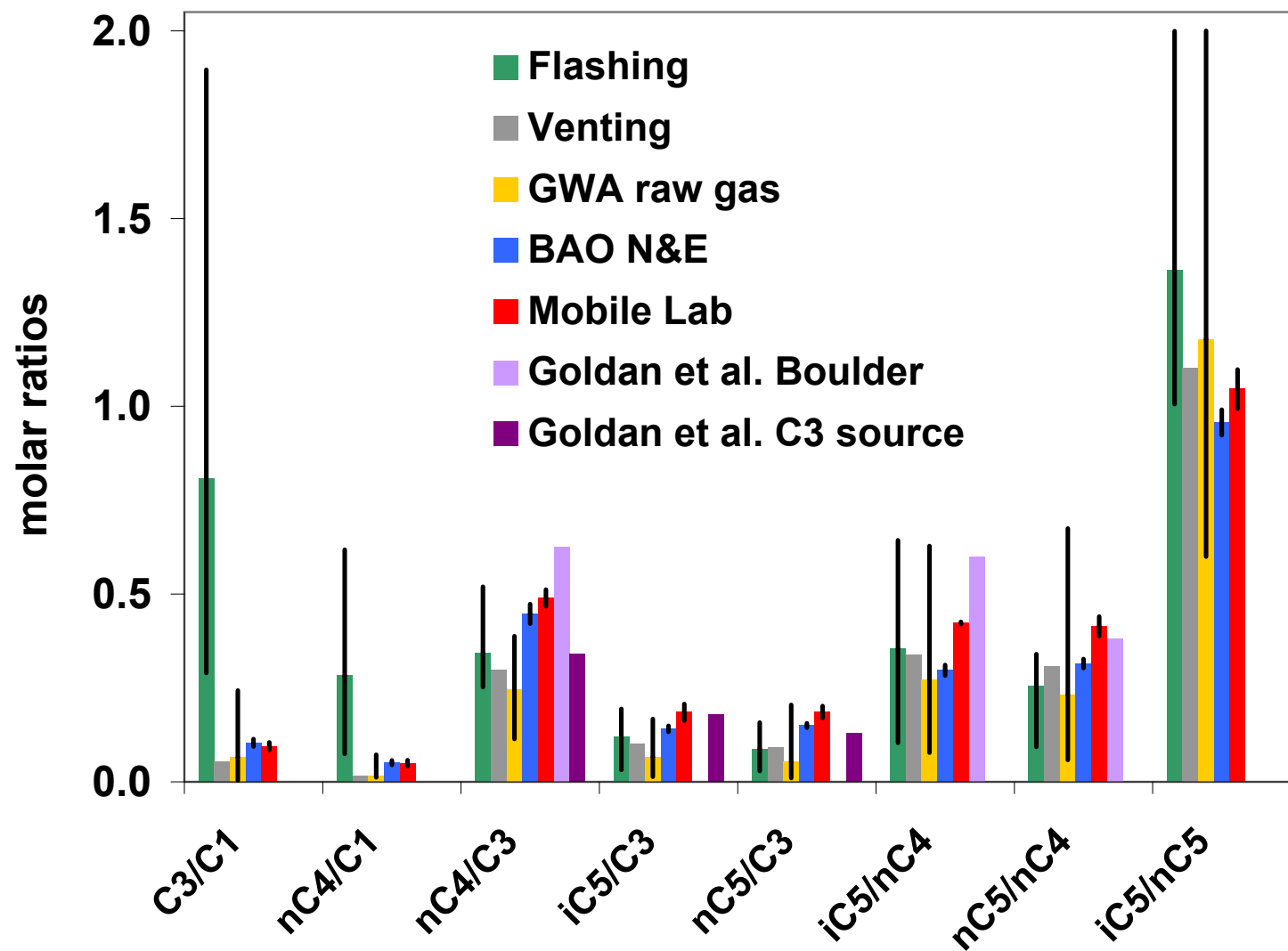




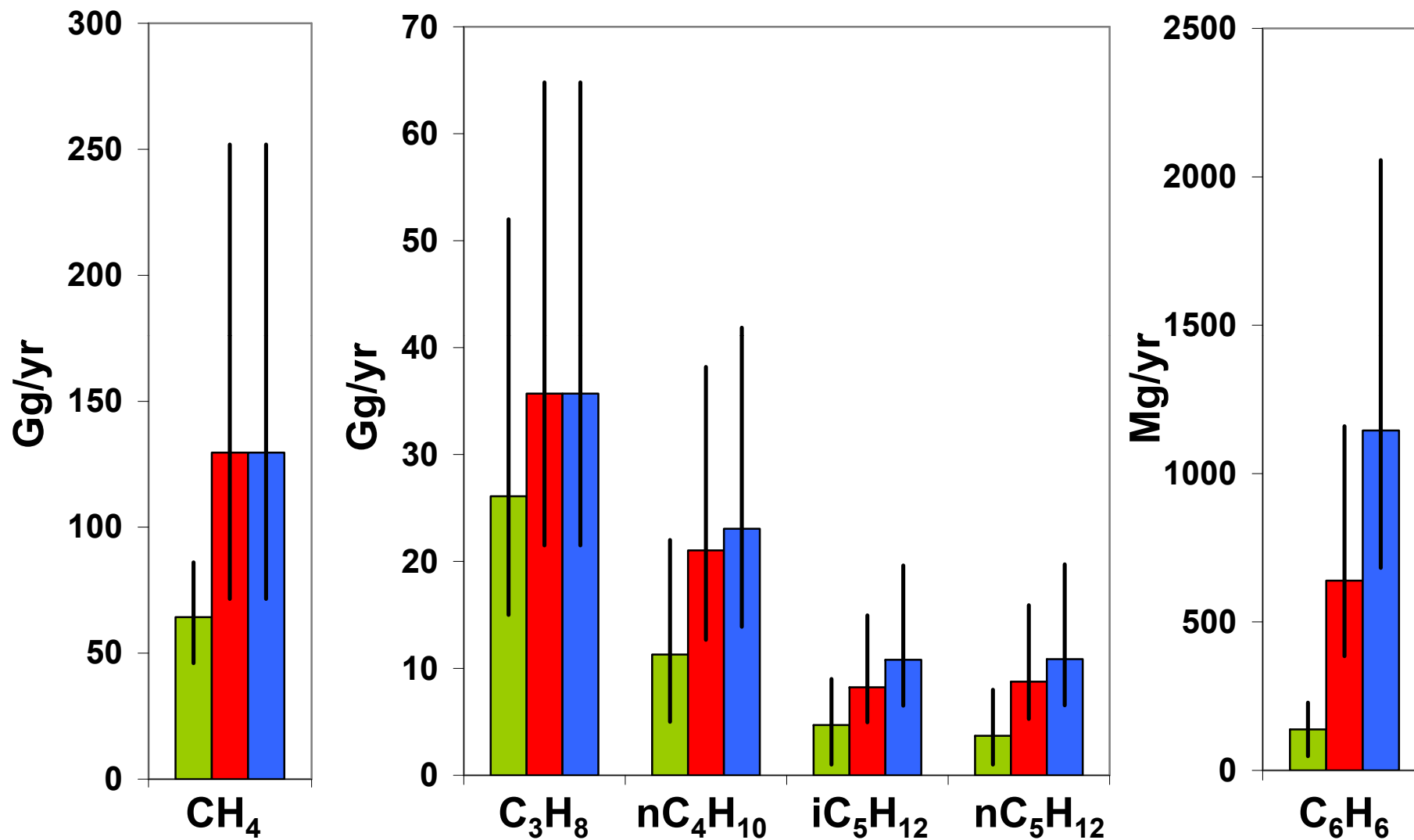








■ Bottom-up ■ BAO- Top-Down ■ Mobile Lab-Top-Down



## Supplementary Tables

Table 1S: Methane source estimates in Colorado (Gg CH<sub>4</sub> /yr, for 2005)

Table 2S: Natural gas and crude oil production in Weld County, Colorado, and the US for 2005 and 2008 (Bcf=Billion cubic feet)

Table 3S: Total VOC and benzene source estimates for Weld County in different bottom-up inventories. Source categories may not sum to total due to rounding.

