

25 **Abstract**

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

44

45 **1) Introduction**

46

47 Since 2004, the National Oceanic and Atmospheric Administration Earth System
48 Research Laboratory (NOAA ESRL) has increased its measurement network density over
49 North America, with continuous carbon dioxide (CO₂) and carbon monoxide (CO)
50 measurements and daily collection of discrete air samples at a network of tall towers
51 [Andrews et al., in preparation] and bi-weekly discrete air sampling along vertical aircraft
52 profiles [Sweeney et al., in preparation]. Close to 60 chemical species or isotopes are
53 measured in the discrete air samples, including long-lived greenhouse gases (GHGs) such
54 as CO₂, methane (CH₄), nitrous oxide (N₂O), and sulfur hexafluoride (SF₆), tropospheric
55 ozone precursors such as CO and several volatile organic compounds (VOCs), and
56 stratospheric-ozone-depleting substances. The NOAA multi-species regional data set
57 provides unique information on how important atmospheric trace gases vary in space and
58 time over the continent, and it can be used to quantify how different processes contribute
59 to GHG burdens and/or affect regional air quality.

60 In this study we focus our analysis on a very strong alkane atmospheric signature
61 observed downwind of the Denver-Julesburg Fossil Fuel Basin (DJB) in the Colorado
62 Northern Front Range (Figures 1 and 1S). In 2008, the DJB was home to over 20,000
63 active natural gas and condensate wells. Over 90% of the production in 2008 came from
64 tight gas formations.

65 A few recent studies have looked at the impact of oil and gas operations on air
66 composition at the local and regional scales in North America. Katzenstein et al. [2003]
67 reported results of two intensive surface air discrete sampling efforts over the Anadarko

68 Fossil Fuel Basin in the southwestern United States in 2002. Their analysis revealed
69 substantial regional atmospheric CH₄ and non-methane hydrocarbon (NMHC) pollution
70 over parts of Texas, Oklahoma, and Kansas, which they attributed to emissions from the
71 oil and gas industry operations. More recently, Schnell et al. [2009] observed very high
72 wintertime ozone levels in the vicinity of the Jonah-Pinedale Anticline natural gas field in
73 western Wyoming. Ryerson et al. [2003], Wert et al. [2003], de Gouw et al. [2009] and
74 Mellqvist et al. [2009] reported elevated emissions of alkenes from petrochemical plants
75 and refineries in the Houston area and studied their contribution to ozone formation.
76 Simpson et al. [2010] present an extensive analysis of atmospheric mixing ratios for a
77 long list of trace gases over oil sands mining operations in Alberta during one flight of
78 the 2008 Arctic Research of the Composition of the Troposphere from Aircraft and
79 Satellites campaign. Our study distinguishes itself from previous ones by the fact that it
80 relies substantially on the analysis of daily air samples collected at a single tall-tower
81 monitoring site between August 2007 and April 2010.

82 Colorado has a long history of fossil fuel extraction [Scamehorn, 2002]. Colorado
83 natural gas production has been increasing since the 1980s, and its share of national
84 production jumped from 3% in 2000 to 5.4% in 2008. 1.3% of the nationally produced oil
85 in 2008 also came from Colorado, primarily from the DJB in northeastern Colorado and
86 from the Piceance Basin in western Colorado. As of 2004, Colorado also contained 43
87 natural gas processing plants, representing 3.5% of the conterminous US processing
88 capacity [EIA, 2006], and two oil refineries, located in Commerce City, in Adams
89 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 CH₄ 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 CH₄
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 CH₄ emission

113 estimates from Strait et al. [2007], rough estimates for the 2005 CH₄ source from natural
114 gas production and processing operations and from natural gas condensate/oil production
115 in Weld County are 19.6 Gg and 4.8 Gg, respectively. It is important to stress here that
116 there are large uncertainties associated with these inventory-derived estimates.

117 Other important sources of CH₄ in the state include large open-air cattle feedlots,
118 landfills, wastewater treatment facilities, forest fires, and agriculture waste burning,
119 which are all difficult to quantify. 2005 state total CH₄ emissions from enteric
120 fermentation and manure management were estimated at 143 and 48 Gg/yr, respectively
121 [Strait et al., 2007]; this combined source is of comparable magnitude to the estimate
122 from natural gas systems. On-road transportation is not a substantial source of methane
123 [Nam et al., 2004].

124 In 2006, forty percent of the DNFR NAA's total anthropogenic VOC emissions
125 were estimated to be due to oil and gas operations [CDPHE, 2008b]. Over the past few
126 years, the State of Colorado has adopted more stringent VOC emission controls for oil
127 and gas exploration and processing activities. In 2007, the Independent Petroleum
128 Association of Mountain States (IPAMS, now Western Energy Alliance), in conjunction
129 with the Western Regional Air Partnership (WRAP), funded a working group to build a
130 state-of-the-knowledge process-based inventory of total VOC and NO_x sources involved
131 in oil and gas exploration, production and gathering activities for the western United
132 State's fossil fuel basins, hereafter referred to as the WRAP Phase III effort
133 (<http://www.wrapair.org/forums/ogwg/index.html>). Most of the oil and gas production in
134 the DJB is concentrated in Weld County. Large and small condensate storage tanks in the
135 County are estimated to be the largest VOC fossil fuel production source category (59%

136 and 9% respectively), followed by pneumatic devices (valve controllers) and unpermitted
137 fugitives emissions (13% and 9% respectively). A detailed breakdown of the WRAP oil
138 and gas source contributions is shown in Figure 2S for 2006 emissions and projected
139 2010 emissions [Bar-Ilan et al., 2008a,b]). The EPA NEI 2005 for Weld County, used
140 until recently by most air quality modelers, did not include VOC sources from oil and
141 natural gas operations (Table 3S).

142 Benzene (C_6H_6) is a known human carcinogen and it is one of the 188 hazardous
143 air pollutants (HAPs) tracked by the EPA National Air Toxics Assessment (NATA).
144 Benzene, like VOCs and CH_4 , can be released at many different stages of oil and gas
145 production and processing. Natural gas itself can contain varying amounts of aromatic
146 hydrocarbons, including C_6H_6 [EPA, 1998]. Natural gas associated with oil production
147 (such sources are located in several places around the DJB) usually has higher C_6H_6
148 levels [Burns et al., 1999] than non-associated natural gas. Glycol dehydrators used at
149 wells and processing facilities to remove water from pumped natural gas can vent large
150 amounts of C_6H_6 to the atmosphere when the glycol undergoes regeneration [EPA, 1998].
151 Condensate tanks, venting and flaring at the well-heads, compressors, processing plants,
152 and engine exhaust are also known sources of C_6H_6 [EPA, 1998]. C_6H_6 can also be
153 present in the liquids used for fracturing wells [EPA, 2004].

154 In this paper, we focus on describing and interpreting the measured variability in
155 CH_4 and C_{3-5} alkanes observed in the Colorado Northern Front Range. We use data from
156 daily air samples collected at a NOAA tall tower located in Weld County as well as
157 continuous CH_4 observations and discrete targeted samples from an intensive mobile
158 sampling campaign in the Colorado Northern Front Range. These atmospheric

159 measurements are then used together with other emissions data sets to provide an
160 independent view of methane and non-methane hydrocarbon emissions inventory results.

161 The paper is organized as follows. Section 2 describes the study design and
162 sampling methods. Section 3 presents results from the tall tower and the Mobile Lab
163 surveys, in particular the strong correlation among the various alkanes measured. Based
164 on the multi-species analysis in the discrete air samples, we were able to identify two
165 major sources of C_6H_6 in Weld County. In section 4.1 we discuss the results and in
166 section 4.2 we compare the observed ambient molar ratios with other relevant data sets,
167 including raw natural gas composition data from 77 gas wells in the DJB. The last
168 discussion section, 4.3, is an attempt to shed new light on methane and VOC emission
169 estimates from oil and gas operations in Weld County. We first describe how we derived
170 speciated bottom-up emission estimates based on the WRAP Phase III total VOC
171 emission inventories for counties in the DJB. We then used 1) an average ambient
172 propane-to-methane molar ratio, 2) a set of bottom-up estimates of propane and methane
173 flashing emissions in Weld County and 3) three different estimates of the propane-to-
174 methane molar ratio for the raw gas leaks to build top-down methane and propane
175 emission scenarios for venting sources in the county. We also scaled the top-down
176 propane (C_3H_8) estimates with the observed ambient alkane ratios to calculate top-down
177 emission estimates for n-butane ($n-C_4H_{10}$), i- and n-pentane ($i-C_5H_{12}$, $n-C_5H_{12}$), and
178 benzene. We summarize our main conclusions in section 5.

179

180 **2) The Front Range Emissions Study: Sampling Strategy,**
181 **Instrumentation, and Sample Analysis**

182 **2.1. Overall Experimental Design**

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

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

197

198 **2.2. BAO and other NOAA cooperative Tall Towers**

199 The BAO tall tower has been used as a research facility of boundary layer
200 dynamics since the 1970s [Kaimal and Gaynor, 1983]. The BAO tower was instrumented
201 by the NOAA ESRL Global Monitoring Division (GMD) in Boulder in April 2007, with
202 sampling by a quasi-continuous CO₂ non-dispersive infrared sensor and a CO Gas Filter
203 Correlation instrument, both oscillating between three intake levels (22, 100 and 300 m
204 above ground level) [Andrews et al., in preparation]. Two continuous ozone UV-

205 absorption instruments have also been deployed to monitor ozone at the surface and at the
206 300-m level.

207 The tower is equipped to collect discrete air samples from the 300-m level using a
208 programmable compressor package (PCP) and a programmable flasks package (PFP)
209 described later in section 2.4. Since August 2007 one or two air samples have been taken
210 approximately daily in glass flasks using PFPs and a PCP. The air samples are brought
211 back to GMD for analysis on three different systems to measure a series of compounds,
212 including methane (CH_4 , also referred to as C_1), CO, propane (C_3H_8 , also referred to as
213 C_3), n-butane ($\text{n-C}_4\text{H}_{10}$, nC_4), isopentane ($\text{i-C}_5\text{H}_{12}$, iC_5), n-pentane ($\text{n-C}_5\text{H}_{12}$, nC_5),
214 acetylene (C_2H_2), benzene, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons
215 (HCFCs) and hydrofluorocarbons (HFCs). Ethane and i-butane were not measured.

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

223 In 2008, NOAA and its collaborators were operating a regional air sampling
224 network of eight towers and 18 aircraft profiling sites located across the continental US
225 employing in-situ measurements (most towers) and flask sampling protocols (towers and
226 aircraft sites) that were similar to those used at BAO. Median mixing ratios for several
227 alkanes, benzene, acetylene, and carbon monoxide from BAO and a subset of five other

228 NOAA towers and from one aircraft site are presented in the Results (Section 3). Table 1
229 provides the three letter codes used for each sampling site, their locations and sampling
230 heights. STR is located in San Francisco. WGC is located 34 km south of downtown
231 Sacramento in California's Central Valley where agriculture is the main economic sector.
232 Irrigated crop fields and feedlots contribute to the higher CH₄ observed at WGC. The
233 LEF tower in northern Wisconsin is in the middle of the Chequamegon National Forest
234 which is a mix of temperate/boreal forest and lowlands/wetlands [Werner et al., 2003].
235 Air samples from NWF (surface elevation 3050m), in the Colorado Rocky Mountains,
236 mostly reflect relatively unpolluted air from the free troposphere. The 457m tall Texas
237 tower (WKT) is located between Dallas/Fort Worth and Austin. It often samples air
238 masses from the surrounding metropolitan areas. In summer especially, it also detects air
239 masses with cleaner background levels arriving from the Gulf of Mexico. The SGP
240 NOAA aircraft sampling site [Sweeney et al., in preparation;
241 <http://www.esrl.noaa.gov/gmd/ccgg/aircraft/>] in northern Oklahoma is also used in the
242 comparison study. At each aircraft site, twelve discrete air samples are collected at
243 specified altitudes on a weekly or biweekly basis. Oklahoma is the fourth largest state for
244 natural gas production in the USA [EIA, 2008] and one would expect to observe
245 signatures of oil and gas drilling operations at both SGP and BAO. Additional
246 information on the tower and aircraft programs is available at
247 <http://www.esrl.noaa.gov/gmd/ccgg/>. Median summer mixing ratios for several alkanes,
248 C₂H₂, C₆H₆ and CO are presented in the Results section.

249

250

2.3. Mobile Sampling

251 Two mobile sampling strategies were employed during this study. The first, the
252 Mobile Lab, consisted of a fast response CO₂ and CH₄ analyzer (Picarro, Inc.), a CO gas-
253 filter correlation instrument from Thermo Environmental, Inc., an O₃ UV-absorption
254 analyzer from 2B Technologies and a Global Positioning System (GPS) unit. All were
255 installed onboard a vehicle. A set of 3 parallel inlets attached to a rack on top of the
256 vehicle brought in outside air from a few meters above the ground to the instruments.
257 Another simpler sampling strategy was to drive around and collect flask samples at
258 predetermined locations in the Front Range region. A summary of the on-road surveys is
259 given in Table 2.

260 The Mobile Lab's Picarro EnviroSense CO₂/CH₄/H₂O analyzer (model G1301,
261 unit CFADS09) employs Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-
262 CRDS), a time-based measurement utilizing a near-infrared laser to measure a spectral
263 signature of the molecule. CO₂, CH₄, and water vapor were measured at a 5-second
264 sampling rate (0.2 Hz), with a standard deviation of 0.09 ppm in CO₂ and 0.7 ppb for
265 CH₄. The sample was not dried prior to analysis, and the CO₂ and CH₄ mole fractions
266 were corrected for water vapor after the experiment based on laboratory tests. For water
267 mole fractions between 1% and 2.5%, the relative magnitude of the CH₄ correction was
268 quasi-linear, with values between 1 and 2.6%. CO₂ and CH₄ mole fractions were assigned
269 against a reference gas tied to the relevant World Meteorological Organization (WMO)
270 calibration scale. Total measurement uncertainties were 0.1 ppm for CO₂ and 2 ppb for
271 CH₄ [Sweeney et al., in preparation]. The CO and ozone data from the Mobile Lab are
272 not discussed here. GPS data were also collected in the Mobile Lab at 1 Hz, to allow data
273 from the continuous analyzers to be merged with the location of the vehicle.

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

279 Each Mobile Lab drive lasted from four to six hours, after a ~30 min warm-up on
280 the NOAA campus for the continuous analyzer before switching to battery mode. The
281 first two Mobile Lab drives, which did not include discrete air sampling, were surveys
282 around Denver (July 9) and between Boulder and Greeley (July 15). The last two drives
283 with the Mobile Lab (July 25 and 31) combined in-situ measurements with discrete flask
284 sampling to target emissions from specific sources: the quasi-real-time display of the data
285 from the continuous CO₂/CH₄ analyzer was used to collect targeted flask samples at
286 strong CH₄ point sources in the vicinity of BAO. Discrete air samples were always
287 collected upwind of the surveying vehicle and when possible away from major road
288 traffic.

289

290 **2.4. Chemical Analyses of Flask Samples**

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

297 were leak-checked then flushed and pressurized to ~ 1.4 atm with synthetic dry zero-air
298 containing approximately 330 ppm of CO_2 and no detectable CH_4 . During sampling, the
299 manifold and flasks were flushed sequentially, at $\sim 5 \text{ L min}^{-1}$ for about 1 min and 10 L
300 min^{-1} for about 3 minutes respectively, before the flasks were pressurized to 2.7 atm.
301 Upon returning to the NOAA lab, the PFP manifold was leak-checked and meta-data
302 recorded by the PFP during the flushing and sampling procedures were read to verify the
303 integrity of each air sample collected. In case of detected inadequate flushing or filling,
304 the affected air sample is not analyzed.

305 Samples collected in flasks were analyzed for close to 60 compounds by NOAA
306 GMD (<http://www.esrl.noaa.gov/gmd/ccgg/aircraft/analysis.html>). In this paper, we focus
307 on eight species: 5 alkanes (CH_4 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $i\text{-C}_5\text{H}_{12}$, $n\text{-C}_5\text{H}_{12}$) as well as CO , C_2H_2
308 and C_6H_6 . CH_4 and CO in each flask were first quantified on one of two nearly identical
309 automated analytical systems (MAGICC 1 & 2). These systems consist of a custom-made
310 gas inlet system, gas-specific analyzers, and system-control software. Our gas inlet
311 systems use a series of stream selection valves to select an air sample or standard gas,
312 pass it through a trap for drying maintained at $\sim -80^\circ\text{C}$, and then to an analyzer.

