

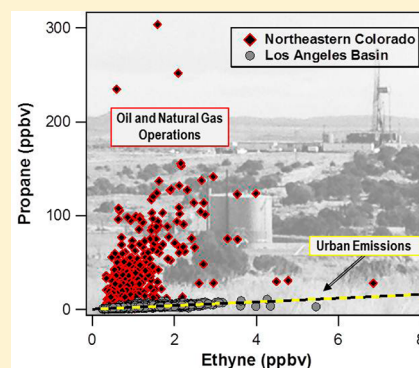
# Source Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado

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**S** Supporting Information

**ABSTRACT:** An extensive set of volatile organic compounds (VOCs) was measured at the Boulder Atmospheric Observatory (BAO) in winter 2011 in order to investigate the composition and influence of VOC emissions from oil and natural gas (O&NG) operations in northeastern Colorado. BAO is 30 km north of Denver and is in the southwestern section of Wattenberg Field, one of Colorado's most productive O&NG fields. We compare VOC concentrations at BAO to those of other U.S. cities and summertime measurements at two additional sites in northeastern Colorado, as well as the composition of raw natural gas from Wattenberg Field. These comparisons show that (i) the VOC source signature associated with O&NG operations can be clearly differentiated from urban sources dominated by vehicular exhaust, and (ii) VOCs emitted from O&NG operations are evident at all three measurement sites in northeastern Colorado. At BAO, the reactivity of VOCs with the hydroxyl radical (OH) was dominated by C<sub>2</sub>–C<sub>6</sub> alkanes due to their remarkably large abundances (e.g., mean propane = 27.2 ppbv). Through statistical regression analysis, we estimate that on average 55 ± 18% of the VOC–OH reactivity was attributable to emissions from O&NG operations indicating that these emissions are a significant source of ozone precursors.



## INTRODUCTION

Natural gas is a nonrenewable fossil fuel that currently provides 25% of the total energy consumed in the United States.<sup>1</sup> Of the domestic natural gas produced today, 46% is from “unconventional” reserves (i.e., shale and tight sands). Since 2005, there has been an increase in “shale gas” production, which is expected to continue through 2035.<sup>1</sup> The recent and projected increase in oil and natural gas (O&NG) extraction from “unconventional” reservoirs has heightened environmental concerns regarding increased emissions of the greenhouse gas methane (CH<sub>4</sub>),<sup>2–6</sup> exposure to air toxics,<sup>7</sup> and degradation of local air quality.<sup>4,8,9</sup>

Raw, unprocessed natural gas is approximately 60–90% CH<sub>4</sub> by molecule.<sup>10</sup> The remaining fraction differs by reservoir, and is typically composed of a mixture of volatile organic compounds (VOCs) including alkanes (paraffins), cycloalkanes (naphthenes), aromatics, nonhydrocarbon gases (e.g., CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, He, etc.), and water.<sup>10</sup> Certain byproducts in raw natural gas will condense to the liquid phase depending on their vapor pressure and the conditions under which they are processed, transported, or stored. Natural gas condensate is a low-density, hydrocarbon solution composed of hydrocarbons with a range of boiling points similar to gasoline, whereas crude oil is a higher-density fluid composed primarily of higher molecular weight, and less volatile hydrocarbons.<sup>10</sup> A single well may produce crude oil, raw natural gas, condensate, and water depending on the reservoir.

Specialized equipment located at each well site is designed to separate gases and oil from the liquid condensate and produced water. These byproducts represent a small fraction of the raw natural gas or crude oil composition; however, they are often concentrated in storage tanks at each well site until the liquids are removed by tanker truck or pipeline. The industrial equipment required for O&NG operations includes diesel trucks, drilling rigs, power generators, phase separators, dehydrators, storage tanks, compressors, and pipelines. Each piece of equipment used to install, operate, or service a well is a known or potential emission source of CH<sub>4</sub>, VOCs, nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>), and other gases or particulate matter (PM). Emissions of CH<sub>4</sub> and VOCs may occur at any stage of exploration and production by way of venting, flashing, flaring, or fugitive/nonpermitted emissions.<sup>11</sup> When there are thousands of wells concentrated in a relatively small area, emissions from these individual point sources can accumulate and represent a substantial area source of VOCs and other trace gases to the atmosphere.<sup>12</sup> The focus of this study is to characterize VOC emissions associated with O&NG operations in northeastern Colorado.

Enhanced levels of C<sub>2</sub>–C<sub>5</sub> alkanes have been observed in ambient air samples collected near areas of O&NG

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production.<sup>2,4,13</sup> These emissions were attributed to primary emissions from the oil and gas industry.<sup>2,4,13</sup> Based on current U.S. emissions inventories, “natural gas and petroleum systems” are estimated to be the largest anthropogenic source of CH<sub>4</sub> (38%), and O&NG production contributes 11.3% of anthropogenic VOC emissions.<sup>14,15</sup> Top-down estimates of CH<sub>4</sub> emission rates in Colorado and the southwestern U.S. indicate that current emission inventories of this potent greenhouse gas may be underestimated.<sup>2,4</sup> This suggests that the coemission of associated VOCs during the exploration for and the production of O&NG may also be underestimated.<sup>4,16</sup>