Sources: WRAP for year 2006 [Bar Ilan et al., 2008a], CDPHE for 2008 [CDPHE, personal communication], NEI 2005 [EPA, 2008], NEI 2008 [EPA, 2011b]

Table 4S: Inventory and measurement derived molar ratios for the various data sets plotted on Figure 9. Flashing emissions composition is based on EPA TANK model runs for 16 condensate tanks located in the DJB and sampled in 2002 [CDPHE, personal communication 2010]. Venting emissions composition is based on an average raw gas weight composition profile provided by Bar-Ilan et al. [2008a] and derived private data from several natural gas producing companies in the DJB. To get a range of distribution for vented emissions, we use the molar composition provided by COGCC for raw gas samples collected at 77 wells in the DJB in December 2006. The BAO NE summer data and Mobile Lab data are the same as in Table 3. The Goldan et al. data for samples collected west of Boulder in February 1991 are based on Goldan et al. [1995] Table 1 and Figure 5.

## Supplementary Figures

Figure 1S: Time series of the Boulder Atmospheric Observatory flask data (collected between 17 and 21 UTC).

Figure 2S: Denver - Northern Front Range NAA VOC emissions inventories for oil and gas exploration, production and processing operations, developed by Bar-Ilan et al. [2008a,b]. The 2006 inventory is based on reported emissions for large condensate tanks and other permitted source categories identified with a (\*) in the legend. Other source estimates are based on activity data and emissions factors. The 2010 ?projection? inventory was extrapolated based on oil and gas production trends, the 2006 emissions data, and federal and state regulations for emissions control of permitted sources that were ?on the book as of early 2008?. We distinguish three types of emissions based on distinct VOC speciation profiles used in the WRAP inventory: (1) flashing emissions from small and large condensate tanks; (2) venting emissions associated with leaks of raw natural gas at the well site or in the gathering network of pipelines; and (3) other emissions such as compressor engines (3% of total source), truck loading of condensate (1%), heaters, drill rigs, workover rigs, exempt engines, and spills which have different VOC emissions profiles.

Figure 3S: PFP samples collected during the mobile survey on July 14, 2008. The size of the symbols indicates the mixing ratio of PFP methane (red circles) and propane (green circles). The labels indicate the PFP

sample number. NGP Plant = natural gas processing plant, WWT = Lafayette wastewater treatment plant.

Figure 4S: Molar composition of the venting (grey) and flashing (green) emissions data used to construct the bottom-up VOC emissions inventory for the DJB (average venting profile shared by Bar-Ilan et al. [2008a], flashing emissions profile based on EPA TANK runs for 16 condensate tanks in the DJB [CDPHE, personal communication]). For flashing emissions we show the average (green bar) and the minimum and maximum (error bars) molar fractions for all species. Also shown are the average (yellow bars) and the minimum and maximum molar fractions (error bars) of the various alkanes derived from the COGCC raw gas composition data for 77 wells in the Greater Wattenberg Area (GWA) (no aromatics data for this data set).

Figure 5S: Flow diagram of the calculation of speciated bottom-up emission estimates.

Figure 6S: Bottom-up flashing and venting emission estimates for Weld County in 2008. The colored bars indicate the mean emission estimates while the error bars indicate the minimum and maximum estimates. The WRAP inventory for the DJB used only one vented gas profile and therefore the corresponding Venting-WRAP emission estimates do not have error bars.

Table 1S: Methane source estimates in Colorado (Gg CH<sub>4</sub> /yr, for 2005)

Source: Strait et al., 2007

Natural gas systems	238
Coal mining	233
Enteric fermentation	143
Landfills	71
Manure management	48
Waste water treatment plants	24
Petroleum systems	10
Colorado total	767



**Table 2S: Natural gas and crude oil production in Weld County, Colorado, and the US for 2005 and 2008 (Bcf=Billion cubic feet)**

Source: COGCC (Weld County) and EIA (Colorado and US)

<b>Year</b>	<b>2005</b>			<b>2008</b>		
<b>Gross withdrawal/production</b>	Natural gas <i>Bcf/yr</i>	Crude oil <i>Million barrels/yr</i>	Lease condensate <i>Million barrels/yr</i>	Natural gas <i>Bcf/yr</i>	Crude oil <i>Million barrels/yr</i>	Lease condensate <i>Million barrels/yr</i>
<b>Weld County</b> <b>(% of Colorado)</b>	188.5 (16.5%)	11.7 (51.3%)	na	202.1 (15.3%)	17.3 (71.8%)	na
<b>DNFR NAA</b>	201.1	12.6	na	214.1	18.5	na
<b>Colorado</b>	1144	22.8	5	1403	24.1	7
<b>USA</b>	23457	1890.1	174	25636	1811.8	173

**Table 3S: Total VOC and benzene source estimates for Weld County in different bottom-up inventories.** Source categories may not sum to total due to rounding.