313 CH_4 was measured by gas chromatography (GC) with flame ionization detection
314 (± 1.2 ppb = average repeatability determined as 1 s.d. of ~ 20 aliquots of natural air
315 measured from a cylinder) [Dlugokencky et al., 1994]. We use the following
316 abbreviations for measured mole fractions: ppm = $\mu\text{mol mol}^{-1}$, ppb = nmol mol^{-1} , and ppt
317 = pmol mol^{-1} . CO was measured directly by resonance fluorescence at $\sim 150 \text{ nm}$ (± 0.2
318 ppb) [Gerbig et al., 1999; Novelli et al., 1998]. All measurements are reported as dry air

319 mole fractions relative to internally consistent calibration scales maintained at NOAA
320 (<http://www.esrl.noaa.gov/gmd/ccl/scales.html>).

321 Gas chromatography/mass spectrometric (GC/MS) measurements were also
322 performed on ~200 mL aliquots taken from the flask samples and pre-concentrated with a
323 cryogenic trap at near liquid nitrogen temperatures [Montzka et al., 1993]. Analytes
324 desorbed at ~110°C were then separated by a temperature-programmed GC column
325 (combination 25 m x 0.25 mm DB5 and 30 m x 0.25 mm Gaspro), followed by detection
326 with mass spectrometry by monitoring compound-specific ion mass-to-charge ratios.
327 Flask sample responses were calibrated versus whole air working reference gases which,
328 in turn, are calibrated with respect to gravimetric primary standards (NOAA scales:
329 benzene on NOAA-2006 and all other hydrocarbons (besides CH₄) on NOAA-2008). We
330 used a provisional calibration for n-butane based on a diluted Scott Specialty Gas
331 standard. Total uncertainties for analyses from the GC/MS reported here are <5%
332 (accuracy) for all species except n-C₄H₁₀ and C₂H₂, for which the total uncertainty at the
333 time of this study was of the order of 15-20%. Measurement precision as repeatability is
334 generally less than 2% for compounds present at mixing ratios above 10 ppt.

335 To access the storage stability of the compounds of interest in the PFPs, we
336 conducted storage tests of typically 30 days duration, which is greater than the actual
337 storage time of the samples used in this study. Results for C₂H₂ and C₃H₈ show no
338 statistically significant enhancement or degradation with respect to our "control" (the
339 original test gas tank results) within our analytical uncertainty. For the remaining
340 species, enhancements or losses average less than 3% for the 30 day tests. More

341 information on the quality control of the flask analysis data is available at
342 <http://www.esrl.noaa.gov/gmd/ccgg/aircraft/qc.html>.

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

349

350 **3) Results**

351

352 **3.1 BAO tall tower: long-term sampling platform for regional** 353 **emissions**

354

355 **3.1.1 Comparing BAO with other sampling sites in the US**

356

357 Air samples collected at BAO tower have a distinct chemical signature (Figure 2),
358 showing enhanced levels of most alkanes (C_3H_8 , nC_4H_{10} , iC_5H_{12} and nC_5H_{12}) in
359 comparison to results from other NOAA cooperative tall towers (see summary of site
360 locations in Table 1 and data time series in Figure 1S). The midday summer time median
361 mixing ratios for C_3H_8 and $n-C_4H_{10}$ at BAO were at least 6 times higher than those
362 observed at most other tall tower sites. For $i-C_5H_{12}$ and $n-C_5H_{12}$, the summertime median
363 mixing ratios at BAO were at least 3 times higher than at the other tall towers.

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

370 Similarly to BAO, the northern Oklahoma aircraft site, SGP, exhibits high alkane
371 levels in the boundary layer and the highest methane summer median mixing ratio of all
372 sites shown in Figure 2 (1889 ppb at SGP vs. 1867 ppb at BAO). As for BAO, SGP is
373 located in an oil- and gas-producing region. Oklahoma, the fourth largest state in terms of
374 natural gas production in the US, has a much denser network of interstate and intrastate
375 natural gas pipelines compared to Colorado. Katzenstein et al. [2003] documented the
376 spatial extent of alkane plumes around the gas fields of the Anadarko Basin in Texas,
377 Oklahoma, and Kansas during two sampling intensives. The authors estimated that
378 methane emissions from the oil and gas industry in that entire region could be as high as
379 4-6 Tg CH₄/yr, which is 13-20% of the US total methane emission estimate for year 2005
380 reported in the latest EPA US GHG Inventory [EPA, 2011a].

381 Enhancements of CH₄ at BAO are not as striking in comparison to other sites.
382 CH₄ is a long-lived gas destroyed predominantly by its reaction with OH radicals. CH₄
383 has a background level that varies depending on the location and season [Dlugokencky et
384 al., 1994], making it more difficult to interpret differences in median summer CH₄ mixing
385 ratios at the suite of towers. Since we do not have continuous measurements of CH₄ at
386 any of the towers except WGC, we cannot clearly separate CH₄ enhancements from

387 background variability in samples with levels between 1800 and 1900 ppb if we only
388 look at CH₄ mixing ratios by themselves (see more on this in the next section).

389

390 **3.1.2 Influence of different sources at BAO**

391

392 *3.1.2.1. Median mixing ratios in the three wind sectors*

393 To better separate the various sources influencing air sampled at BAO, Figure 3
394 shows the observed median mixing ratios of several species as a function of prevailing
395 wind direction. For this calculation, we only used samples for which the associated 30-
396 minute average wind speed (prior to collection time) was larger than 2.5 m/s. We
397 separated the data into three wind sectors: NE, including winds from the north, northeast
398 and east (wind directions between 345° and 120°); S, including south winds (120° to
399 240°); and W, including winds from the west (240° to 345°).

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

406 Air masses from the NE sector pass over the oil and gas wells in the DJB and
407 exhibit large alkane enhancements. In winter, median mole fractions of C₃-C₅ alkanes are
408 8 to 11 times higher in air samples from the NE compared to the samples from the W

409 sector, while the median CH₄ value is 76 ppb higher. The NE wind sector also shows the
410 highest median values of C₆H₆, but not CO and C₂H₂.

411 C₃H₈, n-C₄H₁₀ and the C₅H₁₂ isomers in air samples from the NE wind sector are
412 much higher than in air samples coming from the Denver metropolitan area in the South
413 wind sector. Besides being influenced by Denver, southern air masses may pass over two
414 operating landfills, the Commerce City oil refineries, and some oil and gas wells (Figure
415 1). The S sector BAO CO and C₂H₂ mixing ratios are higher than for the other wind
416 sectors, consistent with the higher density of vehicular emission sources [Harley et al.,
417 1992; Warneke et al., 2007; Baker et al., 2008] south of BAO. There are also occasional
418 spikes in CFC-11 and CFC-12 mixing ratios in the S sector (not shown). These are most
419 probably due to leaks from CFC-containing items in the landfills. Air parcels at BAO
420 coming from the east pass over Interstate Highway 25, which could explain some of the
421 high mole fractions observed for vehicle combustion tracers such as CO, C₂H₂, and C₆H₆
422 in the NE sector data (see more discussion on C₆H₆ and CO in section 4.4 & Figure 4).

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

427

428 ***3.1.2.2. Strong alkane source signature***

429 To detect if the air sampled at BAO has specific chemical signatures from various
430 sources, we looked at correlation plots for the species shown in Figure 3. Table 3
431 summarizes the statistics for various tracer correlations for the three different wind

432 sectors. Figure 4 (left column) shows correlation plots of some of these BAO species for
433 summer data in the NE wind sector.

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

440 The tight correlations between the alkanes suggest a common source located in
441 the vicinity of BAO. Since large alkane enhancements are more frequent in the NE wind
442 sector, this common source probably has larger emissions north and east of the tower.
443 This NE wind sector encompasses Interstate Highway 25 and most of the DJB oil and gas
444 wells. The C_3 - C_5 alkane mole fractions do not always correlate well with combustion
445 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 : $r^2 <$
446 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
447 samples). These results indicate that the source responsible for the elevated alkanes at
448 BAO is not the major source of CO or C_2H_2 , which argues against vehicle combustion
449 exhaust as being responsible. Northeastern Colorado is mostly rural with no big cities.
450 The only operating oil refineries in Colorado are in the northern part of the Denver
451 metropolitan area, south of BAO. The main industrial operations in the northeastern Front
452 Range are oil and natural gas exploration and production and natural gas processing and
453 transmission. We therefore hypothesize here that the oil and gas operations in the DJB, as
454 noted earlier in Section 2, are a potentially substantial source of alkanes in the region.

455

456 **3.1.2.3. At least two sources of benzene in BAO vicinity**

457 The median winter C₆H₆ mixing ratio at BAO is higher for the NE wind sector
458 compared to the South wind sector, which comprises the Denver metropolitan area. The
459 C₆H₆-to-CO winter correlation is highest for the S and W wind sectors BAO samples
460 ($r^2=0.85$ and 0.83 respectively) compared to the NE wind sector data ($r^2=0.69$). The
461 C₆H₆-to-CO correlation slope is substantially higher for the NE wind sector data
462 compared to the other two wind sectors, suggesting that there may be a source of benzene
463 in the NE that is not a significant source of CO. The C₆H₆-to-C₂H₂ correlation slope is
464 slightly higher for the NE wind sector data compared to the other two wind sectors. C₆H₆
465 in the BAO data from the NE wind sector correlates more strongly with C₃H₈ than with
466 CO. The C₆H₆-to-C₃H₈ summer correlation slope for the NE wind sector is 10.1 ± 1.2
467 ppt/ppb ($r^2=0.67$).

468 For the S and W wind sectors BAO data, the C₆H₆-to-C₂H₂ (0.27 - 0.32 ppt/ppt)
469 and C₆H₆-to-CO (1.57 - 1.81 ppt/ppb) slopes are larger than observed emissions ratios for
470 the Boston/New York City area in 2004: 0.171 ppt/ppt for C₆H₆-to-C₂H₂ ratio and 0.617
471 ppt/ppb for C₆H₆-to-CO ratio [Warneke et al., 2007]. Baker et al. [2008] report an
472 atmospheric molar C₆H₆-to-CO ratio of 0.9 ppt/ppb for Denver in summer 2004, which is
473 in between the Boston/NYC emissions ratio value reported by Warneke et al. [2007] and
474 the BAO S and W wind sectors correlation slopes.

475 The analysis of the BAO C₆H₆ data suggests the existence of at least two distinct
476 C₆H₆ sources in the vicinity of BAO: an urban source related mainly to mobile emissions,

477 and a common source of alkanes and C₆H₆ concentrated in northeastern Colorado. We
478 discuss C₆H₆ correlations and sources in more detail in section 4.4.

479

480 **3.2. On-road surveys: tracking point and area source chemical signatures**

481

482 Road surveys with flask sampling and the Mobile Lab with the fast-response CH₄
483 analyzer were carried out in June-July 2008 (Table 2). The extensive chemical analysis of
484 air samples collected in the Front Range provides a snapshot of a broader chemical
485 composition of the regional boundary layer during the time of the study. The Mobile Lab
486 surveys around the Front Range using the in situ CH₄ analyzer allowed us to detect large-
487 scale plumes with long-lasting enhancements of CH₄ mixing ratios as well as small-scale
488 plumes associated with local CH₄ point sources. In the last two Mobile Lab surveys
489 (surveys 8 and 9), we combined the monitoring of the continuous CH₄ analyzer with
490 targeted flask sampling, using the CH₄ data to decide when to collect flask samples in and
491 out of plumes.

492 The regional background CH₄ mixing ratio at the surface (interpreted here as the
493 lowest methane level sustained for ~10 minutes or more) was between 1800 ppb and
494 1840 ppb for most surveys. Some of the highest “instantaneous” CH₄ mixing ratios
495 measured during the Mobile Lab surveys were: 3166 ppb at a wastewater treatment plant,
496 2329 ppb at a landfill, 2825 ppb at a feedlot near Dacono, over 7000 ppb close to a
497 feedlot waste pond near Greeley, and 4709 ppb at a large natural gas processing and
498 propane plant in Fort Lupton (Figure 1).

499 The analysis of the summer 2008 intensive data suggests that regional scale
500 mixing ratio enhancements of CH₄ and other alkanes are not rare events in the Colorado
501 Northern Front Range airshed. Their occurrence and extent depends on both emissions
502 and surface wind conditions, which are quite variable and difficult to predict in this area.
503 During the Mobile Lab road surveys, the high-frequency measurements of CO₂ and CH₄
504 did not exhibit any correlation. Unlike CO₂, the CH₄ enhancements were not related to
505 on-road emissions. Below we present two examples of regional enhancements of CH₄
506 observed during the Front Range Mobile Lab surveys.

507

508 **3.2.1. Survey 9: C₃₋₅ alkane levels follow large-scale changes in methane**

509 Figure 5 shows a time series of the continuous CH₄ mixing ratio data and alkane
510 mixing ratios measured in twelve flask samples collected during the Front Range Mobile
511 Lab survey on 31 July 2008 (flasks #1 to 12, sampled sequentially as shown in Figure 6).
512 The wind direction on that day was from the ENE or E at the NCAR Foothills Lab and
513 BAO tower. The Mobile Lab left the NOAA campus in Boulder around 11:40 am and
514 measured increasing CH₄ levels going east towards the BAO tower (Figure 6). An air
515 sample was collected close to the peak of the CH₄ broad enhancement centered around
516 11:55 am. The CH₄ mixing ratio then decreased over the next 25 minutes and reached a
517 local minimum close to 1875 ppb. The CH₄ level stayed around 1875 ppb for over one
518 hour and then decreased again, more slowly this time, to ~ 1830 ppb over the next two
519 hours.

520 Flasks # 1 to 3 were collected before, at the peak, and immediately after the broad
521 CH₄ feature between 11:40 and 12:15. Flasks # 4 & 5 were sampled close to a wastewater

522 treatment plant and flasks # 7 to 8 were sampled in a landfill. The in situ measurements
523 showed that CH₄ was still elevated above background as these samples were collected.
524 After a 90-minute stop at BAO to recharge the Mobile Lab UPS batteries, flasks # 9 to 11
525 were collected in a corn field while the in situ measurements showed lower CH₄ levels.
526 The last flask sample was collected on the NOAA campus just before 17:00 MDT, about
527 5.5 hours after the first flask sample was collected. The flask samples were always
528 collected upwind of the Mobile Lab car exhaust.

529 Sharp spikes in the continuous CH₄ data reflect local point sources (wastewater
530 treatment plant, landfill). The highly variable signals in both the continuous and discrete
531 CH₄ close to these sources are driven by the spatial heterogeneity of the CH₄ emissions
532 and variations in wind speed and direction. Broader enhancements in the continuous CH₄
533 data reflect larger (regional) plumes. The last flask (#12) sampled at NOAA has much
534 higher levels of combustion tracers (CO, C₂H₂, C₆H₆) than the other samples.

535 Figure 7 shows correlation plots for C₃H₈ versus CH₄ and n-C₄H₁₀ versus C₃H₈ in
536 the 12 flasks taken on 31 July. Air samples not directly influenced by identified point
537 sources (flasks #1-3, 6-7, 9-12) show a very strong correlation between the various
538 measured alkanes. Using the data from the air samples not directly influenced by
539 identified point sources (flasks #1-3, 6-7, 9-12), we derive a C₃H₈-to-CH₄ (C₃/C₁) mixing
540 ratio slope of 0.097± 0.005 ppb/ppb (Figure 7A). This slope is very similar to the one
541 observed for the summertime NE wind sector data at BAO (0.104± 0.005; Table 3).
542 Three air samples collected downwind of the waste water treatment plant and the landfill
543 (flasks # 4-5 and 8) are off the C₃H₈-to-CH₄ correlation line and have higher CH₄ than air
544 samples collected nearby but not under the influence of these local CH₄ sources (flasks 3

545 and 6). Flask # 8 also has elevated CFC-11 (310 ppt) compared to the other samples
546 collected that day (< 255 ppt), probably related to leaks from old appliances buried in the
547 landfill.

548 The C₃-C₅ alkane mixing ratios in samples collected on 31 July are tightly
549 correlated for flasks # 1 to 11 with $r^2 > 0.95$ (Figure 7B). As concluded for the BAO
550 alkane mixing ratio enhancements earlier, this tight correlation suggests that the non-
551 methane alkanes measured during the surveys are coming from the same source types.
552 The nC₄/C₃ correlation slope on 31 July (0.47 ppb/ppb; flasks # 1-11) is similar to the
553 summer slope in the BAO NE samples (0.45 ppb/ppb), while the 31 July iC₅/C₃ and
554 nC₅/C₃ slopes are slightly higher (0.17 and 0.17 ppb/ppb, respectively) than for BAO
555 (0.14 and 0.15 ppb/ppb, respectively).

556

557

558 **3.2.2. Survey 6: Alkane enhancements in the Denver-Julesburg oil and gas** 559 **production zone and cattle feedlot contributions to methane**

560

561 The flask-sampling-only mobile survey on 14 July 2008 focused on the
562 agricultural and oil and gas drilling region south of Greeley. Eleven of the twelve air
563 samples collected on 14 July were taken over the Denver-Julesburg Basin (flasks# 2-12
564 in Figure 3S in Supplementary Material). Figure 8A shows a correlation plot of C₃H₈
565 versus CH₄ mixing ratios in these air samples. Flasks collected NE of BAO and not near
566 feedlots (# 4, 6-8, and 10-12) fall on a line: $y=0.114(x-1830)$ ($r^2=0.99$). This slope and
567 the correlation slope calculated for the BAO NE wind sector data are indistinguishable

568 (within the 1- σ uncertainties in the slopes). Four samples collected in the vicinity of four
569 different cattle feedlots (flasks # 2, 3, 5, and 9) exhibit a lower C₃H₈-to-CH₄ correlation
570 slope (0.083 ppb/ppb, $r^2=0.93$). The r^2 for the C₃H₈-to-CH₄ correlation using all the flasks
571 is 0.91.