Emissions associated with O&NG operations can affect air quality. For example, collocated emissions of VOCs and NO<sub>x</sub> from oil and natural gas operations have been associated with high wintertime ozone levels (O<sub>3</sub> >150 ppbv hourly mean) in Wyoming’s Green River Basin<sup>9</sup> and Utah’s Uintah Basin.<sup>17</sup> As of 2007, portions of northeastern Colorado have been designated as a nonattainment area (NAA) for exceeding the 8-h federal O<sub>3</sub> standard of 0.08 ppmv during the summertime. The NAA encompasses the Denver metropolitan area and surrounding cities where roughly one-half of Colorado’s population resides, and Wattenberg Field where approximately 68% of the crude oil and 11% of the natural gas in Colorado is produced.<sup>18</sup> Since 2008, the O&NG industry in northeastern Colorado has been subjected to much tighter regulations aimed at reducing emissions of CH<sub>4</sub>, VOCs, and NO<sub>x</sub> in concurrence with the State Implementation Plan to reduce ambient O<sub>3</sub> levels.<sup>19</sup>

The primary objectives of this study are to (i) characterize primary VOC emissions from O&NG operations in northeastern Colorado, and (ii) estimate the relative contribution of VOC emissions from O&NG operations to OH reactivity, a metric that identifies the key reactive species that are involved in photochemical O<sub>3</sub> formation. This study expands on previous observations<sup>2,4</sup> by providing a more detailed chemical analysis of VOCs at higher temporal resolution. This enhanced level of detail is required to clearly distinguish the VOC source signature associated with O&NG operations from that associated with urban activities.

## METHODS

**Measurement Locations.** Wintertime measurements were conducted at NOAA’s Boulder Atmospheric Observatory (BAO, 40.05° N, 105.00° W) as part of the NACHTT (Nitrogen, Aerosol Composition, and Halogens on a Tall Tower) experiment from February 18 to March 7, 2011. BAO is ~4 km east of Erie, Colorado and ~30 km north of the Denver metropolitan area, and is located within the southwestern section of Wattenberg Field of the greater Denver-Julesburg Basin (see map in Supporting Information, Figure S1).<sup>2,20</sup> At the time of these measurements, there were >15,000 active oil and natural gas wells within a 100-km radius and 22 wells within a 0.8-km (0.5 mile) radius from BAO. The nearest well pad was 300 m to the west.

Two summertime studies were also conducted in northeastern Colorado. Measurements in Boulder, Colorado took place at NOAA’s David Skaggs Research Center ~15 km west of BAO (39.99° N, 105.26° W) from September 7 to 9, 2010 during the Fourmile Canyon wildfire that was burning nearby and intermittently impacting the site (Figure S1).<sup>21</sup> Measurements were conducted near Fort Collins, Colorado, ~80 km north of BAO in an agricultural research field operated by

Colorado State University (40.67° N, 105.00° W) from July 20 to 24, 2011.

For comparison, we include ship-borne measurements conducted in the Houston, Texas and Galveston Bay Area from August to September 2006 as part of TexAQSG/GoMACCS 2006 (Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study)<sup>22</sup> in addition to measurements conducted in Pasadena, California (34.14° N, 118.12° W) as part of CalNex 2010 (California Nexus) from May 15 to June 15, 2010.<sup>23</sup>

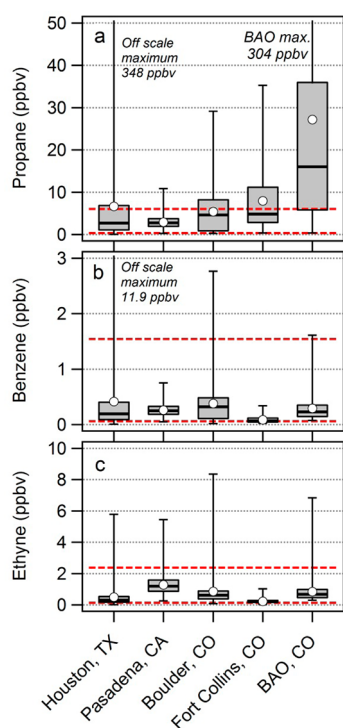
**Instrumentation.** VOCs were measured in situ by a custom-built, two-channel gas chromatograph–mass spectrometer (GC-MS).<sup>24</sup> An unheated PFA inlet (20 m length, 4 mm i.d.) was continuously flushed with 7 SLPM of ambient air so that the inlet residence time was <3 s. Inlet heights ranged from 8 m (at BAO) to 2.5 m (at Boulder and Fort Collins sites) above ground level. From the high-volume inlet flow, two 350-mL ambient air samples are simultaneously collected for 5 min. During sample acquisition, water, CO<sub>2</sub>, and O<sub>3</sub> are removed prior to cryogenically trapping the VOCs.<sup>12</sup>

The two samples collected in parallel are subsequently analyzed on their respective chromatographic columns. Channel 1 utilizes an Al<sub>2</sub>O<sub>3</sub>/KCl PLOT column ramped from 55 to 150 °C in 3.5 min to separate the C<sub>2</sub>–C<sub>5</sub> hydrocarbons. The C<sub>5</sub>–C<sub>11</sub> hydrocarbons, oxygen-, nitrogen-, and halogen-containing VOCs are analyzed on Channel 2, which consists of a semipolar DB-624 capillary column ramped from 38 to 130 °C in 11 min. The effluent from each column is sequentially analyzed by a linear quadrupole mass spectrometer (Agilent 5973N). The combined sample acquisition (5 min) and analysis (25 min) cycle repeats every 30 min. The limit of detection, precision, and accuracy are compound dependent, but are typically better than 0.010 ppbv, 15%, and 25%, respectively.<sup>22,24</sup> Each compound reported is individually calibrated for using dynamic dilutions of several independent, multicomponent gas-phase standards.<sup>22</sup>

## RESULTS AND DISCUSSION

**Comparison of U.S. cities.** Measurements of propane, benzene, and ethyne in northeastern Colorado are compared to those of other U.S. cities in order to highlight the influence of various emission sources on the observed mixing ratios of these compounds (Figure 1). Statistics for observations at BAO are summarized in Table 1 (see Supporting Information, Table S1 for statistics for all VOCs reported).