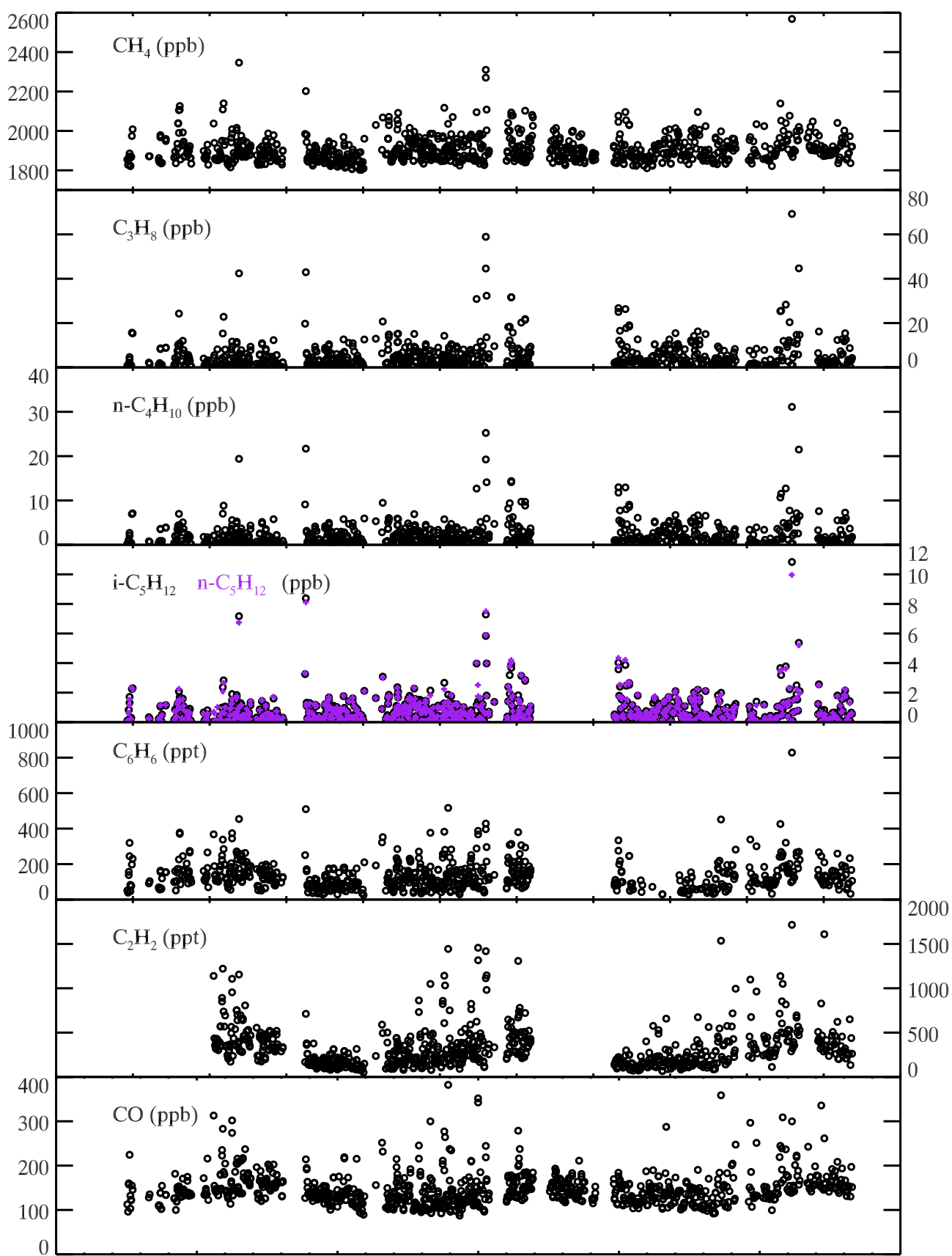
Sources: WRAP for year 2006 [Bar Ilan et al., 2008a], CDPHE for 2008 [CDPHE, personal communication], NEI 2005 [EPA, 2008], NEI 2008 [EPA, 2011b]