572 The n-C₄H₁₀ versus C₃H₈ correlation plot and its slope, along with the n-C₄H₁₀-
573 to-C₃H₈ and C₅H₁₂-to-C₃H₈ correlation slopes for air samples not collected downwind of
574 feedlots are shown in Figure 8B. The r^2 for the n-C₄H₁₀-to-C₃H₈ correlation using all the
575 flasks is 0.98, which is slightly higher than the r^2 for the C₃H₈-to-CH₄ correlation using
576 all flasks (0.91). The r^2 for the i-C₅H₁₂-to-n-C₄H₁₀ and n-C₅H₁₂-to-n-C₄H₁₀ correlations
577 using all the flasks are 0.96 ppb/ppb and 0.99 ppb/ppb, respectively. These results
578 suggest that cattle feedlots have no substantial impact on n-C₄H₁₀ and the C₅H₁₂ levels.

579 The strong correlation observed between the various alkane mixing ratios for air
580 samples not collected downwind of feedlots once again suggests that a common source
581 contributes to most of the observed alkanes enhancements. It is possible that some of the
582 C₃H₈ enhancements seen near the feedlots are due to leaks of propane fuel used for farm
583 operations [Ronald Klusman, personal communication]. Two flask samples were
584 collected downwind of a cattle feedlot near Dacono during Mobile Lab survey #8, on 25
585 July 2008. The analysis of these samples revealed large CH₄ enhancements (1946 and
586 2335 ppb), but no enhancement in C₃H₈ (~ 1ppb), n-C₄H₁₀ (<300ppt), the C₅H₁₂ (<
587 130ppt) or C₆H₆ (< 30ppt).

588 For survey #6, the n-C₄H₁₀-to-C₃H₈ correlation slope (0.56 ppb/ppb) is 16%
589 higher than the summer slope observed at BAO for the NE wind sector data, while the 14
590 July i-C₅H₁₂-to-C₃H₈ and n-C₅H₁₂-to-C₃H₈ correlation slopes (0.24 and 0.23 ppb/ppb,

591 respectively) are 76% and 53% higher, respectively, than the summer NE BAO data.
592 These slopes are higher than for flasks from survey #9. The difference in the C_5/C_3 slopes
593 between the various Mobile Lab surveys data and the BAO NE summer data may reflect
594 the spatial variability in the alkane source molar composition.

595

596 **3.2.3. Benzene source signatures**

597

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

604 The first subset of 39 samples has C_3H_8 mixing ratios smaller than 3 ppb and it
605 includes flasks collected mostly during surveys #2, 3 and 4. For this subset influenced
606 mostly by urban and mobile emissions, C_6H_6 correlates well with CO (slope=1.82
607 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
608 C_6H_6 -to-CO correlation slope for this subset is similar to the correlation slopes for the
609 BAO S and W wind sector winter samples.

610 The second subset of 46 samples corresponds to flasks with a C_3H_8 mixing ratio
611 larger than 3ppb. These flasks were collected mostly during surveys #1, 6, 8 and 9. For
612 this second subset influenced mostly by emissions from the DJB, C_6H_6 correlates well
613 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-

614 C₃H₈ slope for these samples is almost twice as big as the slope calculated for the BAO
615 NE wind sector data (10.1 ppt/ppb) (Table 3).

616

617

618 **4) Discussion**

619

620

621 **4.1. Comparing the alkane enhancements in the BAO and Mobile** 622 **Lab data sets**

623

624 In the previous section we showed two examples of enhanced alkanes in northeast
625 Colorado using mobile sampling (surveys 6 and 9 on 14 and 31 July 2008, respectively).
626 With lifetimes against OH removal on the order of 3.5, 1.7 and 1.0 days in the summer at
627 40°N [Finlayson-Pitts and Pitts, 2000; Spivakovsky et al., 2000] respectively, C₃H₈, n-
628 C₄H₁₀ and the C₅H₁₂ isomers do not accumulate over the continent. Instead their
629 atmospheric mixing ratios and the slopes of correlations between different alkanes reflect
630 mostly local or regional sources within a few days of atmospheric transport.

631 The source responsible for the alkane enhancements observed at BAO and in
632 multiple surveys during the Front Range Study appears to be located in the northeastern
633 part of the Front Range region within the Denver-Julesburg Basin, so we call it the DJB
634 source. The small differences in alkane correlation slopes for the BAO and Mobile Lab
635 samples likely reflect differences in the emitted alkane molar ratios across this distributed

636 source, as well as the mix of chemical ages for the air samples collected at a variety of
637 locations and on different days.

638 In Table 3 and Figure 4, we compare the alkane correlation slopes in the Mobile
639 Lab flask data set with the correlation slopes in the BAO data set. To calculate the DJB
640 source C₃H₈-to-CH₄ correlation slope from the Mobile Lab data set, we have removed air
641 samples collected downwind of feedlots, the wastewater treatment plant, and the natural
642 gas and propane processing plant (Figure 1). The Mobile Lab flasks C₃H₈-to-CH₄
643 correlation slope is 0.095±0.007 ppb/ppb (R²=0.76, 77 samples), similar to the slope
644 calculated for the BAO NE wind sector data. Samples collected downwind of the natural
645 gas processing plant exhibit variable chemical signatures, reflecting a complex mix of
646 contributions from leaks of gas and combustion exhaust from flaring units and
647 compressor engines.

648 To calculate the DJB source n-C₄H₁₀-to-C₃H₈, i-C₅H₁₂-to-C₃H₈ and n-C₅H₁₂-to-
649 C₃H₈ correlation slopes from the Mobile Lab data set, we have removed the three air
650 samples collected downwind of the natural gas and propane processing plant (Figure 1).
651 The C₄/C₃, i-C₅/C₃ and n-C₅/C₃ correlation slopes in the Mobile Lab data are 0.49, 0.19
652 and 0.19 ppb/ppb, respectively (r²> 0.8, 85 samples). The i-C₅/C₃ and n-C₅/C₃ correlation
653 slopes are 40% and 30% higher, respectively, than the BAO NE sector summer slopes. If
654 we remove the 11 data points from survey #6 samples collected in the middle of the DJB,
655 the C₅H₁₂-to-C₃H₈ ratios are only 15% higher than calculated for the NE sector at BAO.

656 High correlations among various alkanes were reported in this region by Goldan
657 et al. [1995]. In that study, hourly air samples were analyzed with an in-situ gas
658 chromatograph deployed on a mesa at the western edge of Boulder for two weeks in

659 February 1991. CH₄ was not measured during that study. The correlation coefficient (r^2)
660 between C₃H₈, n-C₄H₁₀, and the C₅H₁₂ isomers was around 0.86, with a clear minimum
661 slope for the abundance ratios (see Figure 4 in Goldan et al. [1995]). The authors
662 proposed that the C₄-C₆ alkanes shared one common source with propane (called the “C₃
663 source” in the next section and in Figure 9), with additional emissions contributing to
664 some C₄-C₆ alkane enhancements.

665

666 **4.2. Comparing the Front Range observed alkane signatures with VOC** 667 **emissions profiles for oil and gas operations in the Denver-Julesburg** 668 **Basin**

669

670 In this section we compare the alkane ratios calculated from the BAO NE wind
671 sector and the Mobile Lab samples to emissions profiles from the DJB oil and gas
672 exploration and production sector. Most of these profiles were provided by the WRAP
673 Phase III inventory team, who developed total VOC and NO_x emission inventories for oil
674 and gas production and processing operation in the DJB for 2006 [Bar-Ilan et al., 2008a].
675 Emissions and activity data were extrapolated by the WRAP Phase III inventory team to
676 derive emission estimates for 2010 based on projected production numbers and on state
677 and federal emissions control regulations put in place in early 2008 for oil and gas
678 permitted activities in the DNFR NAA [Bar-Ilan et al., 2008b]. The VOCs included in the
679 inventories are: C₃H₈, i,n-C₄H₁₀, i,n-C₅H₁₂ and higher alkanes, C₆H₆, toluene, ethyl-
680 benzene, xylenes and 224-trimethylpentane. The WRAP Phase III inventories for 2006
681 and 2010 were only provided as total VOC and NO_x emitted at the county level for all

682 the counties in the Colorado part of the DJB. The emission estimates are based on various
683 activity data (including the number of new wells (spuds), the total number of wells,
684 estimates of oil, condensate and gas production, and equipment counts) and
685 measured/reported or estimated VOC speciation profiles for the different source
686 categories. Supplementary Figure 2S and Bar-Ilan et al. [2008a,b] present more details on
687 how the inventory emission estimates are derived.

688 We focus primarily on flashing and venting sources here, since the WRAP Phase
689 III inventory indicates that these two sources are responsible for 95% of the total VOC
690 emissions from oil and gas exploration and production operations in Weld County and in
691 the NAA [Bar-Ilan et al., 2008a,b] (see Figure 2S). In 2006, all the oil produced in the
692 DJB was from condensate wells. Condensate tanks at well pads or processing plants store
693 a mostly-liquid mix of hydrocarbons and aromatics separated from the lighter gases in the
694 raw natural gas. Flash losses or emissions happen for example when the liquid
695 condensate is exposed to decreasing atmospheric pressure: gases dissolved in the liquid
696 are released and some of the heavier compounds may be entrained with these gases.
697 Flashing emissions from condensate storage tanks are the largest source of VOCs from
698 oil and gas operations in the DJB. In the DNFR NAA, operators of large condensate
699 tanks have to control and report emission estimates to the Colorado Department of Public
700 Health and the Environment (CDPHE). In 2006 and 2010 flashing emissions represented
701 69% and 65% respectively of the total VOC source from oil and gas exploration,
702 production and processing operations, for the nine counties in the NAA (see
703 supplementary Figure 2S and Bar-Ilan et al. [2008a] for more details on how the
704 estimates are derived).

705 Venting emissions are related to loss of raw natural gas when a new oil or gas
706 well is drilled or when an existing well is vented (blowdown), repaired or restimulated
707 (recompletion). Equipment at active well sites (e.g. well head, glycol dehydrators and
708 pumps) or in the midstream network of compressors and pipelines gathering the raw
709 natural gas can also leak significant amounts of natural gas. In the WRAP Phase III
710 inventory, venting emissions represented 27% and 21% respectively of the total VOC
711 estimated source from the NAA oil and gas operations in 2006 and 2010 ([Bar-Ilan et al.,
712 2008a,b], Figure 2S).

713 The molar compositions of venting and flashing emissions are quite different (see
714 supplementary Figure 4S). Emissions from flash losses are enriched in C₂₊ alkanes
715 compared to the raw natural gas emissions. To convert the total VOC bottom-up source
716 into speciated emission ratio estimates, we use molar ratio profiles for both flashing and
717 venting emissions reported in three data sets:

- 718 ▪ Bar-Ilan et al. [2008a]: mean venting profile used for the 2006 DJB
719 inventory, also called the "Venting-WRAP" profile;
- 720 ▪ Colorado Oil and Gas Conservation Commission [COGCC, 2007]:
721 composition of 77 samples of raw natural gas collected at different wells
722 in the Greater Wattenberg Area in December 2006, also called "Venting-
723 GWA" profiles. Note that C₆H₆ was not reported in this data set;
- 724 ▪ Colorado Department of Public Health and the Environment (CDPHE,
725 personal communication): flashing emissions profiles based on condensate
726 composition data from 16 different storage tanks in the DJB and EPA
727 TANK2.0 (flashing emissions model) runs.

728 Figure 9 shows a comparison of the alkane molar ratios for the raw natural gas
729 and flash emissions data sets with the correlation slopes derived for the Mobile Lab 2008
730 samples and for air samples collected at BAO in the summer months only (between
731 August 2007 and April 2010) for the NE wind sector (cf. Table 4S to get the plotted
732 values). The alkane correlation slopes observed at BAO and across the Northern Front
733 Range with the Mobile Lab are all within the range of ratios reported for flashing and/or
734 venting emissions. The C₃₋₅ alkane ratios for both flashing and venting emissions are too
735 similar for their atmospheric ratios to be useful in distinguishing between the two source
736 processes. The ambient C₃H₈-to-CH₄ and n-C₄H₁₀-to-CH₄ molar ratios are lower than
737 what could be expected from condensate tank flashing emissions alone, indicating that
738 most of the CH₄ observed came from the venting of raw natural gas. In the next section,
739 we will describe how we derive bottom-up emission estimates for CH₄ and C₃H₈ as well
740 as three top-down emissions scenarios consistent with the observed atmospheric slopes.

741

742 Figure 9 also shows the correlation slopes calculated by Goldan et al. [1995] for
743 the 1991 Boulder study. These slopes compare very well with the BAO and Mobile Lab
744 results and the oil and gas venting and flashing emissions ratios. Goldan et al. [1995]
745 compared the measured C₄/C₃ and C₅/C₃ ratios for the Boulder C₃ source (see definition
746 in Section 4.1) with the ratios reported in the locally distributed pipeline-quality natural
747 gas for February 1991, and concluded that the common C₃H₈ and higher alkane source
748 was not linked with the local distribution system of processed natural gas. However, the
749 composition of the raw natural gas at the extraction well is quite different from the
750 purified pipeline-quality natural gas distributed to end-users. Processed pipeline-quality

751 natural gas delivered throughout the USA is almost pure CH₄ [Gas Research Institute,
752 1992]. Since Goldan et al. [1995] did not measure CH₄ in their 1991 study, they could not
753 determine if the atmospheric C₃₊/C₁ alkane ratios were higher than expected in processed
754 natural gas.

755

756 **4.3. Estimation of the alkane source in Weld County**

757 *Bottom-up speciated emission estimates*

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

769 The WRAP Phase III total VOC emission from venting sources for Weld County
770 was calculated by averaging industry estimates of the volume of natural gas vented or
771 leaked to the atmosphere by various processes shown in Figure 2S (well blowdown, well
772 completion, pneumatic devices...). A basin-wide average of gas composition analyses
773 provided by oil and gas producers was then used to compute a bottom-up estimate of the

774 total mass of VOC vented to the atmosphere by oil and gas exploration, production and
775 processing operations. Uncertainties attached to the venting source can be related to
776 uncertainties in leak rates or intensity of out-gassing events, as well to the variability in
777 the composition of raw natural gas, none of which were quantitatively taken into account
778 in the WRAP Phase III inventory.

779 Next we describe the calculations, summarized in Figure 5S, to derive bottom-up
780 estimates of venting and flashing emissions for the various trace gases we measured
781 using information from the WRAP Phase III inventory and the COGCC GWA raw
782 natural gas composition data set (Table 4 and supplementary Figure 6S). From the total
783 annual vented VOC source and the average vented emission profile provided by Bar-Ilan
784 et al. [2008a] (Table 2S), we derived an estimate of the volume of natural gas that we
785 assumed is vented to the atmosphere by the oil and gas production and processing
786 operations in Weld County. Following Bar-Ilan et al. inventory data and assumptions
787 [2008a], we used the weight fraction of total VOC in the vented gas (18.74%), the molar
788 mass of the vented gas (21.5g/mol) and standard pressure and temperature with the ideal
789 gas law to assume that 1 mole of raw natural gas occupies a volume 22.4 L (as was done
790 in the WRAP Phase III inventory). The total volume of vented gas we calculate for Weld
791 County in 2008 is 3.36 billion cubic feet (Bcf), or the equivalent of 1.68% of the total
792 natural gas produced in the county in 2008 (202.1 Bcf). We then use the estimate of the
793 volume of vented gas and the molar composition profiles for the 77 raw natural gas
794 samples reported in the COGCC GWA study to compute average, minimum, and
795 maximum emissions for CH₄, each of the C₃₋₅ alkanes we measured, and C₆H₆. Using this

796 procedure, 2008 Weld County average venting CH₄ and C₃H₈ bottom-up source estimates
797 are 53.1 Gg/yr and 7.8 Gg/yr, respectively (Table 4).

798 For flashing emissions, we distributed the WRAP 2008 total annual VOC source
799 estimate (41.3 Gg/yr) using the modeled flash loss composition profiles for 16 different
800 condensate tanks provided by the CDPHE. Average CH₄ and C₃H₈ emissions as well as
801 the minimum and maximum estimates are reported in Table 4. The 2008 average flashing
802 CH₄ and C₃H₈ bottom-up emission estimates are 11.2 Gg/yr and 18.3 Gg/yr, respectively
803 (Table 4). The total flashing + venting CH₄ and C₃H₈ bottom-up estimates range from 46
804 to 86 Gg/yr and from 15 to 52 Gg/yr, respectively.