The mean mixing ratio of propane at BAO (27 ± 1 ppbv, mean ± standard error of mean) exceeds the range reported for 28 U.S. cities,<sup>25</sup> indicating the presence of a large propane source that is unique to the area. The mean propane level at BAO is 3–9 times larger than the observed means in the highly industrialized area of Houston, TX (6.7 ± 0.8 ppbv),<sup>22</sup> the large urban area of Pasadena, CA (2.92 ± 0.03 ppbv), and the two other Colorado sites (Boulder = 5.4 ± 0.5 ppbv, Fort Collins = 8.0 ± 0.5 ppbv) that lie outside of Wattenberg Field (Figure S1). Urban propane sources include the use of liquefied petroleum gas (LPG) and a minor source from fossil fuel combustion.<sup>26,27</sup> Propane is produced during biomass burning (BB); however, the maximum observed value in Boulder was not associated with BB and there was no evidence of BB affecting the other data sets. Industrial sources of propane include raw natural gas processing and use as a feedstock in the petrochemical industry. The maximum propane level at BAO (304 ppbv) is most comparable to Houston (347 ppbv), where



**Figure 1.** Box and whisker plots (maximum, 75th, 50th, 25th percentiles, and minimum) including mean values (open circles) for (a) propane, (b) benzene, and (c) ethyne. Range of mean values for 28 U.S. cities (Baker et al.<sup>25</sup>) is indicated by red dashed lines.

several fossil fuel refineries and petrochemical facilities are located.

Mean mixing ratios for benzene and ethyne for all data sets are within the range reported for 28 U.S. cities.<sup>25</sup> Houston has the highest mean ( $0.42 \pm 0.03$  ppbv) and maximum (11.9 ppbv) benzene due to the industrial sources in the area.<sup>22</sup> Pasadena has the highest mean ethyne ( $1.27 \pm 0.01$  ppbv) due to the preponderance of on-road combustion sources. The maximum values for benzene (2.77 ppbv) and ethyne (8.36 ppbv) in Boulder were observed in biomass burning plumes. BAO and Fort Collins have elevated mean propane levels, but mean benzene and ethyne levels similar to those of other U.S. cities (Figure 1), indicating that both these sites are influenced by an area propane source that is unrelated to combustion.

At BAO, the  $C_2$ – $C_7$  alkanes and  $C_5$ – $C_6$  cycloalkanes are also highly abundant and are tightly correlated with propane (coefficients of determination,  $r_{\text{propane}} > 0.90$ ) but less so with ethyne ( $r_{\text{ethyne}} < 0.78$ , Table 1). This is in accordance with long-term measurements at the top of the 300-m tower at BAO by Pétron et al. who showed that the  $C_3$ – $C_5$  alkanes (i) are significantly enhanced compared to other measurements on tall towers in the U.S., (ii) strongly correlate with one another, but do not always correlate well with combustion tracers such as carbon monoxide, and (iii) are enhanced by a factor of  $\sim 1.75$  in the winter compared to summer due to longer photochemical lifetimes and more stable/stratified boundary layer conditions during the colder winter months.<sup>2</sup> In comparison, the 2011 wintertime propane levels at BAO are  $>3$  times greater than the summertime levels in Boulder and Fort Collins suggesting that enhancements in propane at BAO cannot be explained by seasonal differences alone. The strong correlations of the  $C_2$ –

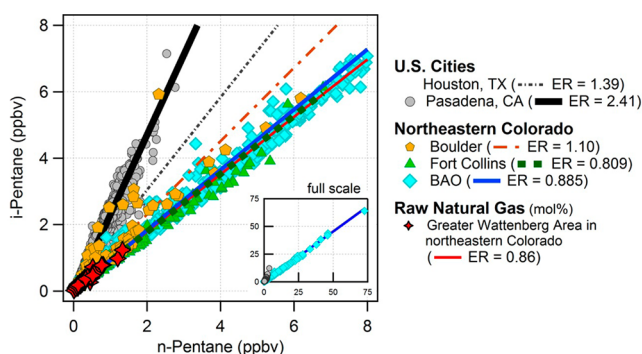
**Table 1. Statistics and Analysis Results of a Subset of VOCs Measured at the Boulder Atmospheric Observatory (BAO) in Northeastern Colorado February 18 to March 7, 2011 ( $n = 554$  Samples)<sup>a</sup>**