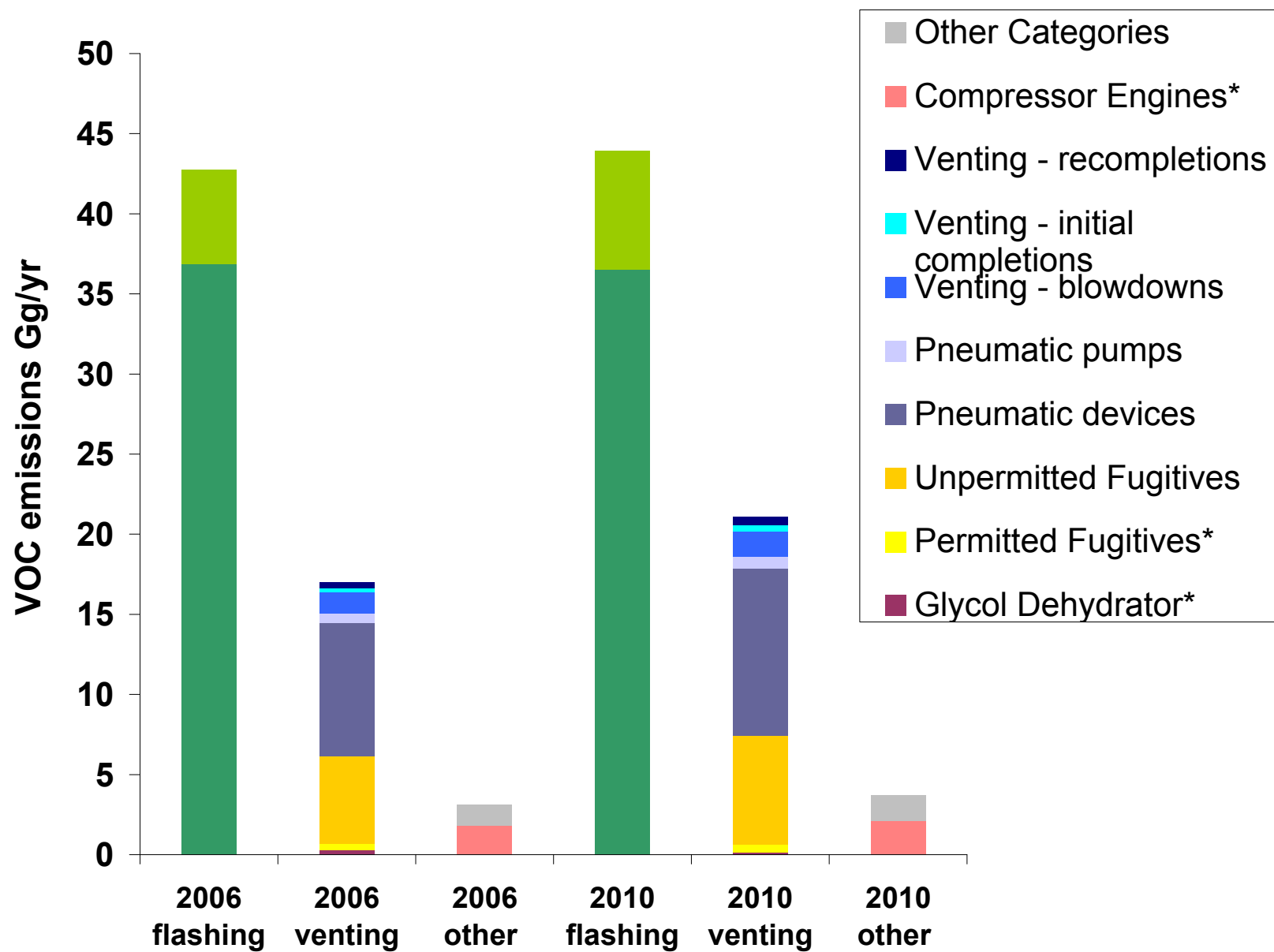
Species		Total VOC				Benzene		
Year		2006	2008	2008	2005	2008	2008	2005
Source		WRAP	CDPHE	NEI	NEI	CDPHE	NEI	NEI
unit		Gg/yr				Mg/yr		
On-Road			2533	2968	3532	95.4	121.4	160.1
Non-road + rail + aircraft			1596	1313	1626	44.2	36.0	45.9
Wood burning			232	-	187	8.8	-	5.7
Solvent utilization			201	1914	2819	-	-	31.6
Surface coating			1235	-	421	-	-	0.8
Oil and gas area		21145*	-	-	-	-	-	-
Oil and gas point	Large Condensate tanks	34790	17811	18163	-	21.3	21.5	1120.0
	Glycol dehydrators	218	220	-	-	15.1	-	47.6
	Gas sweetening	11	11	-	-	6.6	-	7.8
	Internal Combustion Engines	1996	1692	-	-	16.0	-	-
	Other	304	844	646	-	2.8	23.1	1.6
	<b>Total</b>	<b>37015</b>	<b>20628</b>	<b>18810</b>	<b>-</b>	<b>61.8</b>	<b>44.6</b>	<b>1177.0</b>
Gas stations/Gasoline bulk terminals			697	965	1270	8.0	11.1	11.8
Forest and prescribed fires			110		207	8.3	-	2.4
Fossil Fuel combustion Point (non O&G)			196	1880	651	0.5	16.5	3.9
Other point			547	680	335	1.0	15.6	12.3
Other area			1078		605	2.3		4.6
Total for available source categories		58160	29051	28530	11654	230.5	245.2	1454