805

806 *Top-Down emissions scenarios*

807 Finally, we use our atmospheric measurements to bring new independent
808 constraints for the estimation of venting and flashing emissions in Weld County in 2008.
809 The exercise consists in calculating three top-down venting emission scenarios for CH₄
810 and C₃H₈ (x_m , x_p : mass of methane and propane vented respectively) consistent with a
811 mean observed CH₄-to-C₃H₈ atmospheric molar ratio of 10 ppb/ppb (Table 4) in the DJB.
812 We assume, as done earlier in the bottom-up calculations, that the observed C₃H₈-to-CH₄
813 ratio in the DJB results from a combination of flashing and venting emissions. The
814 bottom-up information used here is (1) the set of speciated flashing emissions derived
815 earlier for the 16 condensate tanks provided by CDPHE for CH₄ and C₃H₈ (y_m , y_p)_{tank=1,16},
816 and (2) three scenarios for the basin-average raw (vented) natural gas CH₄-to-C₃H₈ molar
817 ratio, denoted $v_{m/p}$. The three values used for basin-average vented gas CH₄-to-C₃H₈
818 molar ratio are: 18.75, which is the WRAP Phase III inventory assumption (scenario 1);

819 15.43, which is the median of the molar ratios for the COGCC GWA 77 gas samples
 820 (scenario 2); and 24.83, which is the mean of the molar ratios for the COGCC GWA 77
 821 gas samples (scenario 3). For each vented gas profile scenario, we use the set of 16 flash
 822 emission estimates to calculate an ensemble of venting emission estimates for CH₄ (x_m)
 823 and C₃H₈ (x_p) following the two equations below.

824 The first equation formalizes the assumption for CH₄-to-C₃H₈ molar ratio of the
 825 vented raw natural gas, with M_m (16g/mol) and M_p (44g/mol) being the molar masses of
 826 CH₄ and C₃H₈ respectively.:

$$827 \quad v_{m/p} = \frac{M_p}{M_m} \times \frac{x_m}{x_p} \quad (1)$$

828 In the second equation, the mean observed atmospheric CH₄-to-C₃H₈ molar ratio ($a_{m/p}$ =10
 829 ppb/ppb) constrains the overall ratio of methane versus propane emitted by both flashing
 830 and venting sources. Therefore, for each set of 16 bottom-up flashed emission estimates
 831 (y_m, y_p), we have:

$$832 \quad \frac{M_p(x_m + y_m)}{M_m(x_p + y_p)} = a_{m/p} \quad (2)$$

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

$$834 \quad x_p = \frac{1}{(v_{m/p} - a_{m/p})} \times \left(a_{m/p} \times y_p - \frac{M_p}{M_m} y_m \right) \quad (3)$$

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

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

837 The first goal of this top-down estimation exercise is to highlight the many
 838 assumptions required to build the bottom-up and top-down emission estimates. The

839 choices made for the WRAP Phase III inventory or our top-down calculations are all
840 reasonable, and the uncertainty attached to the values chosen (if available) should be
841 propagated to calculate total uncertainty estimates for the final emission products. When
842 the error propagation is done conservatively, the emission uncertainty is close to a factor
843 of 2 for both CH₄ and C₃H₈. This number is much higher than the 30% uncertainty
844 reported by the EPA for the 2009 national CH₄ source estimate from natural gas systems
845 [EPA, 2011c].

846 The scenario 1 mean top-down vented CH₄ source (118.4 Gg/yr) is twice as large
847 as the bottom-up estimate of 53.1 Gg/yr (Table 4). If we assume that 77% (by volume) of
848 the raw gas is CH₄, an average estimate of 118.4 Gg/yr of CH₄ vented would mean that
849 the equivalent of 4% of the 2008 natural gas gross production in Weld County was
850 vented. It is important to note that the top-down scenarios cover a large range (67-229
851 Gg/yr), corresponding to between 2.3% and 7.7% of the annual production being lost to
852 the atmosphere through venting (Table 4). The lowest estimate is, however, larger than
853 what we derived from the WRAP Phase III bottom-up inventory (1.68%). If instead of
854 using the EIA [EIA, 2004] convention for the molar volume of gas (23.6 L/mol), we used
855 the standard molar volume used by WRAP (22.4 L/mol), our top-down calculations of
856 the volume of gas vented would be 5% lower than reported in Table 4.

857 Emissions for the other alkanes measured are all derived from the C₃H₈ total
858 sources scaled with the atmospheric molar ratios observed in the BAO NE summer
859 samples and the Mobile Lab samples. Figure 10 shows a comparison of the bottom-up
860 estimates and the top-down emission scenarios (mean of scenario 1 and overall minimum
861 and maximum of the three scenarios).

862 The main result of this exercise is that for each of the three top-down total
863 emissions scenarios, the mean estimates for CH₄, n-C₄H₁₀ and the C₅H₁₂ isomers are at
864 least 60% higher than the bottom-up mean estimates. The minimum top-down emissions
865 scenarios are lower than (in the case of C₃H₈) or higher than (for CH₄, nC₄H₁₀, i-C₅H₁₂,
866 n-C₅H₁₂) the bottom-up mean estimates.

867 To put the top-down CH₄ source estimate from oil and gas exploration,
868 production and processing operations in perspective, we compare it with an estimate of
869 the passive “geological” CH₄ flux over the entire DJB. Klusman and Jakel [1998]
870 reported an average flux of 0.57 mg CH₄/m²/day in the DJB due to natural microseepage
871 of light alkanes. Multiplied by a rough upper boundary estimate of the DJB surface area
872 (Figure 1), the estimated annual natural flux is 0.66 Gg CH₄ /yr, or less than 1% of the
873 top-down venting source estimated for active exploration and production of natural gas in
874 Weld County.

875

876 **4.4. Benzene sources in the Northern Front Range**

877 On-road vehicles are estimated to be the largest source of C₆H₆ in the US [EPA,
878 2009a]. Emissions from on-road and off-road vehicles and from large point sources
879 (including chemical plants and refineries) have been regulated by the EPA for over thirty
880 years [Fortin et al., 2005; Harley et al., 2006]. When motor vehicle combustion
881 dominates emissions, such as in the BAO S and W wind sectors, C₆H₆ correlates well
882 with CO and C₂H₂.

883 Crude oil and natural gas production and processing emitted an estimated 8333
884 tonnes of benzene nationally in 2005, which represented 2% of the national total C₆H₆

885 source [EPA, 2009a]. C_6H_6 and C_3H_8 have similar photochemical lifetimes (~ 3-4 days in
886 the summer), so the observed atmospheric ratios we report in Table 3 should be close to
887 their emission ratio if they are emitted by a common source. The strong correlation
888 between C_6H_6 and C_3H_8 (Figure 4, Table 3) for the BAO NE wind sector and in the DJB
889 Mobile Lab air samples suggests that oil and gas operations could also be a non-
890 negligible source of C_6H_6 in the Northern Colorado Front Range.

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

898 If we use the mean C_3H_8 emission estimate for scenario 1 described in Section 4.3
899 (35.7 Gg/yr), together with the C_6H_6 -to- C_3H_8 correlation slope for the summer BAO NE
900 wind sector data and that from the Mobile Lab samples (10.1 ppt/ppb and 17.9 ppt/ppb
901 respectively), we derive a C_6H_6 emission estimate for the DJB source in Weld County in
902 2008 of 639 tonnes/yr (min/max range: 478/883 tonnes/yr) and 1145 tonnes/yr (min/max
903 range: 847/1564 tonnes/yr), respectively. As expected, these numbers are much higher
904 than what we derived for the bottom-up flashing and venting emissions (total of 139
905 tonnes/yr, min/max range of 49-229 tonnes/yr). For comparison, C_6H_6 emissions from
906 facilities in Colorado reporting to the US EPA for the Toxics Release Inventory
907 amounted to a total of 3.9 tonnes in 2008 [EPA, 2009b] and on-road emissions in Weld

908 County were estimated at 95.4 tonnes/yr in 2008 [CDPHE, personal communication].
909 Based on our analysis, oil and gas operations in the DJB could be the largest source of
910 C₆H₆ in Weld County.

911 More measurements are needed to further evaluate the various potential sources
912 associated with oil and gas operations (for example, glycol dehydrators and condensate
913 tank flash emissions). The past two iterations of the C₆H₆ emissions inventory developed
914 by the State of Colorado for the National Emissions Inventory and compiled by the EPA
915 do not show much consistency from one year to another. The 2008 and 2005 NEI
916 reported very different C₆H₆ emission estimates for condensate tanks in Weld County
917 (21.5 Mg/yr versus 1120 Mg/yr, respectively; see also Table 3S). Estimates in the 2008
918 NEI are much closer to estimates provided by CDPHE (personal communication) for
919 2008 (21.3 Mg/yr), suggesting the 2005 NEI estimate may be flawed, even though it is in
920 the range of our top-down estimation. We conclude that the current level of
921 understanding of emissions of C₆H₆ from oil and gas operations cannot explain the top-
922 down range of estimates we derive in our study, suggesting that, once again, more field
923 measurements are needed to understand and quantify oil and gas operation sources.

924

925 **5) Conclusion**

926

927 This study provides a regional overview of the processes impacting ambient
928 alkane and benzene levels in northeastern Colorado in the late 2000s. We report
929 atmospheric observations collected by two sampling platforms: a 300-m tall tower
930 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 CH₄, C₃H₈, n-C₄H₁₀, i-C₅H₁₂, n-C₅H₁₂ and C₆H₆
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 CH₄ (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 C₆H₆ in the region: one related to
972 combustion processes, which also emit CO and C₂H₂ (engines and mobile
973 vehicles), and one related to the DJB alkane source. The C₆H₆ 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 C₆H₆ from oil and gas

976 operations. Our top-down source estimates for C₆H₆ 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.

991

992

993

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995

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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 C₃₋₅ 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.

1227

1228 Figure 6: Continuous methane observations (colored squares) and flask (circles) samples
1229 collected during the July 31, 2008 Mobile Lab Survey #9 in Boulder and Weld County.
1230 The size of the symbols (and the symbol color for the continuous methane data)
1231 represents the mixing ratio of continuous/flask methane (squares, green circles) and flask
1232 propane (blue circles). The labels indicate the flask sample number (also shown in the
1233 time series in Figure 5). NCAR = National Center for Atmospheric Research, FL =
1234 NCAR Foothills Laboratory, ML = NCAR Mesa Laboratory, WWT Plant = Lafayette
1235 wastewater treatment plant.

1236

1237 Figure 7: A) Propane versus methane mixing ratios for air samples collected during
1238 Survey #9 on July 31, 2008. B) n-butane versus propane mixing ratios in the same air
1239 samples. The black line in plot A shows the correlation line for samples not impacted by
1240 local sources of methane (all flasks except #4, 5, 8, and 12). The black line in plot B
1241 shows the correlation line for all samples except flask 12. The flask sample number is
1242 shown next to each data point. The twelve samples were filled sequentially (see Figure
1243 6).

1244 Figure 8: A) Propane versus methane mixing ratios for air samples collected during
1245 Survey #6 on July 14, 2008. B) n-butane versus propane mixing ratios in the same air
1246 samples. The black line in plot A shows the correlation line for samples not impacted by
1247 local sources of methane (all flasks except 1-3, 5, and 9). The black line in plot B shows
1248 the correlation line for samples not impacted by local sources of propane.

1249 Figure 9: Alkane correlation slopes in air samples collected at BAO (NE wind sector,
1250 summer samples only, blue) and over the Denver-Julesburg Basin (red) during the Front
1251 Range Study (June-July 2008) are compared with VOC emissions molar ratios for
1252 flashing (green) and venting (grey) sources used by Bar-Ilan et al. [2008a] for the DJB
1253 WRAP Phase III emissions inventory. The error bars indicate the min and max values for
1254 the flashing emissions molar ratios. Also shown are the mean, min and max molar ratios
1255 derived from the composition analysis of gas samples collected in 2006 at 77 different
1256 gas wells in the Great Wattenberg Area (yellow, [Colorado Oil and Gas Conservation
1257 Commission, 2007]). Goldan et al. [1995] data are from a two week measurement
1258 campaign in the Foothills, west of Boulder, in February 1991 (light purple). Goldan et al.
1259 identified a “local” propane source (lower limit for correlation slope) with clear C₄₋₅
1260 alkane ratios to propane (dark propane, see also text). The error bars on the observed
1261 atmospheric molar ratios are the 2-sigma calculated for the ratios with linmix_err.pro
1262 (http://idlastro.gsfc.nasa.gov/ftp/pro/math/linmix_err.pro).

1263 Figure 10: Bottom-up (inventory-derived) emission estimates and top-down emission
1264 scenarios for CH₄, C₃H₈, n-C₄H₁₀, i-C₅H₁₂, n-C₅H₁₂ and C₆H₆ in Weld County. The
1265 vertical bars show scenario 1 average values and the error bars indicate the minimum and
1266 maximum values for the three scenarios described in Table 4.

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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

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* aircraft discrete air samples

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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 ₄ enhancements, Landfill, Corn field	Picarro + 12 flasks

1292

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	0.104 ± 0.005	0.85	81	0.105 ± 0.004	0.9 0	115	0.079 ± 0.008	0.53	130	0.085 ± 0.005	0.73	148	0.095 ± 0.007	0.76	77
nC_4H_{10}/C_3H_8	ppb/ppb	0.447 ± 0.013	1.00	81	0.435 ± 0.005	1.0	120	0.449 ± 0.011	0.98	131	0.434 ± 0.006	1.00	151	0.490 ± 0.011	1.00	85
iC_5H_{12}/C_3H_8	ppb/ppb	0.141 ± 0.004	1.00	81	0.134 ± 0.004	0.9 8	120	0.142 ± 0.009	0.81	121	0.130 ± 0.004	0.94	151	0.185 ± 0.011	0.81	85
nC_5H_{12}/C_3H_8	ppb/ppb	0.150 ± 0.003	1.00	81	0.136 ± 0.004	0.9 8	120	0.142 ± 0.006	0.90	131	0.133 ± 0.003	0.91	151	0.186 ± 0.008	0.92	85
C_6H_6/C_3H_8	ppt/ppb	10.1 ± 1.2	0.67	49	8.2 ± 0.5	0.7 9	117	-	0.33	130	-	0.39	150	17.9 ± 1.1	0.95	46
C_6H_6/CO	ppt/ppb	2.89 ± 0.40	0.58	53	3.18 ± 0.24	0.6 9	112	1.57 ± 0.08	0.85	123	1.81 ± 0.08	0.83	148	1.82 ± 0.12	0.89	39
C_2H_2/CO	ppt/ppb	3.15 ± 0.33	0.85	81	7.51 ± 0.39	0.8 5	100	5.03 ± 0.17	0.92	110	5.85 ± 0.25	0.86	131	4.32 ± 0.28	0.89	39
C_6H_6/C_2H_2	ppt/ppt	0.51 ± 0.09	0.55	50	0.34 ± 0.02	0.9 0	103	0.27 ± 0.02	0.90	111	0.32 ± 0.02	0.96	132	0.37 ± 0.04	0.75	39

1301 **Table 4: Bottom-up (inventory-derived) emission estimates and top-down emissions scenarios for CH₄ and C₃H₈ in Weld**
 1302 **County.**

Gg/yr	Bottom-Up Estimates				Top-Down Scenarios ^c : Venting			Top-Down Scenarios ^c : TOTAL Bottom-Up Flashing + Top-Down Venting			Top-Down Scenarios ^c : % of production vented ^f		
	Flashing ^b	Venting ^c	Flashing + venting	% of production vented ^d	1	2	3	1	2	3	1	2	3
methane	11.2	53.1	64.3	1.68%	118.4	92.5	157	129.6	103.7	168.2	4.0%	3.1%	5.3%
min^a	4	42	46		86.5	67.6	114.7	90.5	71.6	118.7	2.9%	2.3%	3.8%
max^a	23	63	86		172.6	134.9	228.9	195.6	157.9	251.9	5.8%	4.5%	7.7%
propane	18.3	7.8	26.1		17.4	10.2	28	35.7	28.5	46.3			
min^a	14	1	15		12.7	7.5	20.5	26.7	21.5	34.5			
max^a	24	28	52		25.3	14.9	40.8	49.3	38.9	64.8			

1303
 1304 ^a The minimum and maximum values reported here come from the ensemble of 16 condensate tank emissions speciation profiles
 1305 provided by CDPHE.