compound	mean (ppbv)	SD (1 sigma)	median (ppbv)	min. (ppbv)	max. (ppbv)	$r_{\text{propane}}$	$r_{\text{ethyne}}$	bkng (ppbv)	$ER'_{\text{propane}}$ (ppbv [ppbv $C_3H_8$ ] <sup>-1</sup> )	$ER'_{\text{ethyne}}$ (ppbv [ppbv $C_2H_2$ ] <sup>-1</sup> )	mean O&NG contrib. (%)
alkanes											
ethane	35	38	22	1.6	300	0.98	0.61	1.6	1.090	6.6	72
propane	27	33	17	0.58	304	1.00	0.56	0.58	1	0	90
<i>i</i> -butane	6.0	8.5	2.9	0.078	85	0.99	0.55	0.078	0.243	0.00	93
<i>n</i> -butane	14	19	7.3	0.11	184	0.99	0.54	0.11	0.563	0.00	95
<i>i</i> -pentane	4.2	5.9	2.0	0.038	64	0.97	0.55	0.038	0.168	0.00	95
<i>n</i> -pentane	4.7	6.7	2.2	0.028	73	0.97	0.54	0.028	0.190	0.00	96
<i>n</i> -hexane	1.1	1.3	0.6	0.014	12	0.95	0.60	0.014	0.0348	0.213	78
<i>n</i> -heptane	0.32	0.35	0.19	<LOD	2.8	0.92	0.63	0	0.0087	0.096	73
cycloalkanes											
methylcyclopentane	1.3	1.2	1.0	0.030	6.7	0.97	0.78	0.030	0.028	0.28	68
cyclohexane	0.30	0.28	0.20	0.0063	1.4	0.97	0.78	0.0063	0.0062	0.069	67
methylcyclohexane	0.28	0.34	0.17	0.0045	2.6	0.91	0.69	0.0045	0.0074	0.065	72
aromatics											
benzene	0.29	0.21	0.23	0.075	1.6	0.88	0.79	0.075	0.00428	0.166	32
toluene	0.30	0.29	0.21	0.016	2.2	0.76	0.85	0.016	0.0038	0.308	31
<i>m</i> - and <i>p</i> -xylenes	0.11	0.10	0.075	0.005	0.61	0.75	0.86	0.005	0.00099	0.130	23
<i>o</i> -xylene	0.03	0.03	0.023	<LOD	0.19	0.71	0.87	0	0.00026	0.0488	20
alkenes and alkynes											
ethyne	0.84	0.61	0.67	0.30	6.8	0.56	1.00	0.3	0	1	0
ethene	0.74	0.79	0.49	0.052	6.6	0.60	0.94	0.052	0.0025	1.14702	8.6
propene	0.16	0.19	0.09	0.012	1.5	0.47	0.83	0.012	0.0001	0.26195	1.8

<sup>a</sup><LOD = Below limit of detection.  $r_{\text{propane}}$  = Coefficient of determination for observed VOC to propane enhancement ratio.  $r_{\text{ethyne}}$  = Coefficient of determination for observed VOC to ethyne enhancement ratio.  $ER'_{\text{propane}}$  = Emission ratios derived from the multivariate regression analysis for each VOC relative to propane.  $ER'_{\text{ethyne}}$  = Emission ratios derived from the multivariate regression analysis for each VOC relative to ethyne. Mean O&NG contrib. = Mean contribution of VOC emissions from O&NG expressed as a percentage.

$C_7$  alkanes and  $C_5$ – $C_6$  cycloalkanes with propane suggest that these compounds (i) have a similar source as propane, and (ii) there was minimal photochemical processing during the wintertime study at BAO. One would expect to see greater variability (smaller  $r_{\text{propane}}$ ) if there were other VOC sources with disparate emission ratios or from the preferential removal of the more reactive VOCs (e.g., heptane) as an air mass is photochemically aged.

**Source Signature of O&NG Operations in Northeastern Colorado.** The magnitude of observed VOC mixing ratios (Figure 1) will be affected by boundary layer conditions, the proximity to emission sources, and the extent of photochemical processing. To minimize these effects, we utilize the iso-pentane to *n*-pentane ( $iC_5/nC_5$ ) enhancement ratio to identify the VOC source signature of O&NG operations. The  $iC_5/nC_5$  enhancement ratio is equal to the slope of a linear 2-sided fit of an iso-pentane to *n*-pentane correlation plot (Figure 2). This



**Figure 2.** Correlation plots of iso-pentane versus *n*-pentane for BAO, Fort Collins, and Boulder measurement sites in northeastern Colorado. Data from other U.S. cities including Houston, Texas (TexAQs 2006, individual data points not shown) and Pasadena, California (CalNex 2010) are included for comparison. Raw natural gas samples from the Greater Wattenberg Area of the Denver-Julesburg Basin are plotted as mole percent. Enhancement ratios (ER) are determined by linear 2-sided fits. Inset shows the full range of ambient observations.

ratio is largely independent of air mass mixing and dilution as both species are similarly affected;<sup>28</sup> therefore, the ratio will not be unduly influenced by the boundary layer conditions or the proximity to emission sources. The  $iC_5/nC_5$  ratio will also be minimally affected by photochemical processing (which is minimal for the wintertime study) as both species have similar reaction rate coefficients with the hydroxyl radical.<sup>29</sup>

In Figure 2, we compare the observed  $iC_5/nC_5$  enhancement ratios for the same set of U.S. cities included in Figure 1. Pasadena has the highest  $iC_5/nC_5$  ratio of  $2.41 \pm 0.02$  ( $r = 0.94$ ). Literature values for the  $iC_5/nC_5$  ratio for gasoline-related sources range from 2.3 for the composition of liquid gasoline blended for wintertime use in California<sup>30</sup> to 3.80 for the composition of gasoline vapors.<sup>30,31</sup> The  $iC_5/nC_5$  ratio in Pasadena lies within this range and most closely matches the values observed in a Los Angeles tunnel study ( $iC_5/nC_5 = 2.45$ )<sup>32</sup> indicating that emissions from gasoline-fueled vehicles are the main sources of these compounds in Pasadena.