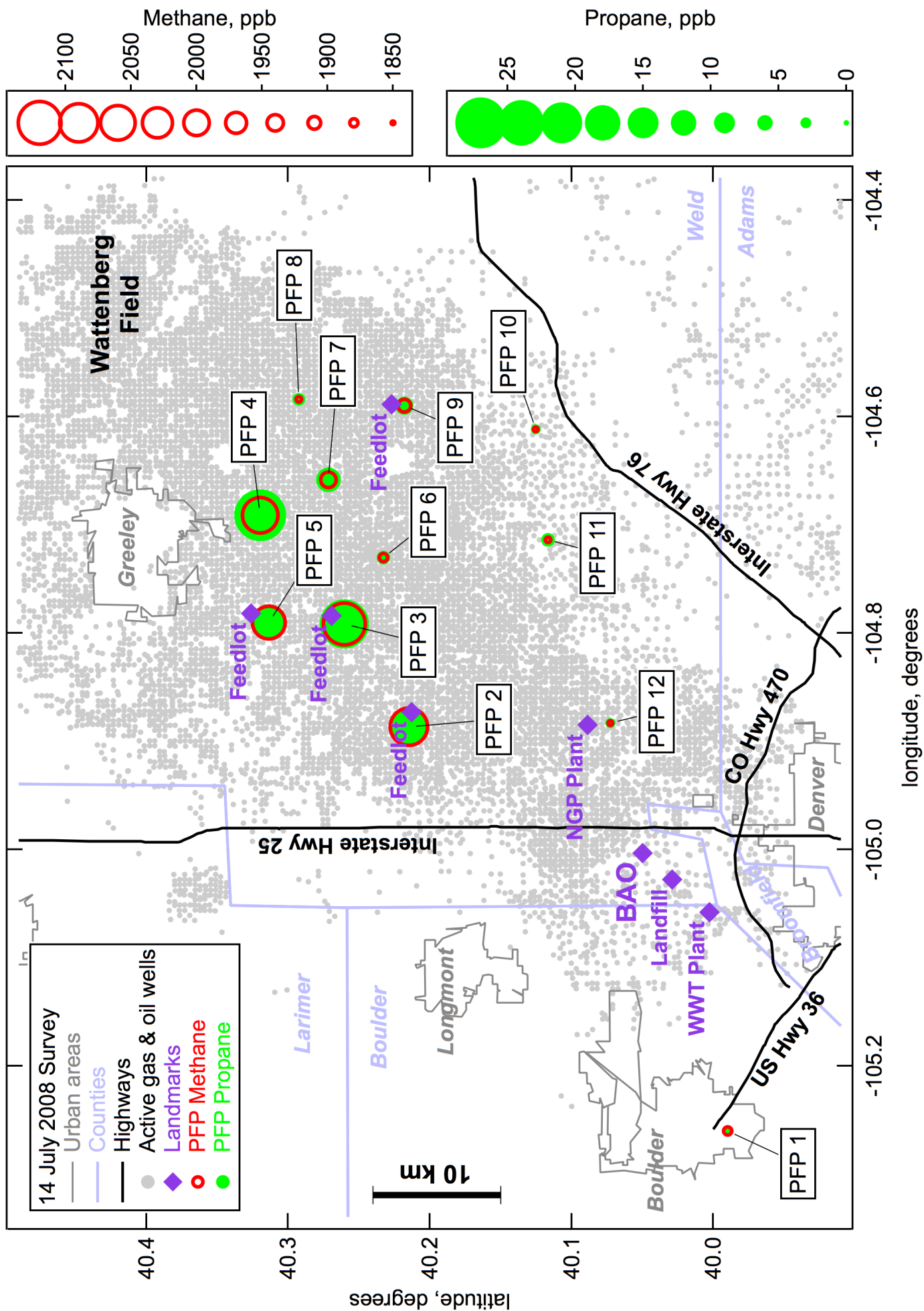
\*Source categories included are: Pneumatic devices and pumps, small condensate tanks, fugitive emissions, heaters, process heaters, venting, truck loading, spills, NG production: flares, flanges and connections, and others.