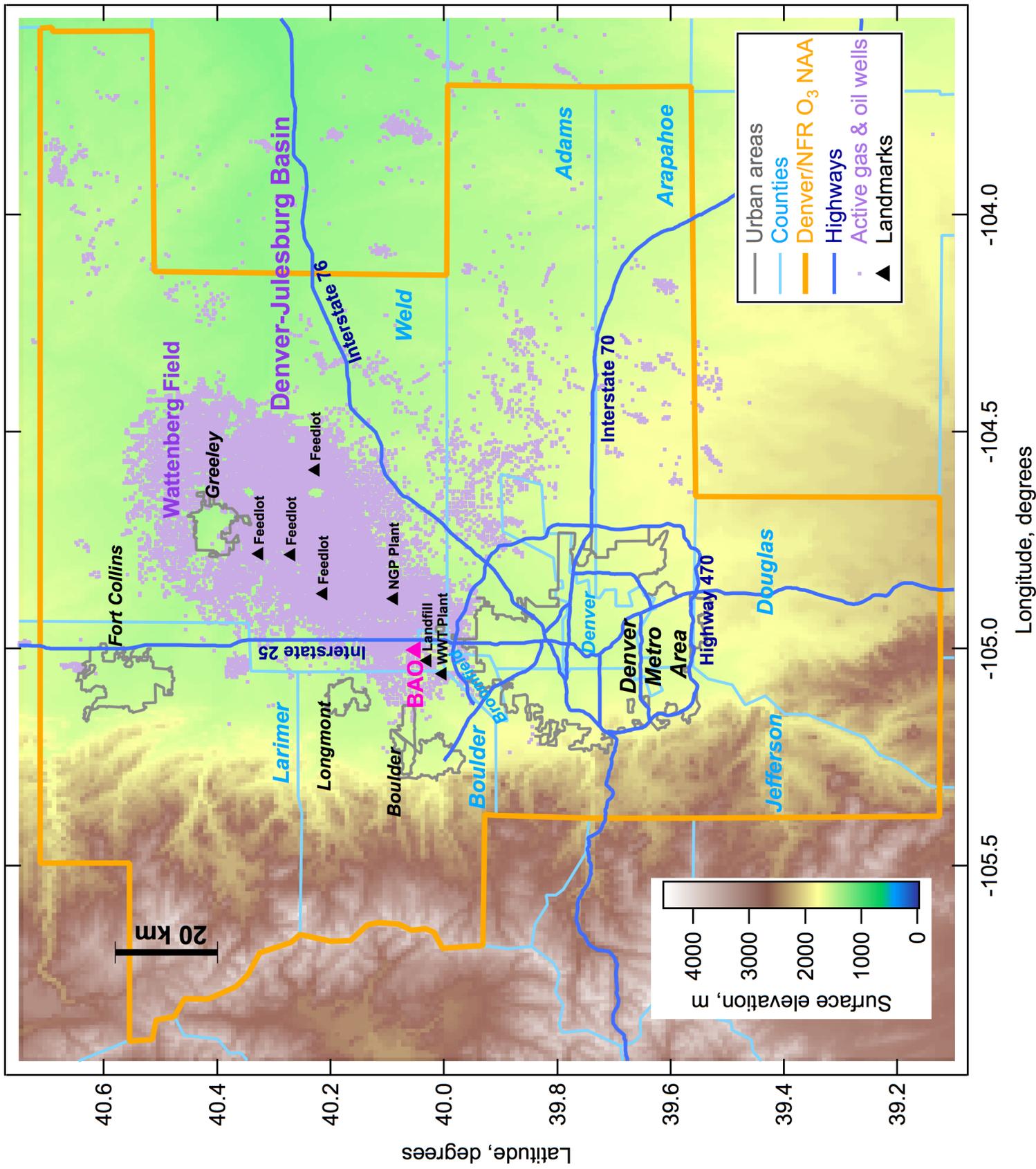
1306 ^b The bottom-up flashing emissions for methane and propane were calculated using the 2008 estimate of total VOC flash emissions
 1307 derived by averaging the WRAP estimate for 2006 and the projection for 2010 (Cf. section 4.3).

1308 ^c The bottom-up venting emissions for methane and propane were calculated using the WRAP Phase III inventory estimate for the
 1309 total volume of natural gas vented and the GWA 77 natural gas composition profiles.

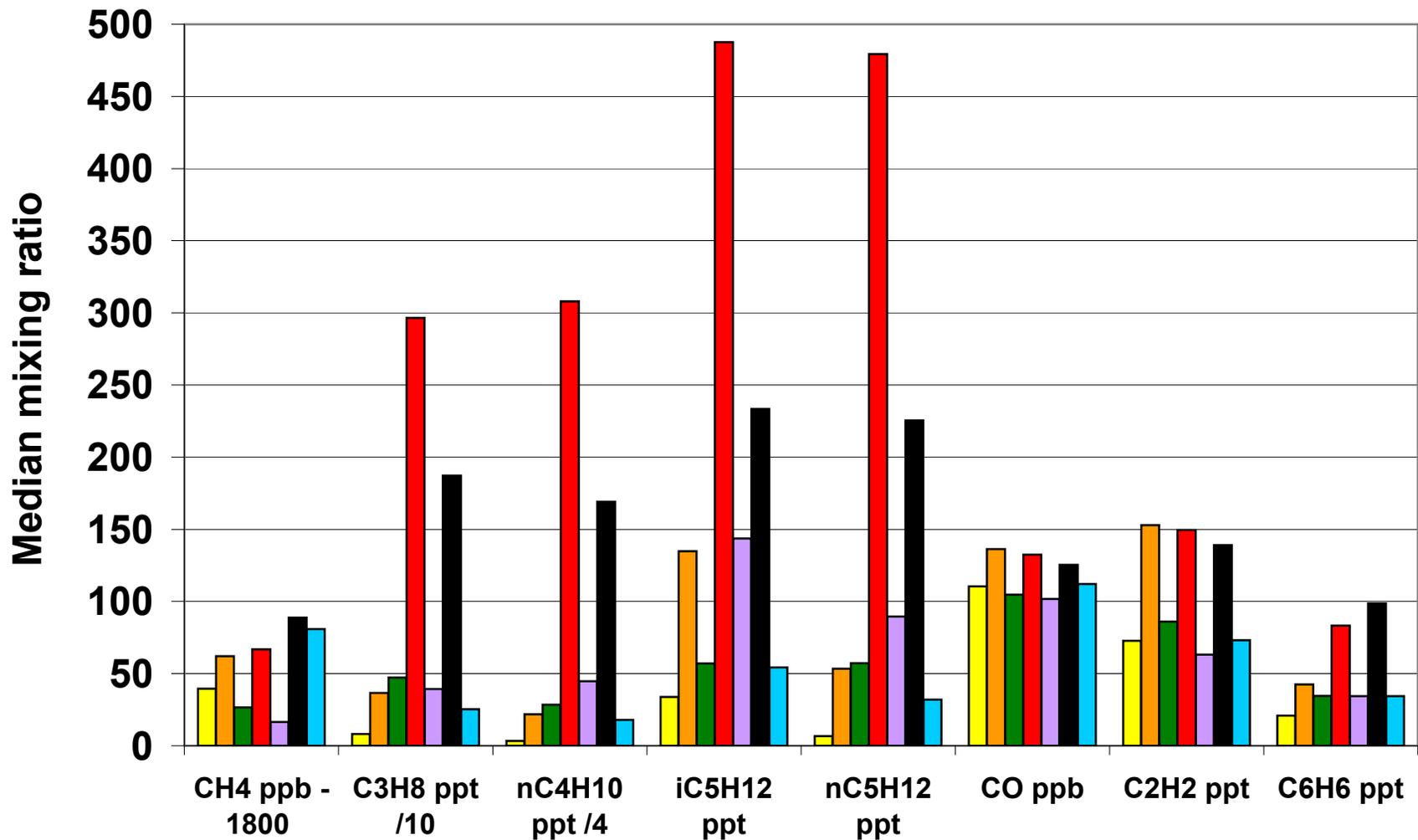
1310 ^d Using the WRAP Phase III inventory data set and assumptions, including a CH₄ mean molar ratio of 77.44% for the vented natural
 1311 gas and a molar volume for the gas of 22.4 L/mol.

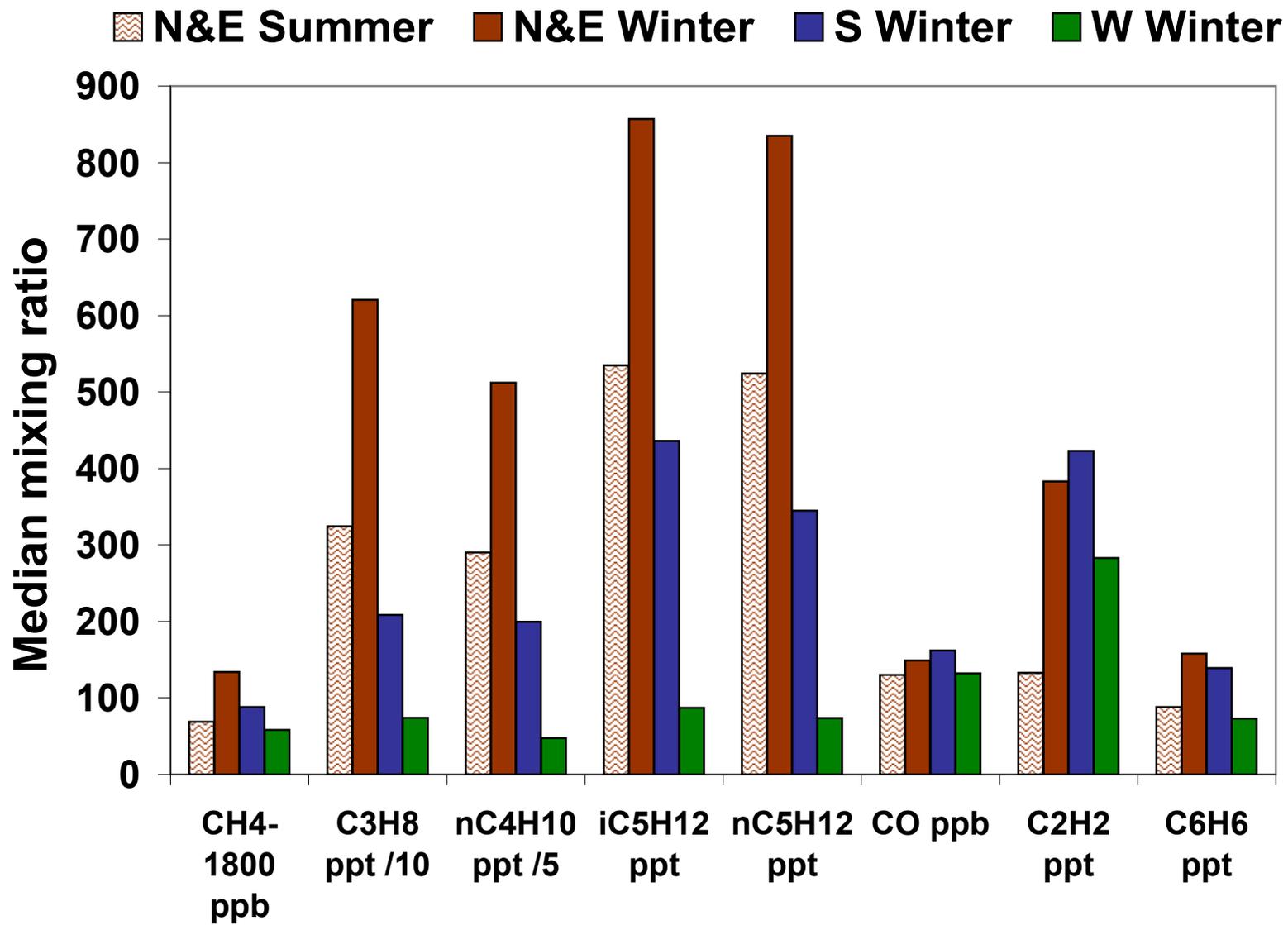
1312 ^e The CH₄-to-C₃H₈ molar ratio for vented natural gas is 18.75 (WRAP report estimate) for scenario 1, 15.43 for scenario 2 (median of
 1313 molar ratios in GWA data set) and 24.83 for scenario 3 (mean of molar ratios in GWA data set).

1314 ^f Using the assumptions of a CH₄ molar ratio of 77% for the vented natural gas and a molar volume for the gas of 23.6 L/mol
 1315 (Pressure= 14.73 pounds per square inch and Temperature= 60°F) as used by the EIA [EIA, 2004].

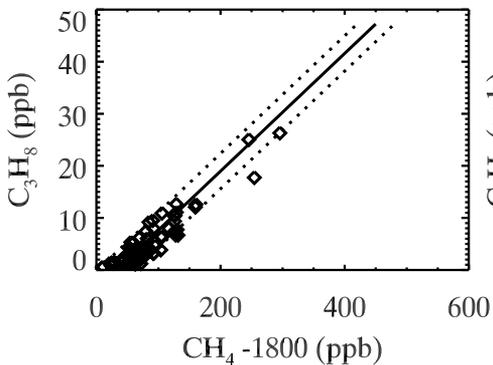


■ STR, CA
 ■ WGC, CA
 ■ NWF, CO - Night
 ■ BAO, CO
 ■ WKT, TX
 ■ SGP, OK
 ■ LEF, WI

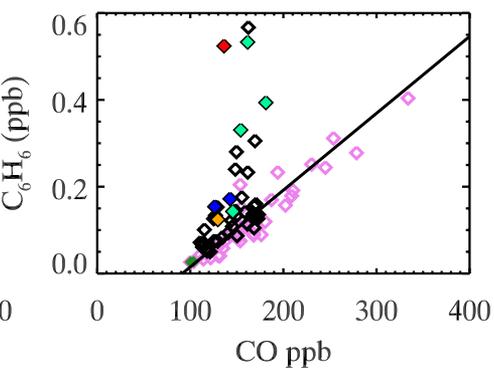
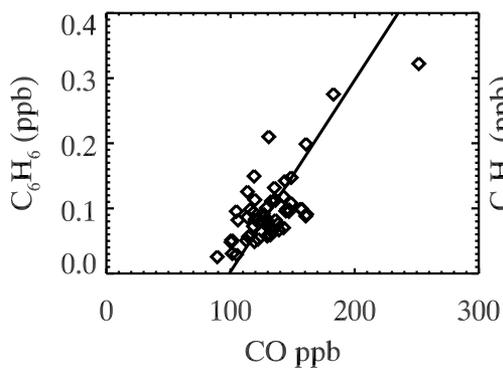
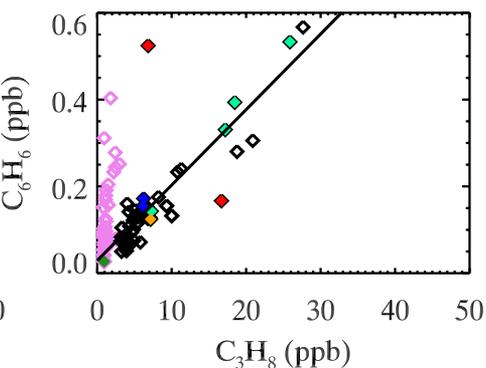
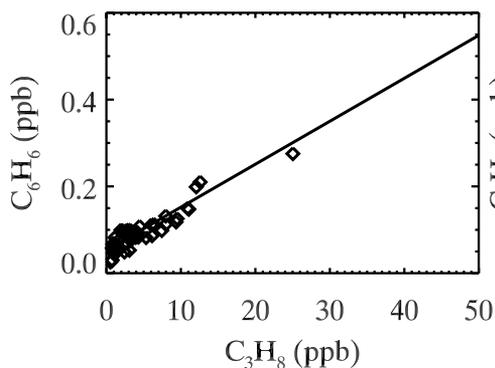
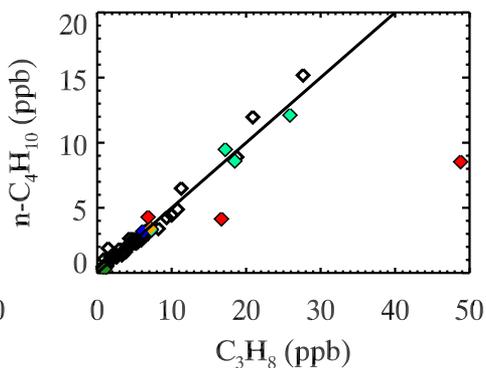
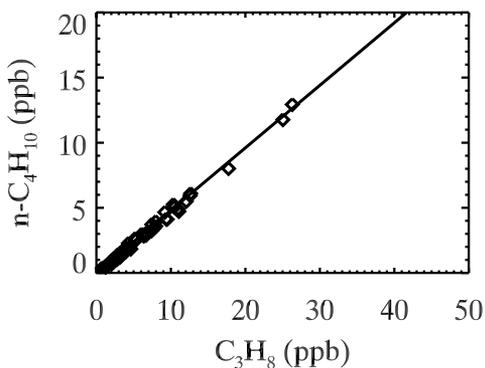
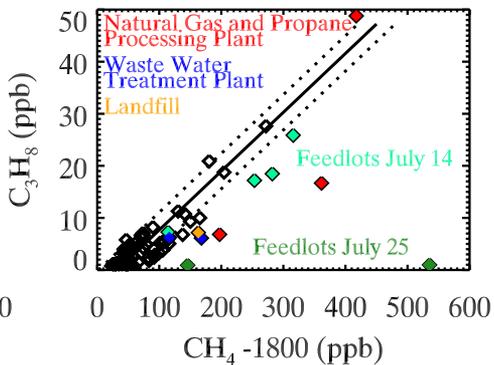