The  $iC_5/nC_5$  ratios observed at BAO ( $0.885 \pm 0.002$ ,  $r = 0.998$ ), Fort Collins ( $0.809 \pm 0.008$ ,  $r = 0.990$ ), and Boulder ( $1.10 \pm 0.05$ ,  $r = 0.91$ ) are significantly lower than that observed in Pasadena indicating that gasoline is not the primary source of these compounds in these data sets. The  $iC_5/nC_5$

enhancement ratio for raw natural gas in the Greater Wattenberg Area of the Denver-Julesburg Basin is  $0.86 \pm 0.02$  ( $r = 0.97$ ),<sup>33</sup> which is statistically equivalent to that observed in ambient air at BAO. The identical  $iC_5/nC_5$  ratios observed in ambient air at BAO and raw natural gas samples collected in Wattenberg Field strongly suggest that O&NG operations in the area are the dominant source of these compounds. For Boulder, the individual data points lie on or between the  $iC_5/nC_5$  ratios for Pasadena and BAO, indicating that both urban activities and O&NG operations impacted air masses in Boulder.<sup>34</sup> Our analysis shows that all three measurement sites in Colorado were influenced by VOC emissions from O&NG operations concentrated in Wattenberg Field of the greater Denver-Julesburg Basin.

The  $iC_5/nC_5$  ratio appears to be similar for different O&NG reservoirs. For example, Gilman et al. reported intercepting an air mass influenced by natural gas activities on Russia's Kola Peninsula with an  $iC_5/nC_5$  ratio of 0.89.<sup>24</sup> Riaz et al. reported an  $iC_5/nC_5$  ratio of 0.84 for natural gas condensate from a reservoir in the North Sea.<sup>35</sup> The composition of the Macondo reservoir fluid that escaped into the Gulf of Mexico after the Deepwater Horizon explosion had an  $iC_5/nC_5$  ratio of 0.82.<sup>36</sup> Additionally, iso-pentane and *n*-pentane have boiling points, vapor pressures, and reaction rate coefficients similar to the hydroxyl radical so that the  $iC_5/nC_5$  ratio will be less susceptible to perturbations during initial processing stages or photochemical oxidation upon release to the atmosphere. The  $iC_5/nC_5$  ratio appears to be a robust indicator of the influence of O&NG operations.

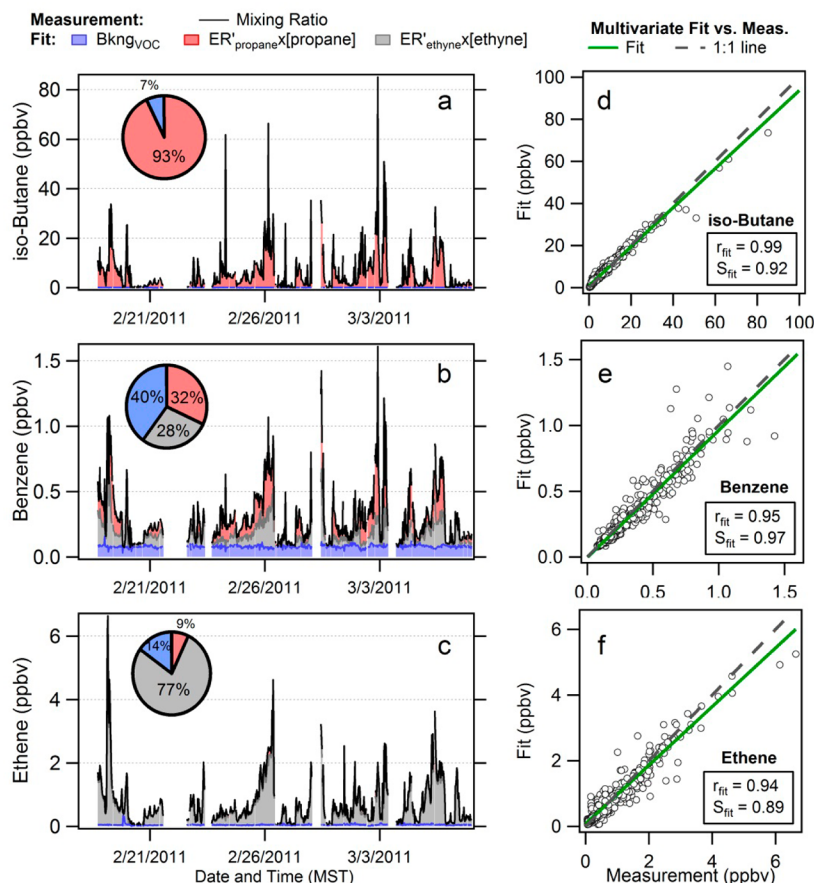
**Source Apportionment of VOCs at BAO in Northeastern Colorado.** At BAO, the  $C_2$ – $C_7$  alkanes and several of the cycloalkanes are tightly correlated with propane ( $r_{\text{propane}} > 0.90$ , Table 1), a predominant byproduct in O&NG production, whereas the  $C_9$  aromatics and ethene are more tightly correlated with ethyne ( $r_{\text{ethyne}} > 0.90$ ), a combustion tracer associated with urban activities. We use these two species in a multivariate regression analysis to show that the variability in propane and ethyne can be used to explain the observed variability of the other VOCs. This allows us to (i) characterize the emission source profiles of various hydrocarbons associated with these sources and (ii) estimate the relative contribution of each emission source.