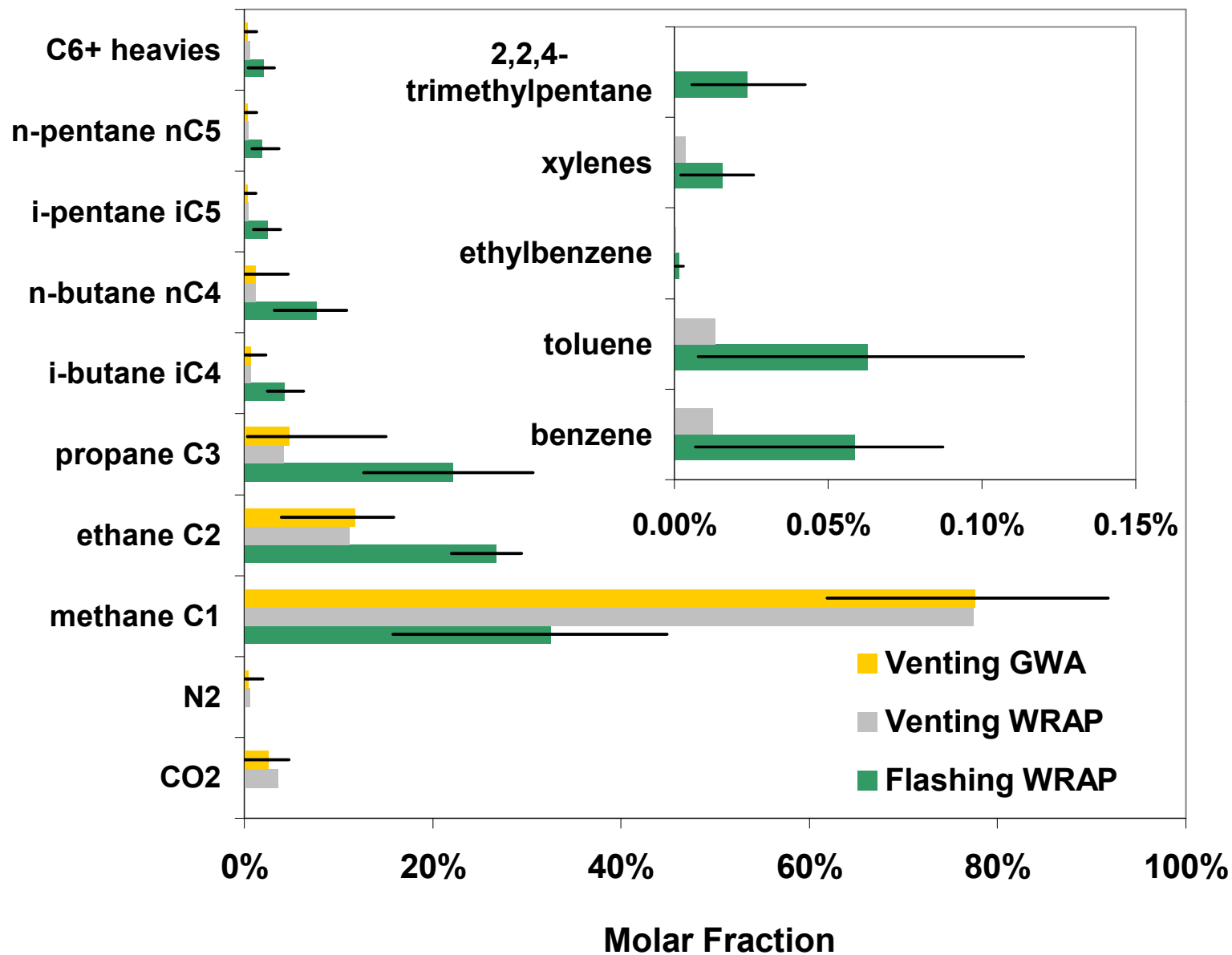
**Table 4S:** Inventory and measurement derived molar ratios for the various data sets plotted on Figure 9. Flashing emissions composition is based on EPA TANK model runs for 16 condensate tanks located in the DJB and sampled in 2002 [CDPHE, personal communication 2010]. Venting emissions composition is based on an average raw gas weight composition profile provided by Bar-Ilan et al. [2008a] and derived private data from several natural gas producing companies in the DJB. To get a range of distribution for vented emissions, we use the molar composition provided by COGCC for raw gas samples collected at 77 wells in the DJB in December 2006. The BAO NE summer data and Mobile Lab data are the same as in Table 3. The Goldan et al. data for samples collected west of Boulder in February 1991 are based on Goldan et al. [1995] Table 1 and Figure 5.