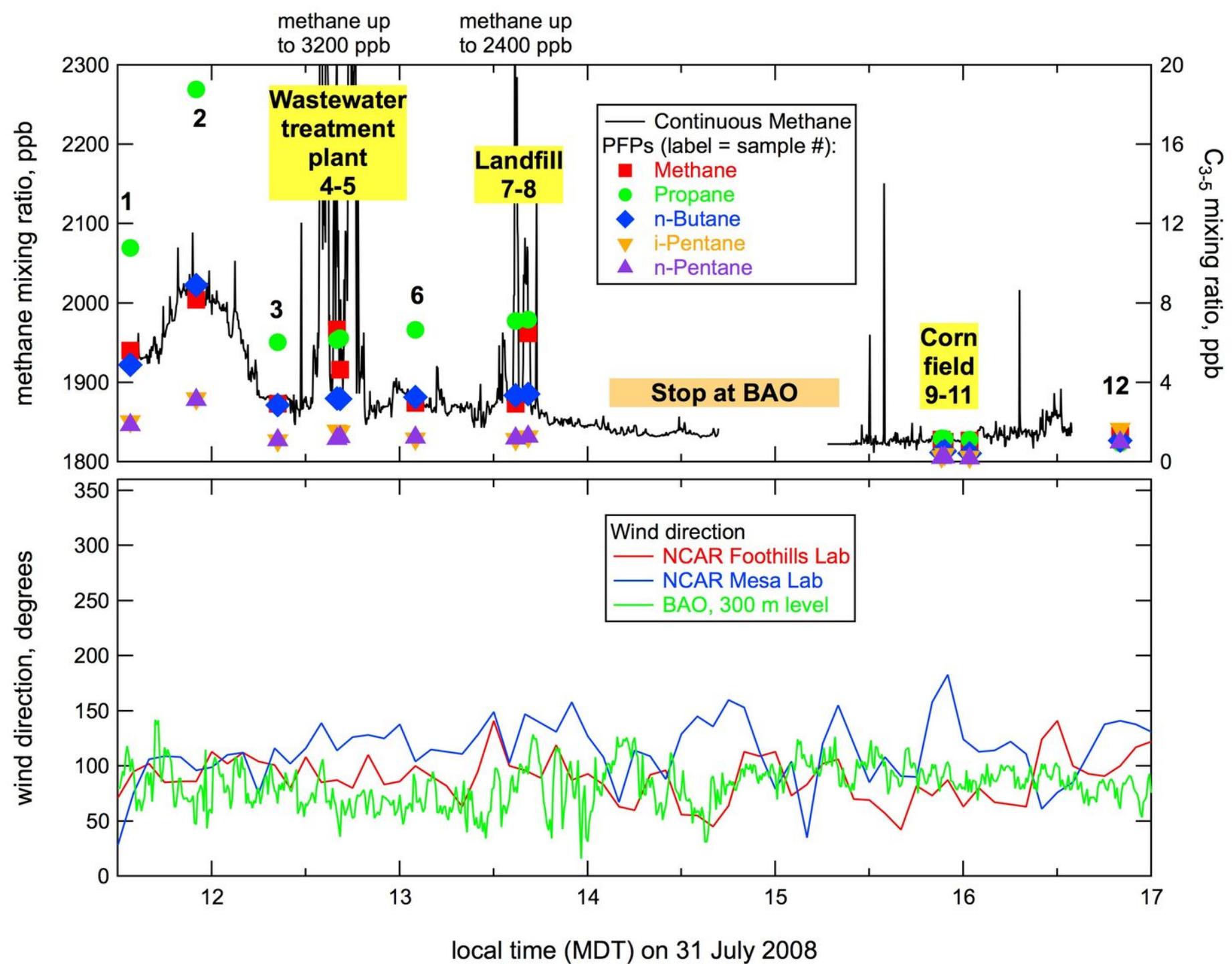


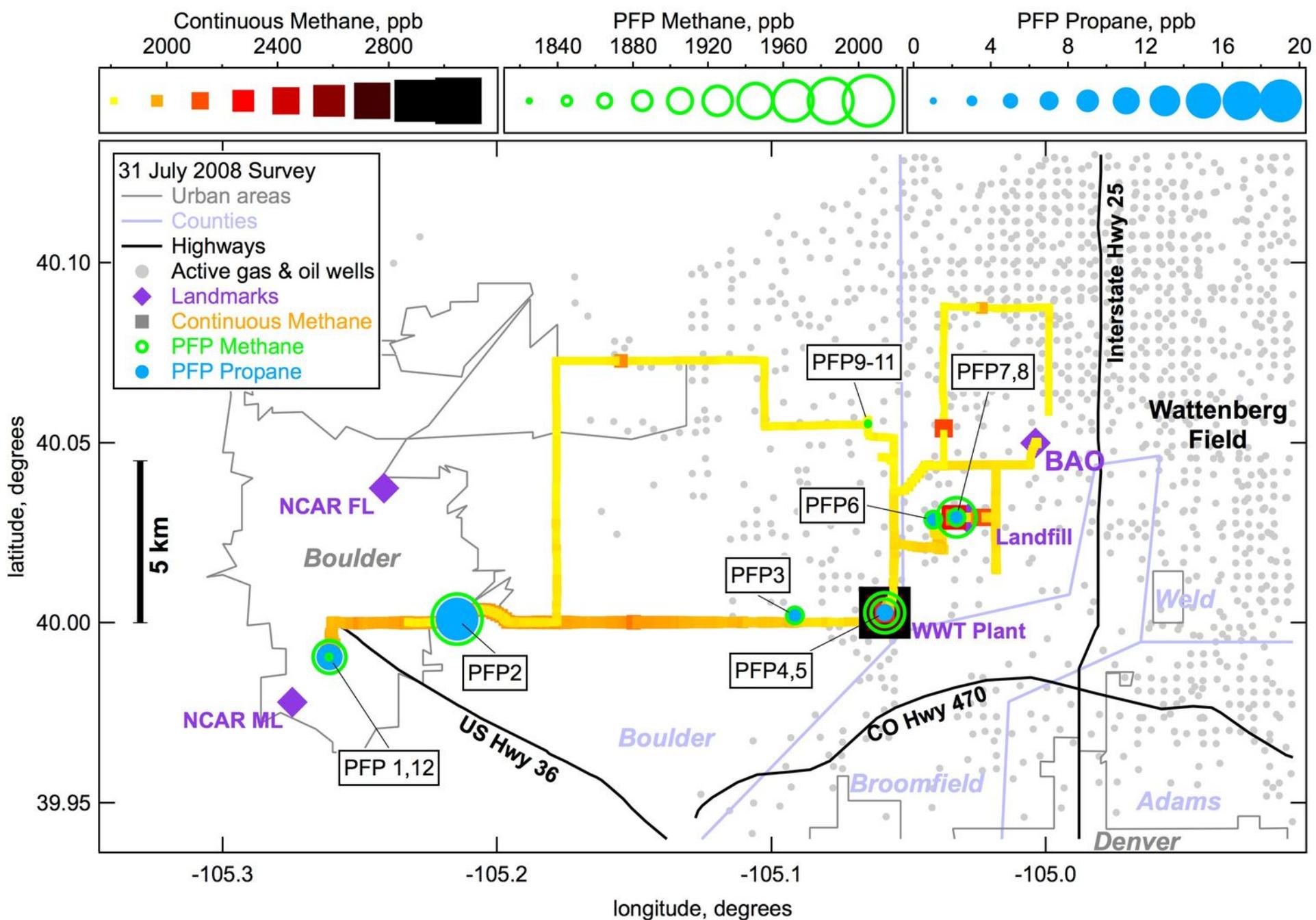
BAO N&E Summer

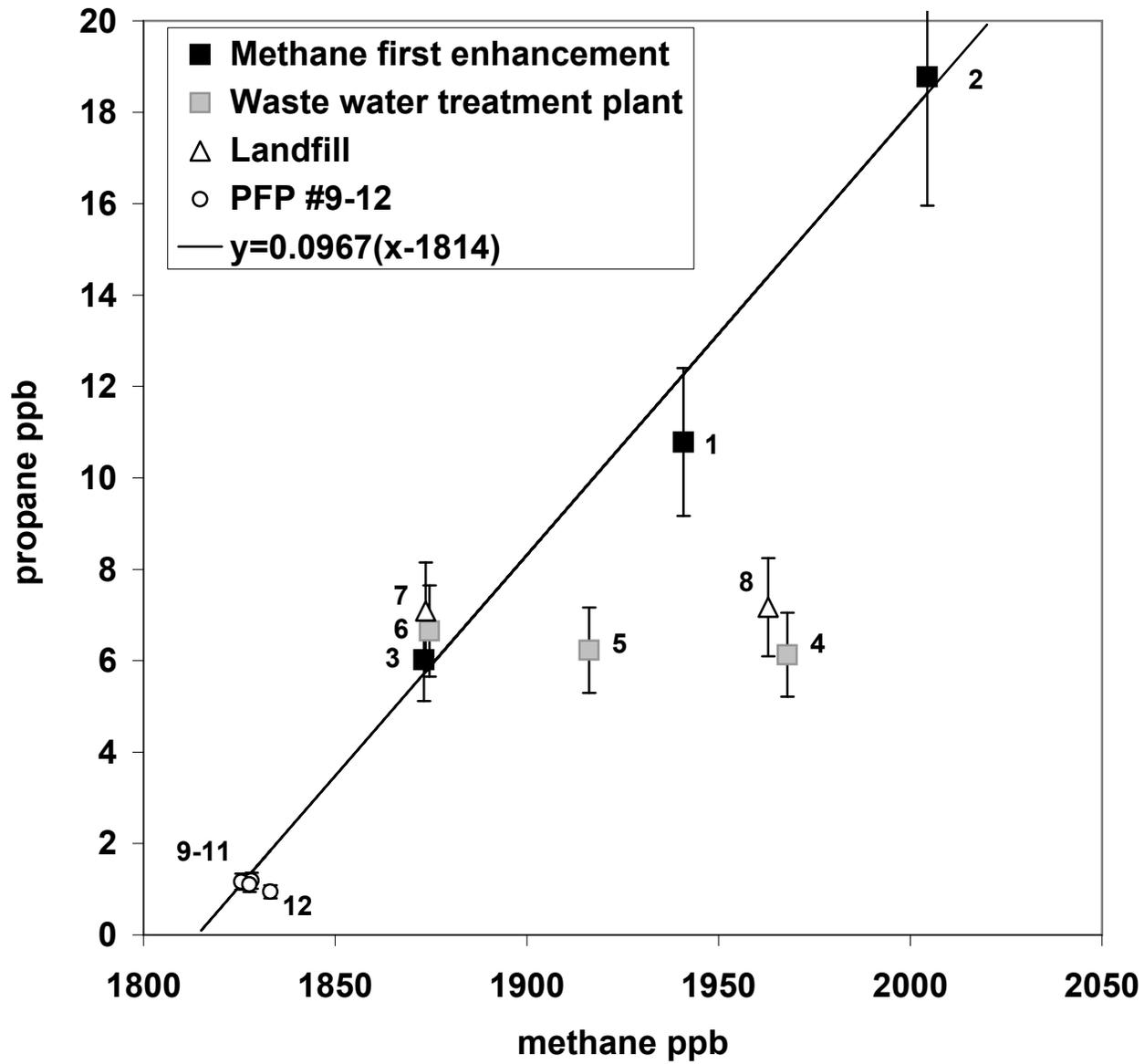


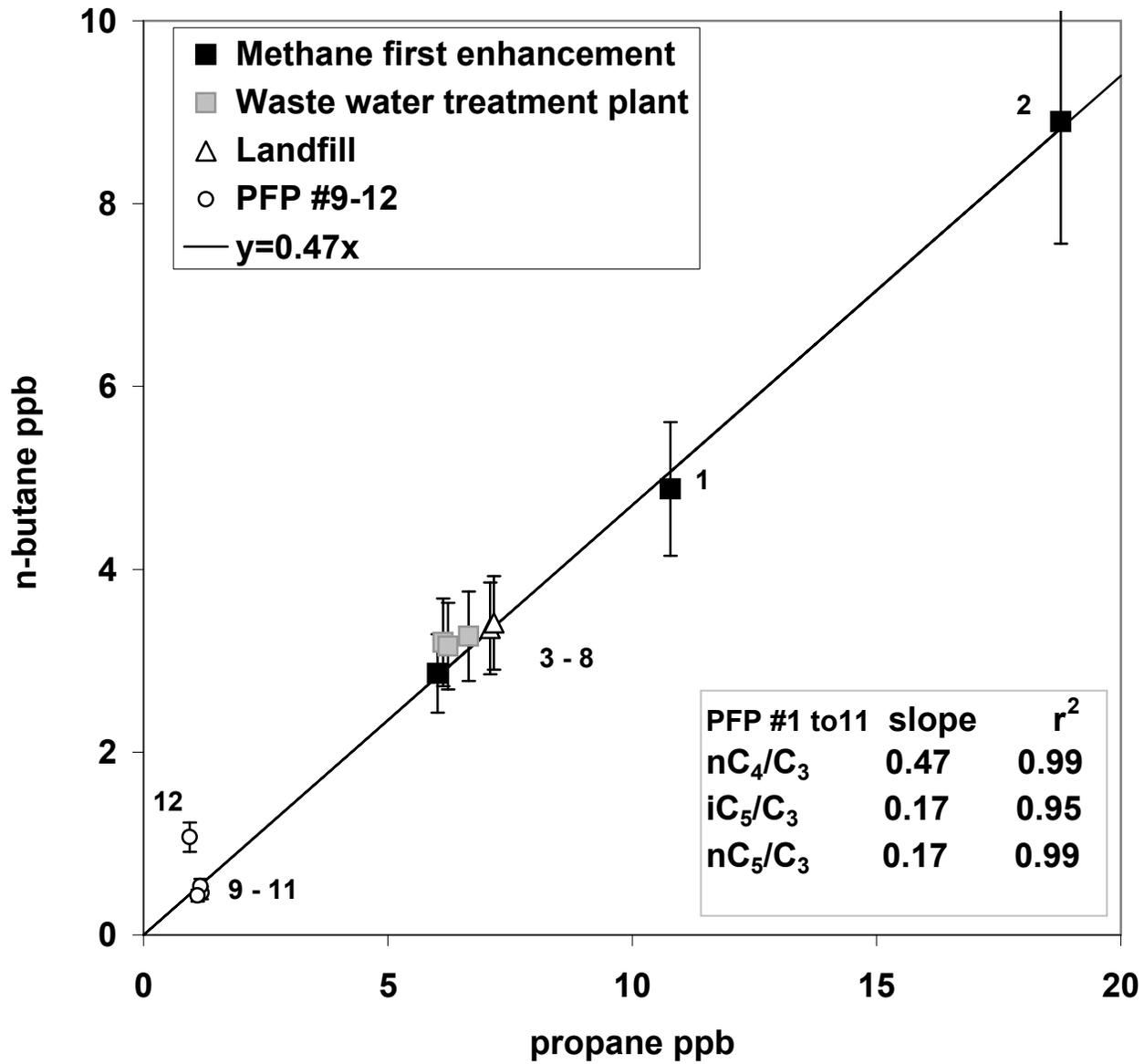
Mobile lab, All samples

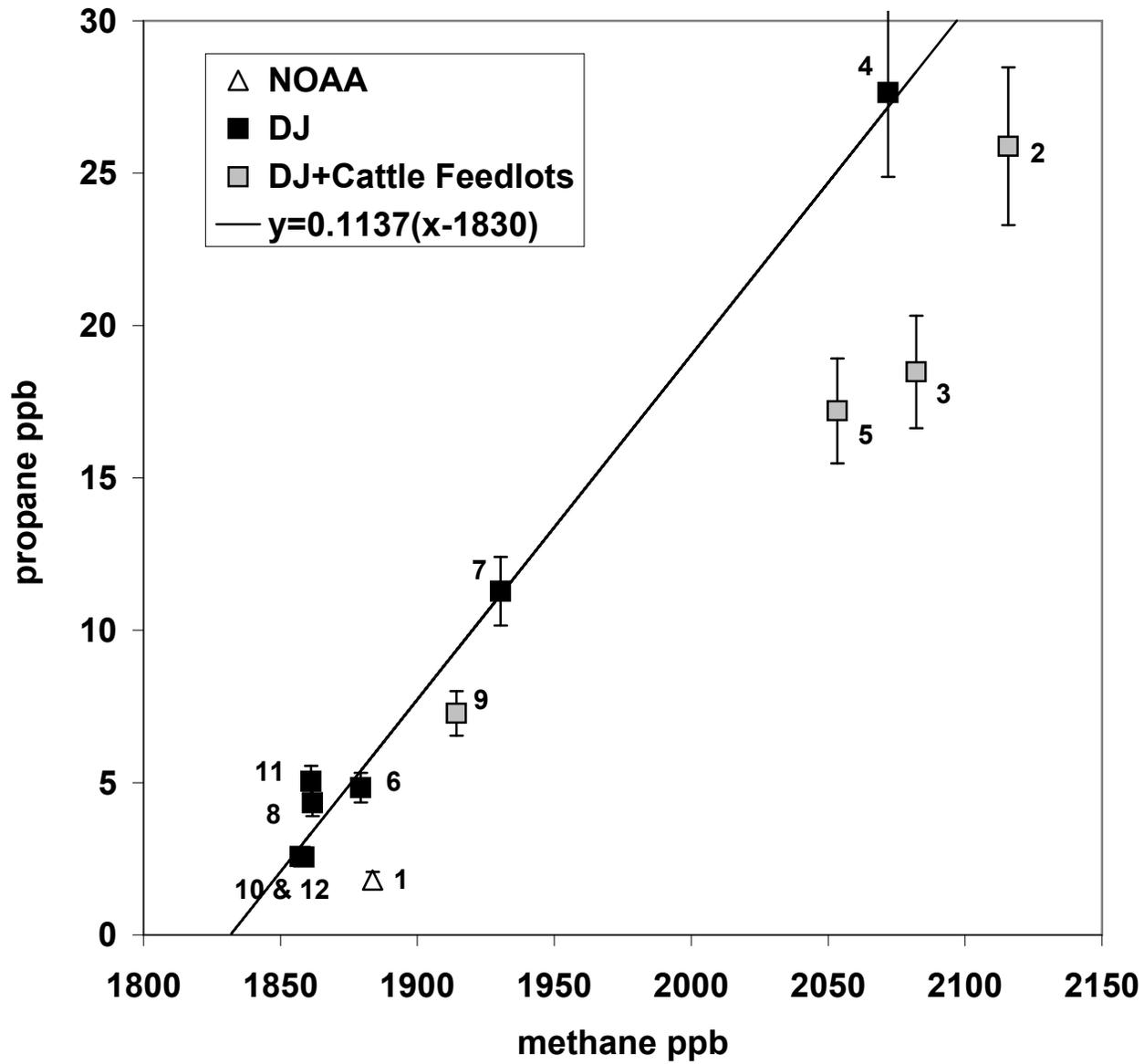


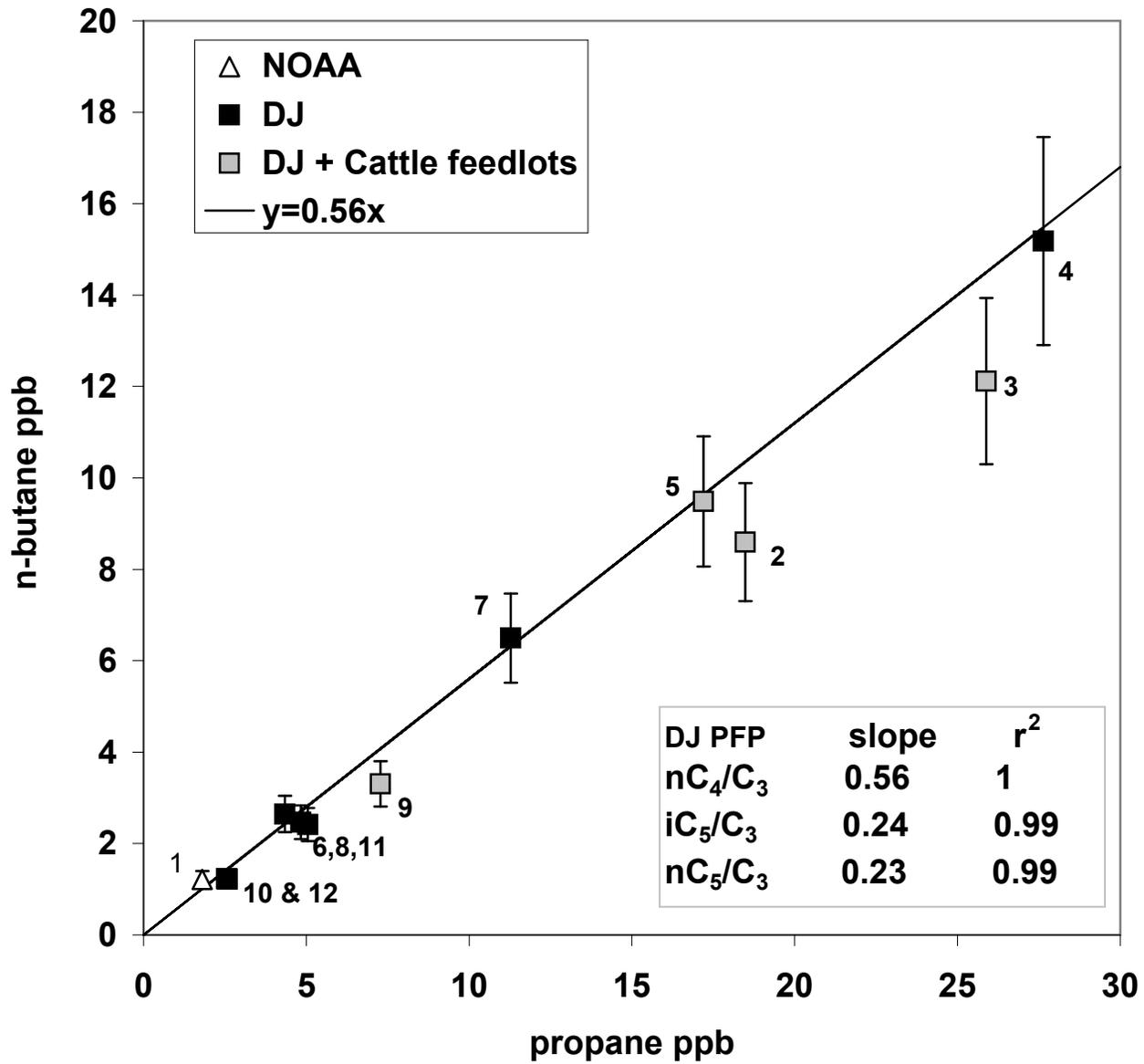


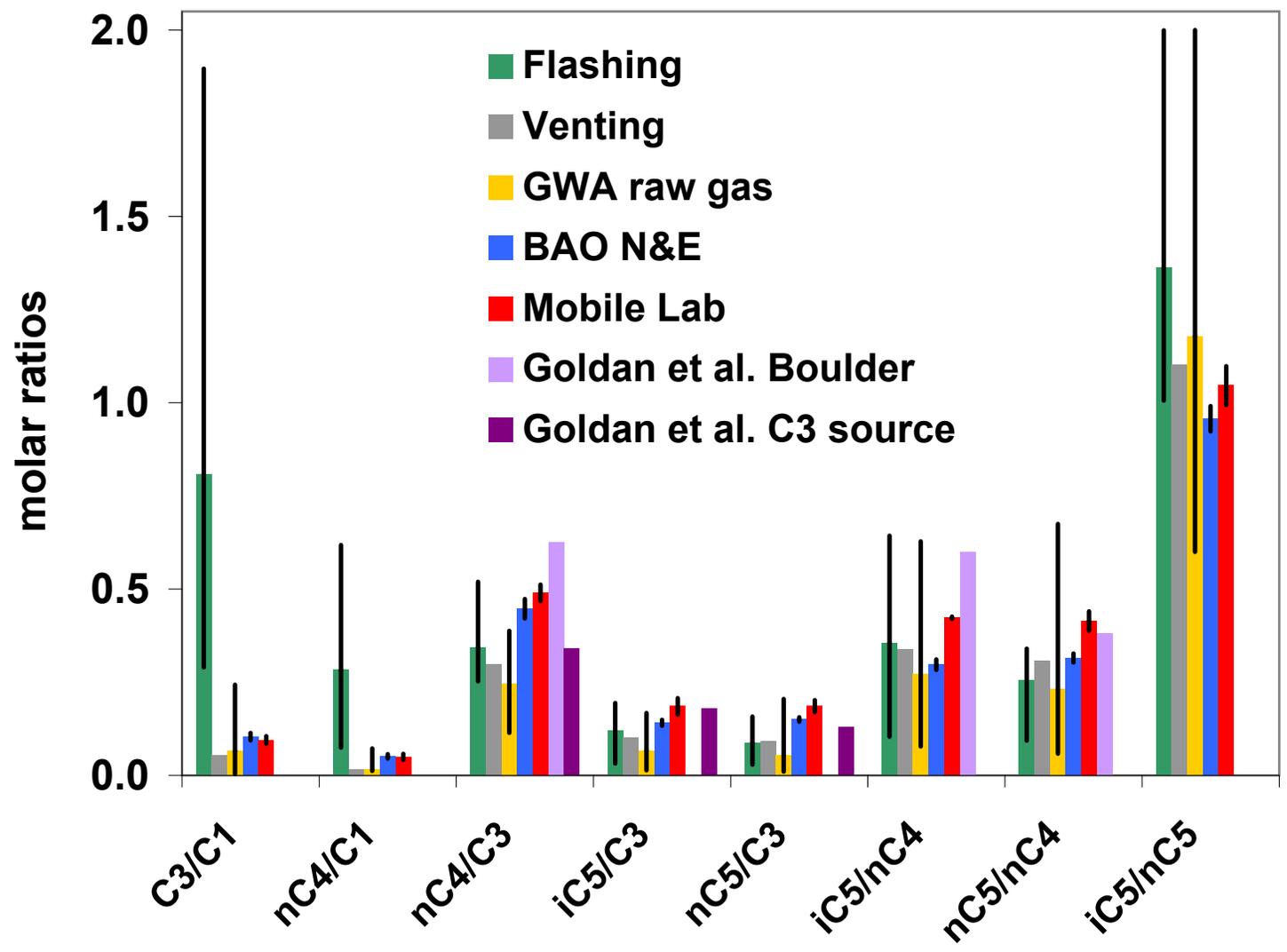




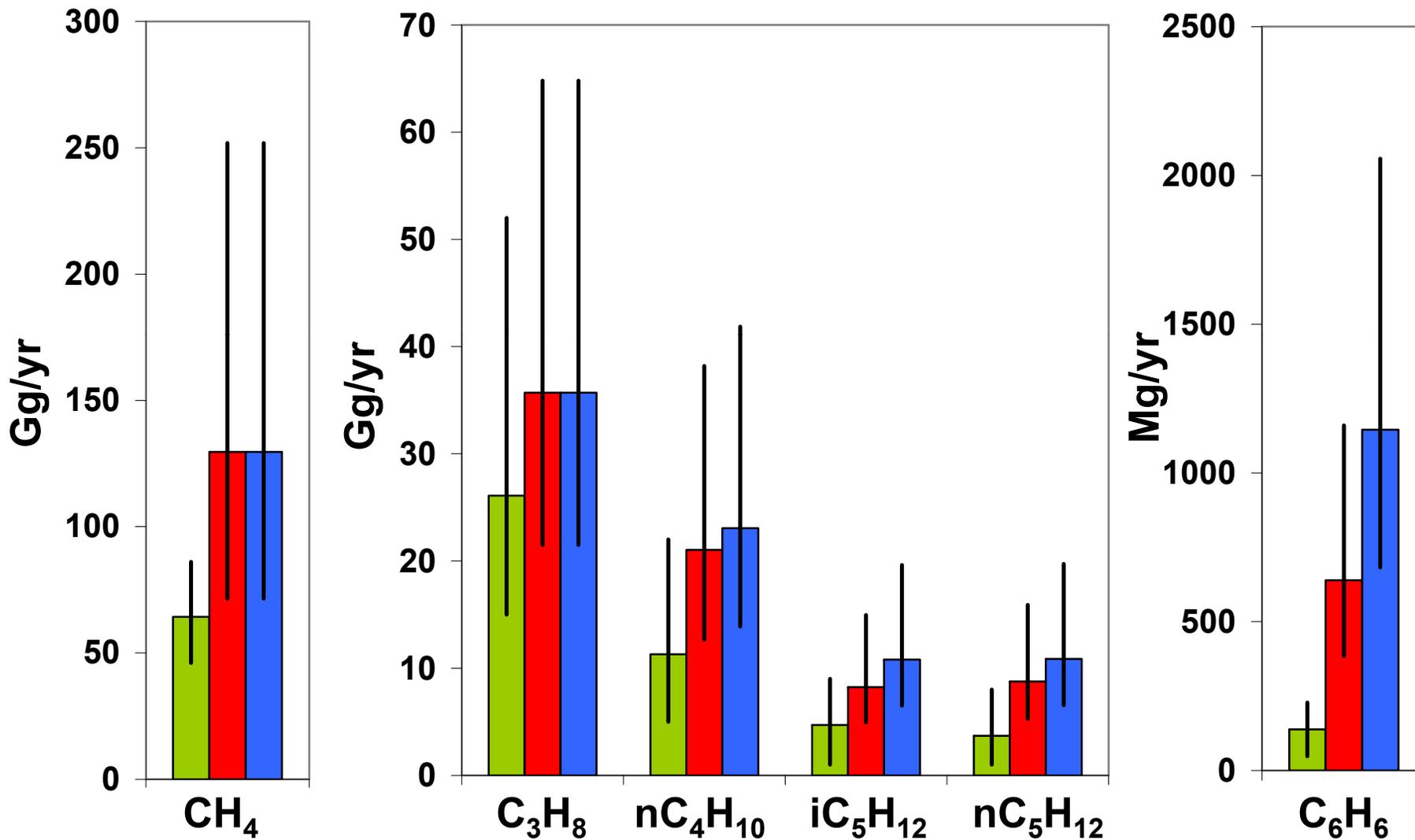








Bottom-up BAO- Top-Down Mobile Lab-Top-Down



1 Supplementary Tables

2

3 Table 1S: Methane source estimates in Colorado (Gg CH₄ /yr, for 2005)

4

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

7

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

11 Sources: WRAP for year 2006 [Bar Ilan et al., 2008a], CDPHE for 2008
12 [CDPHE, personal communication], NEI 2005 [EPA, 2008], NEI 2008 [EPA,
13 2011b]

14

15 Table 4S: Inventory and measurement derived molar ratios for the various
16 data sets plotted on Figure 9. Flashing emissions composition is based on
17 EPA TANK model runs for 16 condensate tanks located in the DJB and
18 sampled in 2002 [CDPHE, personal communication 2010]. Venting emissions
19 composition is based on an average raw gas weight composition profile
20 provided by Bar-Ilan et al. [2008a] and derived private data from several
21 natural gas producing companies in the DJB. To get a range of
22 distribution for vented emissions, we use the molar composition provided
23 by COGCC for raw gas samples collected at 77 wells in the DJB in December
24 2006. The BAO NE summer data and Mobile Lab data are the same as in Table
25 3. The Goldan et al. data for samples collected west of Boulder in
26 February 1991 are based on Goldan et al. [1995] Table 1 and Figure 5.

27

28

29 Supplementary Figures

30

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

33

34 Figure 2S: Denver - Northern Front Range NAA VOC emissions inventories
35 for oil and gas exploration, production and processing operations,