The expression used for the multivariate analysis is given by

$$[\text{VOC}] = Bkgd_{\text{VOC}} + \{ER'_{\text{propane}} \times [\text{propane}_0]\} + \{ER'_{\text{ethyne}} \times [\text{ethyne}_0]\} \quad (1)$$

where [VOC] is the observed mixing ratio of the VOC to be fitted, and  $Bkgd_{\text{VOC}}$  is equal to the minimum observed values (Table S1),  $[\text{propane}_0]$  and  $[\text{ethyne}_0]$  are the observed propane and ethyne mixing ratios minus the minimum observed values for propane (0.58 ppbv) and ethyne (0.30 ppbv), respectively. The expression (eq 1) is solved for  $ER'_{\text{propane}}$  and  $ER'_{\text{ethyne}}$  which represent the derived values of the VOC emission ratio relative to propane, and the VOC emission ratio relative to ethyne, respectively. Equation 1 does not include terms for photochemical production/loss as we assume photochemistry was negligible (see discussion above).

One limitation of this simplified source apportionment analysis is that  $ER'_{\text{propane}} = 1$  and  $ER'_{\text{ethyne}} = 0$  for propane and  $ER'_{\text{propane}} = 0$  and  $ER'_{\text{ethyne}} = 1$  for ethyne by definition. For explicit quantification of  $ER'_{\text{propane}}$  and  $ER'_{\text{ethyne}}$ , the two variables ( $[\text{propane}_0]$  and  $[\text{ethyne}_0]$ ) should be independent of



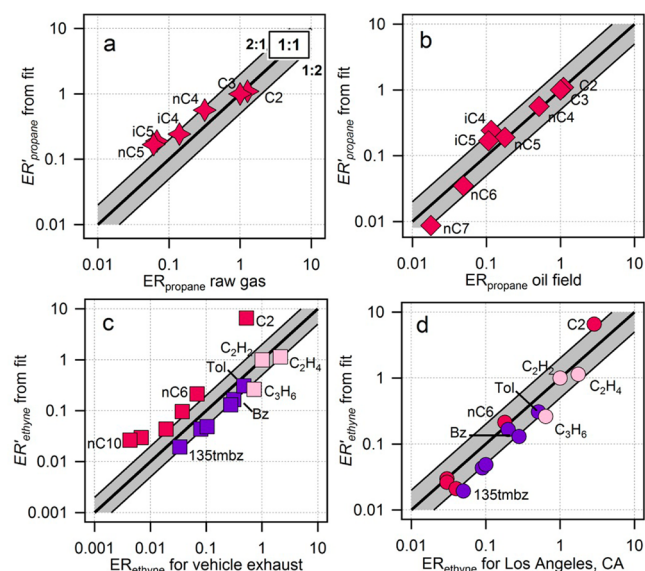
**Figure 3.** Left column shows the time series of the measured mixing ratios at BAO and mixing ratios derived from the multivariate fit for (a) iso-butane, (b) benzene, and (c) ethene. The time series of the derived mixing ratio and the pie charts are colored by the contribution of each term of the multivariate fit analysis. The pie charts depict the mean contribution of each term. The right column shows correlation plots of the derived versus the measured mixing ratios for (d) iso-butane, (e) benzene, and (f) ethene where  $r_{fit}$  is the linear correlation coefficient and  $S_{fit}$  is the slope of the linear 2-sided fit.

one another. Raw and processed natural gas contains propane but not ethyne; however, combustion of fossil fuels often produces small amounts of propane relative to ethyne. Propane to ethyne emission ratios range from  $<0.10$  for tailpipe emissions<sup>32</sup> to 1.2–2.5 for urban areas that may include natural gas sources.<sup>37</sup> These ratios are significantly less than the observed propane to ethyne enhancement ratio at BAO ( $ER_{ethyne} = 97$ , see Table S1 and Table of Contents figure) indicating that ethyne sources will have a small contribution to propane for the vast majority of the samples.

In Figure 3a–f, we compare the observed mixing ratios with those derived from the multivariate analysis for three example compounds: iso-butane, benzene, and ethene. The time series of the derived mixing ratios are colored by the contribution from each of the three terms of the multivariate fit, and the pie charts depict the mean contribution of each term. The variability of the three species is well represented by the multivariate fit ( $r_{fit} > 0.94$ , Figure 3d–3f). For iso-butane, the correlation with propane is so strong ( $r_{propane} = 0.99$ , Table 1) that the propane term ( $ER'_{propane} \times [propane]$ ) completely dominates (Figure 3a). Benzene has significant contributions from both the propane and ethyne terms indicating benzene emissions are from more than one source (Figure 3b), similar to the findings of Pétron et al.<sup>2</sup> For ethene, the ethyne term dominates indicating combustion-related sources are the primary source of this compound.

Results of the multivariate fit for all VOCs reported are compiled in Tables 1 and S1. The multivariate analysis using only propane and ethyne as variables adequately captures the observed variability ( $r_{fit} > 0.80$ ) in the alkanes, cycloalkanes, aromatics, and alkenes including isoprene (see Table S1). The other biogenic VOCs and oxygenated VOCs are not tightly correlated with either propane or ethyne resulting in a poorer fit ( $r_{fit} < 0.80$  and  $slope_{fit} < 0.65$ ) indicating that these compounds have additional sources and/or natural variabilities that are independent of propane and ethyne emissions and will therefore be excluded from further discussion.