Data Set		$C_3/C_1$	$nC_4/C_1$	$nC_4/C_3$	$iC_5/C_3$	$nC_5/C_3$	$iC_5/nC_4$	$nC_5/nC_4$	$iC_5/nC_5$
<b>WRAP Flashing emissions</b>	Median	0.807	0.283	0.343	0.119	0.088	0.354	0.255	1.362
	Mean	0.654	0.271	0.339	0.123	0.088	0.354	0.262	1.271
	Min	0.290	0.074	0.252	0.032	0.029	0.104	0.093	1.006
	Max	1.896	0.618	0.519	0.194	0.158	0.643	0.340	1.999
<b>WRAP Venting emissions</b>		0.053	0.016	0.298	0.100	0.091	0.338	0.307	1.101
<b>GWA raw gas</b>	Median	0.065	0.015	0.245	0.066	0.054	0.270	0.231	1.179
	Mean	0.064	0.017	0.253	0.071	0.061	0.280	0.239	1.226
	Min	0.004	0.015	0.114	0.014	0.010	0.078	0.058	0.600
	Max	0.243	0.072	0.388	0.167	0.205	0.628	0.674	2.000
<b>Bottom-up VOC inventory: WRAP Flashing + GWA Venting (mean profiles)</b>		0.154	0.049	0.316	0.099	0.078	0.313	0.245	1.274
<b>BAO NE -summer</b>		0.104	0.051	0.447	0.141	0.150	0.297	0.315	0.957
<b>Mobile Lab</b>		0.095	0.050	0.510	0.185	0.186	0.423	0.414	1.046
<b>Goldan et al.-all data</b>		-	-	0.340	0.180	0.130	-	-	-
<b>Goldan et al. C<sub>3</sub> source</b>		-	-	0.625	-	-	0.600	0.380	-









## FLASHING

Total VOC emitted in WRAP  
2008: 41.3 Gg

2008=  
average of  
2006 and  
2010  
WRAP  
estimates

## VENTING

Total VOC emitted in WRAP  
2008: 17.3 Gg

Condensate  
flash  
emission  
weight ratios  
calculated for  
16 different  
DJB tanks  
used by  
WRAP

*Set of 16 speciated  
emissions*

***Average, minimum and  
maximum bottom-up F+V  
emission estimates for each  
species***

Mean raw  
natural gas  
composition  
used by  
WRAP

Total volume of gas  
vented

77 GWA raw  
natural gas  
composition  
speciation  
profiles

*Set of 77 speciated  
emissions*