36 developed by Bar-Ilan et al. [2008a,b]. The 2006 inventory is based on
37 reported emissions for large condensate tanks and other permitted source
38 categories identified with a (*) in the legend. Other source estimates
39 are based on activity data and emissions factors. The 2010 ?projection?
40 inventory was extrapolated based on oil and gas production trends, the
41 2006 emissions data, and federal and state regulations for emissions
42 control of permitted sources that were ?on the book as of early 2008?. We
43 distinguish three types of emissions based on distinct VOC speciation
44 profiles used in the WRAP inventory: (1) flashing emissions from small
45 and large condensate tanks; (2) venting emissions associated with leaks
46 of raw natural gas at the well site or in the gathering network of
47 pipelines; and (3) other emissions such as compressor engines (3% of
48 total source), truck loading of condensate (1%), heaters, drill rigs,
49 workover rigs, exempt engines, and spills which have different VOC
50 emissions profiles.

51

52 Figure 3S: PFP samples collected during the mobile survey on July 14,
53 2008. The size of the symbols indicates the mixing ratio of PFP methane
54 (red circles) and propane (green circles). The labels indicate the PFP

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

57

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

68

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

71

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

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Table 1S: Methane source estimates in Colorado (Gg CH₄ /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)

Year	2005			2008		
Gross withdrawal/production	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>
Weld County (% of Colorado)	188.5 (16.5%)	11.7 (51.3%)	na	202.1 (15.3%)	17.3 (71.8%)	na
DNFR NAA	201.1	12.6	na	214.1	18.5	na
Colorado	1144	22.8	5	1403	24.1	7
USA	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*.

