RESEARCH ARTICLE

Atmospheric oil and natural gas hydrocarbon trends in the Northern Colorado Front Range are notably smaller than inventory emissions reductions

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From 2008 to mid-2016, there was more than a 7-fold increase in oil production and nearly a tripling of natural gas production in the Colorado Denver–Julesburg Basin (DJB). This study utilized air samples collected at the Boulder Atmospheric Observatory (BAO) tower in southwestern Weld County in the DJB to investigate atmospheric mole fraction trends of methane and volatile organic compounds (VOCs). Elevated methane and propane mole fractions and low values (<1) in the ratio of i-pentane to n-pentane at BAO were found to be associated with flow patterns that transport air from the northeast (NE) to east (E) sector to the site, the direction where the primary locations of oil and natural gas (O&NG) extraction and processing activities are located. Median mole fractions of the O&NG tracer propane at BAO were 10 times higher than background values when winds came from the NE quadrant. This contrasts with lower mole fractions of O&NG-related constituents in air parcels arriving at BAO from the south, the direction of the major urban area of Denver. None of O&NG tracers, for example, methane and propane, show statistically significant trends in mole fraction (relative to the background) over the study period in air transported from the DJB. Also, longer term acetylene mole fraction changes were not seen in NE quadrant or south sector samples. A significant decline in the mole fraction ratio of i-pentane to n-pentane in the NE sector data provides evidence of an increasing influence of O&NG on the overall composition of VOCs measured at BAO, a change not seen in measurements from the south (urban) sector. These results suggest that O&NG emissions and resulting atmospheric mole fractions have remained relatively constant over 2008–2016. The behavior in the observations is in contrast to the most recent VOC emissions inventory. While the inventory projects O&NG total VOC emission reductions between 2011 and 2020, of –6.5% per year despite the large production increases, the best estimate of the propane emission rate of change for the DJB-filtered data during 2008–2016 is much smaller, that is, –1.5% per year.

Keywords: Hydrocarbons, Methane, Oil and natural gas, Boulder Atmospheric Observatory, O&NG emissions regulations, VOCs

Introduction

The Northern Colorado Front Range (NCFR) located north of the city of Denver includes the midsize municipalities of Boulder, Fort Collins, Longmont, Loveland, and Greeley and encompasses the Denver–Julesburg oil and natural gas (O&NG) basin (DJB) lying primarily in Weld County (**Figure 1**). With the advent of hydraulic fracturing and horizontal drilling techniques in the 2000s, O&NG production has greatly expanded. In the decade from 2000–2009, oil production in Weld County grew from approximately 7.1 million to 18.5 million barrels per year, and natural gas production increased from approximately 141.8 billion to 211.6 billion cubic feet per year. In the subsequent period (2010–2018), oil production further increased from approximately 21.0 million to 157.8 million barrels per year, and natural gas production from 219.8 billion to 807.3 billion cubic feet per year (Colorado Oil & Gas Conservation Commission, 2020). As of December 2018, there were more than 22,000 active O&NG wells in Weld County, which is the highest number of active wells in any county in the United States. In addition to

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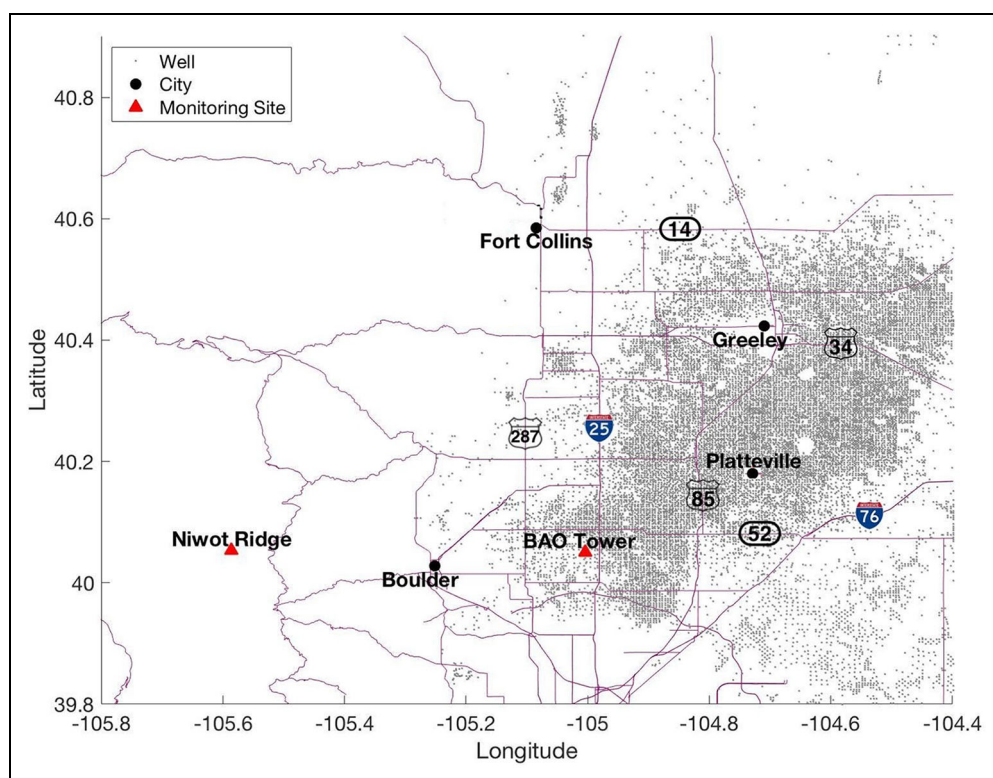Email: samuel.j.oltmans@noaa.gov

Figure 1. Map of Northern Colorado Front Range with the location of towns (black dots), observing locations (red triangles), highways, and oil and gas wells (small grey dots), and the location of the Boulder Atmospheric Observatory tower as well the Niwot Ridge reference sites. DOI: https://doi.org/10.1525/elementa.2020.00136.f1

increases in O&NG-related activities, vehicle miles traveled (VMT) in the Denver Metropolitan Area increased from 72 to 82 million miles per day over the period 2008–2016 (Denver Regional Council of Governments [DRCOG], 2018).