Figure 4 shows the comparison of the derived emission ratios ( $ER'_{propane}$  and  $ER'_{ethyne}$ ) to various emission sources.  $ER'_{propane}$  is compared to VOC to propane ratios determined from the composition of raw natural gas in the Greater Wattenberg Area<sup>33</sup> ( $ER_{propane}$  raw gas, Figure 4a) and to ambient air sampled downwind of an oil storage tank with a working oil well as reported by Katzenstein et al.<sup>4</sup> (Figure 4b). The emission ratios for a majority of the compounds in all three data sets agree within a factor of 2; however, the derived propane source profile (i.e., the composite of the individual  $ER'_{propane}$ ) agrees more closely with the ambient air profile from Katzenstein et al. In Figure 4a, the derived ethane to propane emission ratio is lower in ambient air than expected from the raw natural gas composition ( $ER'_{propane} < ER_{propane}$  raw gas), while the derived emissions of the  $C_4$ – $C_5$  alkanes relative to



**Figure 4.** Comparison of VOC to propane emission ratios derived from the multivariate fit ( $ER'_{\text{propane}}$ ) versus VOC to propane ratios (a) for raw natural gas in the Greater Wattenberg Area of the Denver-Julesburg Basin and (b) reported by Katzenstein et al. for a sample downwind of an oil storage tank with a working oil well. Comparison of the VOC to ethyne emission ratios derived from the multivariate fit ( $ER'_{\text{ethyne}}$ ) to the VOC to ethyne emission ratios published by (c) Schauer et al. for gasoline-powered motor vehicles and (d) Borbon et al. for urban Los Angeles, California. The 2:1, 1:1, and 1:2 lines are shown in all panels, where the shaded area represents a factor of 2 from unity. Each marker represents a different VOC. Alkanes are maroon and are identified by carbon number (e.g., C2 = ethane, iC4 = iso-butane). Aromatics are purple (Bz = benzene, Tol = toluene, and 135tmbz = 1,3,5-trimethylbenzene). Alkenes and ethyne are pink and are identified by empirical formulas (e.g.,  $C_2H_2$  = ethyne).

propane are higher than  $ER_{\text{propane}}$  raw gas. This suggests that the C2–C5 alkanes observed in ambient air at BAO may not be only from direct venting of raw natural gas to the atmosphere, but from the emission of raw natural gas components after some stage of initial processing where the lighter, more volatile components have been partially separated from the heavier, less volatile components; a common industry practice called condensate stabilization.<sup>38</sup> These findings are consistent with previous observations by Pétron et al. at BAO.<sup>2</sup> We note that the iC<sub>5</sub>/nC<sub>5</sub> ratio (see previous discussion) would not be affected by condensate stabilization because they have similar vapor pressures.

The derived  $ER'_{\text{ethyne}}$  values are compared to published VOC to ethyne emission ratios measured in gasoline-powered motor vehicle exhaust<sup>27</sup> (Figure 4c) and in urban Los Angeles<sup>23</sup> (Figure 4d). For the C<sub>3</sub>–C<sub>5</sub> alkanes,  $ER'_{\text{ethyne}}$  derived for BAO is 0 because the fit is overwhelmed by the propane source term; therefore, these compounds do not appear in Figure 4c–4d due to the logarithmic scale. The  $ER'_{\text{ethyne}}$  for the majority of the C<sub>6</sub>–C<sub>11</sub> alkanes, C<sub>6</sub>–C<sub>9</sub> aromatics, and C<sub>2</sub>–C<sub>3</sub> alkenes agree with literature values for ambient air in the urban area of Los Angeles. The derived ethane to ethyne emission ratio is greater than that expected for vehicle exhaust and in Los Angeles ( $ER'_{\text{ethyne}} > ER_{\text{ethyne}}$ ) suggesting that we are overestimating the urban emission ratio of ethane at BAO by more than a factor of 2.

From these comparisons, we conclude that a large fraction of the VOC variability observed at BAO can be explained by a

linear combination of two emission sources. The first source is proportional to propane, has a composition that is similar to that of natural gas itself and to emissions from condensate tanks in Texas and Oklahoma, and is therefore attributed to O&NG operations in the area surrounding BAO. The second source is proportional to ethyne, has a composition similar to that of urban emissions and is therefore attributed to traffic-related sources in the area. The relative contribution of O&NG operations to the observed mixing ratios can now be estimated from eq 1 by a ratio of the three components of the multivariate analysis as shown:

$$\begin{aligned} \text{O\&NG Fraction} = & \left( \{ER'_{\text{propane}} \times [\text{propane}_0]\} \right) \\ & / \left( \text{Bkgd}_{\text{VOC}} + \{ER'_{\text{propane}} \right. \\ & \times [\text{propane}_0]\} \\ & \left. + \{ER'_{\text{ethyne}} \times [\text{ethyne}_0]\} \right) \quad (2) \end{aligned}$$

The mean O&NG fractional contributions for those VOCs included in the subsequent analysis section are compiled in Tables 1 and S1. From this analysis, O&NG operations in northeastern Colorado during the wintertime study at BAO are identified as the dominant source of C<sub>2</sub>–C<sub>8</sub> alkanes and C<sub>5</sub>–C<sub>8</sub> cycloalkanes and a minor source of C<sub>6</sub>–C<sub>8</sub> aromatics and alkenes compared to urban emission sources.