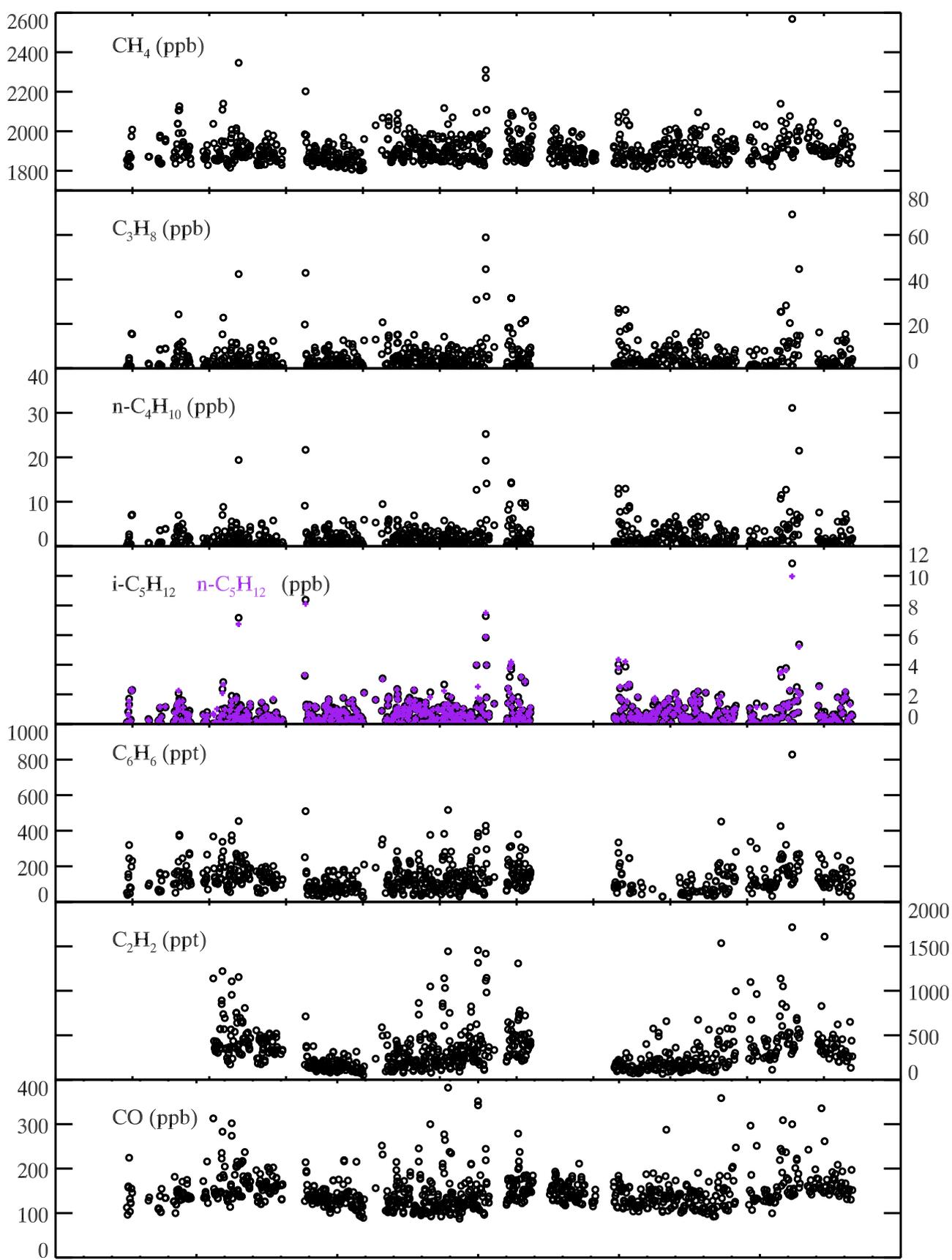
Sources: WRAP for year 2006 [Bar Ilan et al., 2008a], CDPHE for 2008 [CDPHE, personal communication], NEI 2005 [EPA, 2008], NEI 2008 [EPA, 2011b]

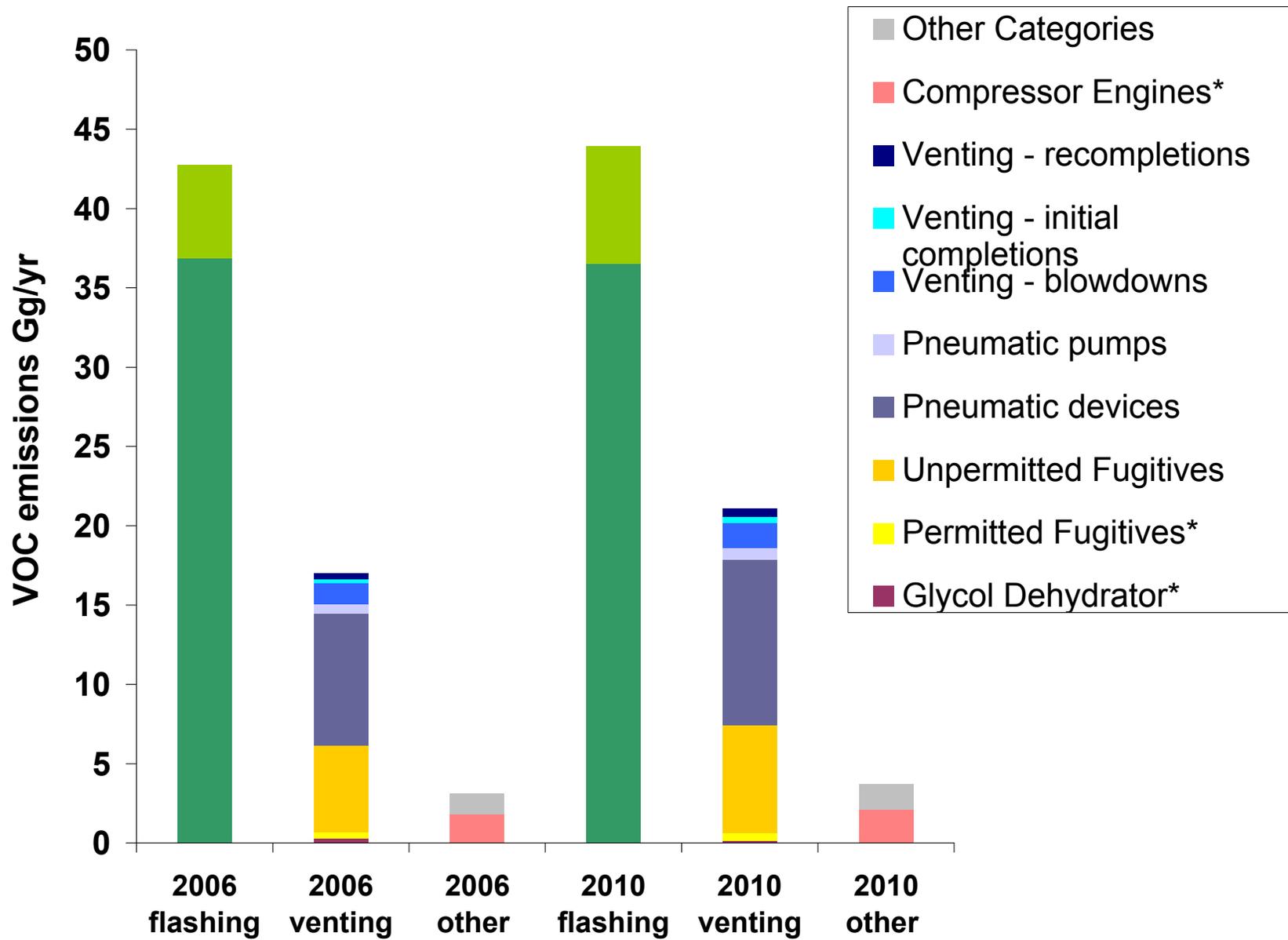
Species		Total VOC				Benzene		
Year		2006	2008	2008	2005	2008	2008	2005
Source		WRAP	CDPHE	NEI	NEI	CDPHE	NEI	NEI
unit		Gg/yr				Mg/yr		
On-Road			2533	2968	3532	95.4	121.4	160.1
Non-road + rail + aircraft			1596	1313	1626	44.2	36.0	45.9
Wood burning			232	-	187	8.8	-	5.7
Solvent utilization			201	1914	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
	Total	37015	20628	18810	-	61.8	44.6	1177.0
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

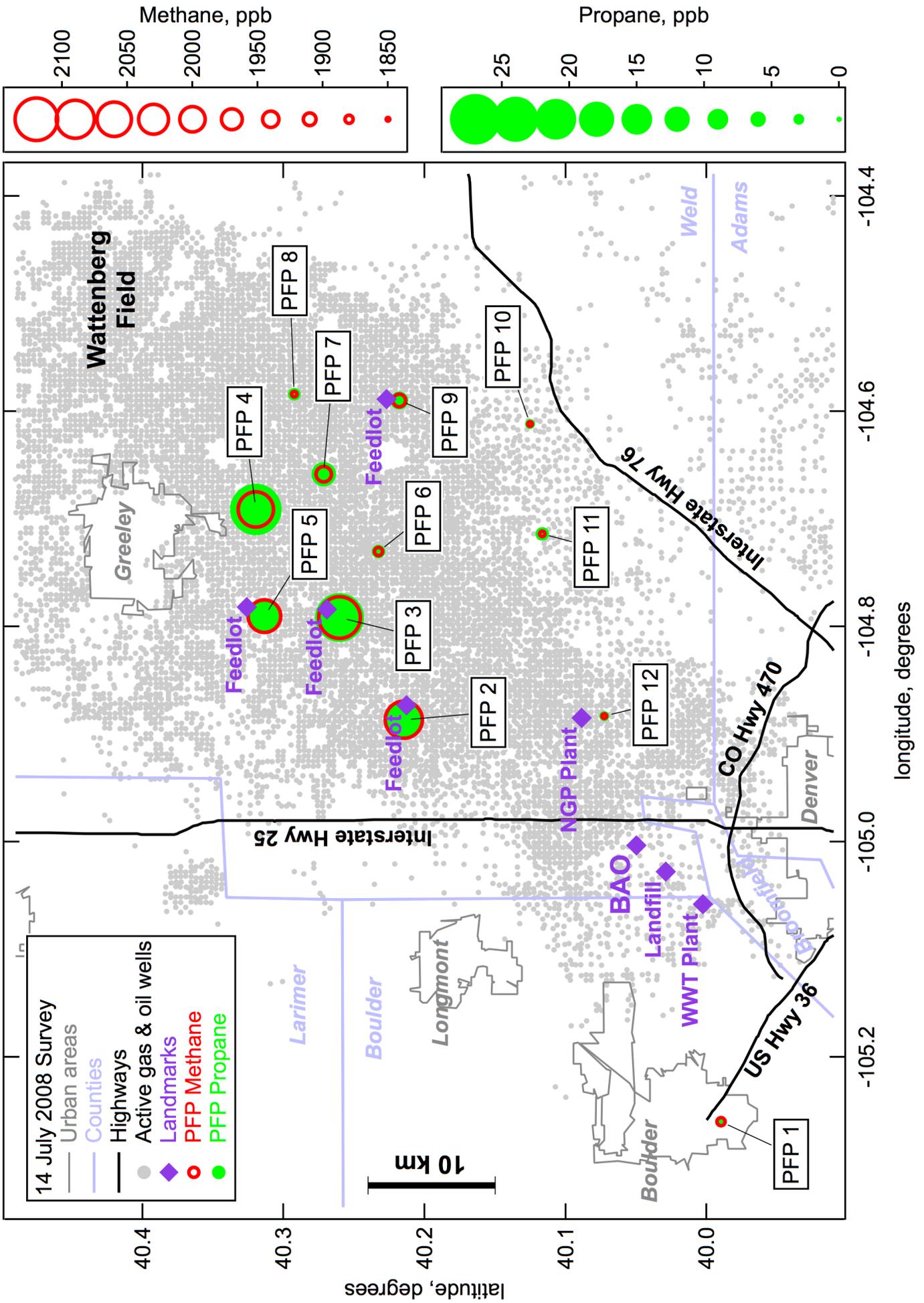
*Source categories included are: Pneumatic devices and pumps, small condensate tanks, fugitive emissions, heaters, process heaters, venting, truck loading, spills, NG production: flares, flanges and connections, and others.

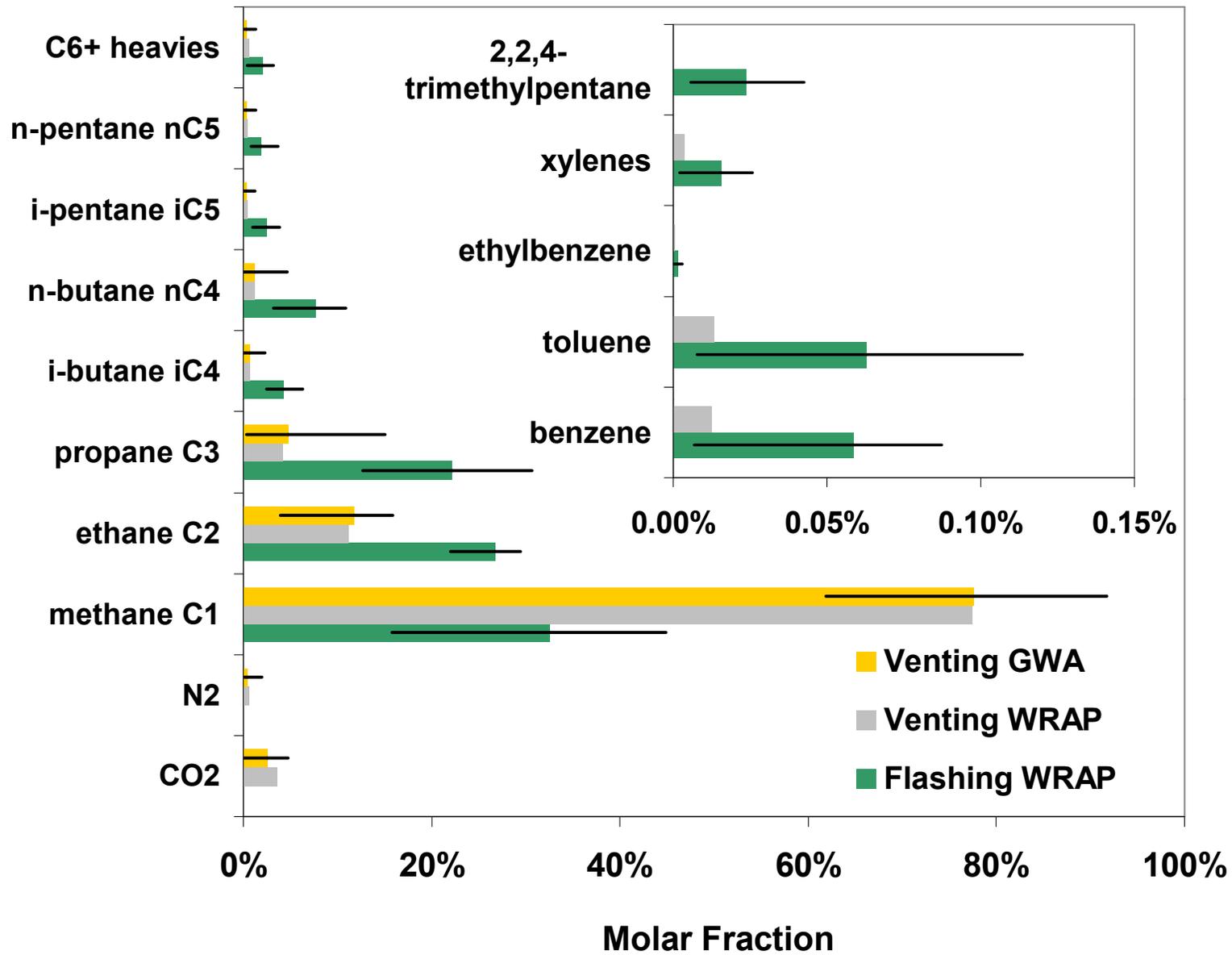
Table 4S: Inventory and measurement derived molar ratios for the various data sets plotted on Figure 9. Flashing emissions composition is based on EPA TANK model runs for 16 condensate tanks located in the DJB and sampled in 2002 [CDPHE, personal communication 2010]. Venting emissions composition is 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
WRAP Flashing emissions	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
WRAP Venting emissions		0.053	0.016	0.298	0.100	0.091	0.338	0.307	1.101
GWA raw gas	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
Bottom-up VOC inventory: WRAP Flashing + GWA Venting (mean profiles)		0.154	0.049	0.316	0.099	0.078	0.313	0.245	1.274
BAO NE -summer		0.104	0.051	0.447	0.141	0.150	0.297	0.315	0.957
Mobile Lab		0.095	0.050	0.510	0.185	0.186	0.423	0.414	1.046
Goldan et al.- all data		-	-	0.340	0.180	0.130	-	-	-
Goldan et al. C₃ source		-	-	0.625	-	-	0.600	0.380	-









FLASHING

Total VOC emitted in WRAP
2008: 41.3 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

2008=
average of
2006 and
2010
WRAP
estimates

VENTING

Total VOC emitted in WRAP
2008: 17.3 Gg

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