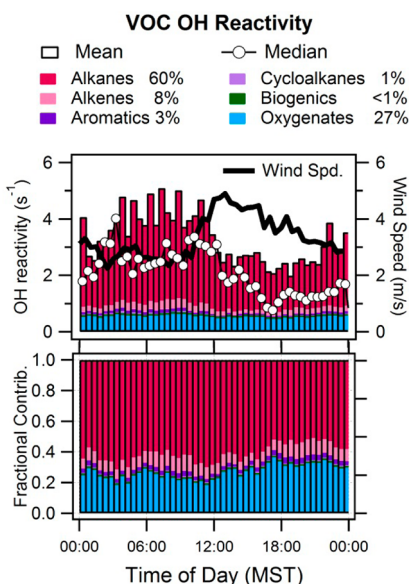
**OH Reactivity.** The primary source of O<sub>3</sub> in the lower troposphere is the photolysis of NO<sub>2</sub> that has been produced from peroxy radical (ROO•) oxidation of NO. In typical urban air masses, a complex, photoinitiated oxidation sequence that involves reactions between NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) and reactive VOCs provides the peroxy radicals required for the fast and efficient photochemical formation of O<sub>3</sub>. Oxidation of VOCs by the hydroxyl radical (•OH) is the initial step in the process. OH reactivity is a simple metric that identifies the key reactants that most readily form ROO•, and therefore, are most likely to play a key role in the potential formation of O<sub>3</sub>. The actual amount of O<sub>3</sub> produced is dependent on the relative abundances of NO<sub>x</sub> and VOCs, which affect the overall oxidation mechanism.

The OH reactivity for the VOCs measured at BAO was calculated using

$$R_{\text{OH+VOC}} = \sum (k_{\text{OH+VOC}} \times [\text{VOC}]) \quad (3)$$

where  $R_{\text{OH+VOC}}$  is the sum of the products of the temperature and pressure dependent reaction rate coefficient,  $k_{\text{OH+VOC}}$ , and the VOC concentration, [VOC], in molecules cm<sup>-3</sup>. The campaign mean and median  $R_{\text{OH+VOC}}$  for the wintertime measurements at BAO are  $3 \pm 3 \text{ s}^{-1}$  and  $2 \text{ s}^{-1}$ , respectively. We compare this to the Texas study where the median  $R_{\text{OH+VOC}}$  ranged from  $0.28 \text{ s}^{-1}$  in the remote marine boundary layer to  $3.02 \text{ s}^{-1}$  near Houston in the summertime.<sup>22</sup>

The diurnal profile of the mean and median  $R_{\text{OH+VOC}}$  (Figure 5a) shows that the OH reactivity is greater in the first half of the day (00:00–12:00 MST). The decrease around 12:00 MST is associated with an increase in both wind speed and boundary layer depth, which effectively dilutes the reactants resulting in a reduction of  $R_{\text{OH+VOC}}$ . The fractional contribution of each VOC class to  $R_{\text{OH+VOC}}$  (Figure 5b) is independent of the boundary layer dynamics.  $R_{\text{OH+VOC}}$  is dominated by the alkanes, which account for 60% of the OH reactivity on average. Reactivity of the oxygenated VOCs (OVOCs), which is dominated by



**Figure 5.** (a) Diurnal profile of the VOC OH reactivity at BAO. The mean VOC OH reactivity is represented by the height of bar and is colored by the contribution from each compound class. Diurnal profiles of the median VOC OH reactivity are given by the markers and mean wind speed is given by the thick black line. (b) The average fractional contribution of each VOC compound class as a function of time of day. The campaign integrated contributions for each compound class are listed as percentages in the figure key.

acetaldehyde and ethanol, accounts for 27% of the VOC reactivity. Alkenes, cycloalkanes, and biogenics are generally more reactive than alkanes; however, their relatively low abundances compared to the alkanes make them only minor contributors to  $R_{\text{OH}+\text{VOC}}$ .

We can estimate the contribution of hydrocarbons emitted from O&NG activities by applying the O&NG fraction from the combination of eqs 2 and 3.

$$R_{\text{OH}+\text{VOC}}^{\text{O\&NG}} = \sum (k_{\text{OH}+\text{VOC}} \times [\text{VOC}] \times \text{O\&NG fraction}) \quad (4)$$

The mean contribution of VOCs attributed to O&NG activities ( $R_{\text{OH}+\text{VOC}}^{\text{O\&NG}}$ ) is  $55 \pm 18\%$  (1 sigma deviation) for the BAO data set. This large contribution directly pertains to the elevated concentrations of the light alkanes, which are known byproducts of and are attributed to O&NG production. The fraction of reactivity due to emissions from O&NG emissions varies strongly among different air masses. The distribution of calculated  $R_{\text{OH}+\text{VOC}}^{\text{O\&NG}}$  values is included in Figure S2 along with a wind directional analysis. Samples with the highest  $R_{\text{OH}+\text{VOC}}^{\text{O\&NG}}$  occur when winds arrive at BAO from the northeast sector where the majority of the O&NG wells are located (Figure S2). Only 4% of all samples at BAO had high  $R_{\text{OH}+\text{VOC}}^{\text{O\&NG}}$  and were from the western sector where the nearest wells are located indicating that they were not the dominant O&NG source at BAO.

The results of this analysis indicate that VOC emissions from O&NG production in northeastern Colorado are a significant source of  $\text{O}_3$ -precursors in this region. The contribution from O&NG operations is expected to decrease somewhat during the summertime " $\text{O}_3$  season" as the relative importance of biogenic VOCs may increase. We have recently conducted summertime measurements at BAO to investigate the relative

role of biogenic VOCs and investigate the products formed during active photochemistry in order to identify the important VOC precursors, which will be detailed in a forthcoming analysis.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Data from the 2011 wintertime study at BAO (NACHTT) are available at <http://www.esrl.noaa.gov/csd/groups/csd7/measurements/2011NACHTT/Tower/DataDownload/>. An expanded table of statistics and analysis results for all 53 VOCs reported in included in Table S1. Additional figures include a detailed map of the measurement sites in northeastern Colorado (Figure S1) and the distribution of calculated  $R_{\text{OH}+\text{VOC}}^{\text{O\&NG}}$  values and associated wind rose frequency plots (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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