The NCFR has been in nonattainment for the surface ozone 8-h national ambient air quality standard (NAAQS) since 2007 (Bien and Helmig, 2018). Over time since then, the State of Colorado has enacted a range of regulations to try to reduce ozone precursor emissions (volatile organic compounds [VOCs] and nitrogen oxides) from certain sources in the region, including those from O&NG operations (Milford, 2014; Colorado Department of Public Health and Environment [CDPHE], 2014, 2019; Rigehetti et al., 2020). The degree to which the large increases in production activity have impacted emissions to the atmosphere of methane and nonmethane hydrocarbons (NMHCs), and consequent impacts on air quality and greenhouse gas related warming, has been the focus of a number of studies over the past decade (Pétron et al., 2012, Pétron et al., 2014; Gilman et al., 2013; LaFranchi et al., 2013; Swarthout et al., 2013; Thompson et al., 2014; McDuffie et al., 2016; Halliday et al., 2016; Evans and Helmig, 2016; Abeleira et al., 2017; Pfister et al., 2017; Cheadle et al., 2017; Peischl et al., 2018; Benedict et al., 2019; Kille et al., 2019; Lindass et al., 2019; Flocke et al., 2020). In 2019, the EPA reclassified the region as a serious ozone nonattainment area (NAA) for the 2008 NAAQS and required new emission mitigation planning to reach attainment.

In previous studies, ambient air hydrocarbon data reported on have relied primarily on measurements obtained during dedicated field campaigns lasting weeks to months. In this work, we analyze a unique 9-year data set of ambient air samples collected during the day on a near daily basis at the top of a 300 m tall tower, the National Oceanic and Atmospheric Administration (NOAA) Boulder Atmospheric Observatory located in Erie in southwest Weld County, CO. These measurements are used to investigate atmospheric mole fractions of several O&NG-related gases at a site influenced by different sources in the NAA. In addition to O&NG tracers, we investigated acetylene, a VOC that is more closely related to urban emission sources, to determine whether urban sources have contributed to changes in the composition of the samples obtained at BAO. A number of the constituents measured at the BAO were also measured in samples collected at a nearby remote location in the Rocky Mountains to the west of BAO and analyzed at the same lab, that is, the NOAA Global Monitoring Laboratory (GML). The NOAA observations spanning over 8 years are unique for this region for the traceability of the measurements to known gas standards, frequency of samples, and their boundary layer representativeness. Back-trajectory analysis categorized the potential source strength of the O&NG signature of air transported to the tower site. With this extensive measurement record, mole fraction enhancements above background levels, year-to-year variability in mole fractions, and longer term changes in atmospheric mole fractions were determined. Seasonal

variability was also analyzed and enabled a focus on changes during the summer photochemical season (May–September) given the impact of O&NG VOC emissions on ground-level ozone in the region (McDuffie et al., 2016; Abeleira et al., 2017; Pfister et al., 2017; Cheadle et al., 2017; Flocke et al., 2020; Helmig, 2020a). The results obtained from the BAO high-quality measurement records are discussed in relation to concurrent long-term changes in O&NG production and regulatory efforts in this region.

Measurements and methods
Flask samples
The BAO, a 300 m tall instrumented tower, was in the southwestern corner of Weld County (40.050°N, 105.038°W, 1,584 meters above sea level [masl], see **Figure 1**) and operated by NOAA. The research facility and tower were originally built in the late 1970s to study boundary layer dynamics and were equipped with temperature, relative humidity, and wind sensors at multiple levels (Wolfe and Lataitis, 2018). An air sampling system for both in situ measurements and flasks collection was installed on site in 2007. Glass flasks were filled from the 300 m agl level of the tower from July 2007 until the decommissioning of the tower in July 2016 (see NOAA GML, 2021a, for a description of the operation and sampling procedures at BAO). For this analysis, only air samples collected between 10:00 AM and 6:00 PM mountain daylight time (MDT; designated as daytime samples) were used; over 95% of these daytime samples were obtained between 12:00 and 3:30 pm MDT. This period of the day was selected in order to eliminate results during nocturnal boundary conditions, when the air can be vertically stratified and inhomogeneous, and its composition can be more strongly influenced by local, nearby emission sources. In contrast, daytime samples from the top of the tower were deemed to most likely represent a well-mixed boundary layer (Stull, 1988; Oltmans et al., 2019). Therefore, daily results are expected to reflect influences from sources in a larger spatial footprint upwind of the tower. Secondly, focusing on daytime data will increase the relevance of the analysis and findings towards photochemical ozone production, which exclusively occurs during the same daytime interval.

Over the 8 years (2008–2015) of complete annual observations, the number of daily daytime methane determinations from the flask measurements ranged from a high of 529 in 2008 to 285 in 2014 (144 in the half years of 2007 and 2016; Table S1). Overall, there were approximately 10% fewer NMHC determinations in the flask samples than for methane. From 2008 to 2012, air samples were generally collected in pairs, while in later years, one daily flask sample was obtained. Consequently, the number of days with samples ranged from 325 in 2008 to 202 in 2011 (Table S1). Although the samples were not evenly distributed over the year, all months are represented for each year, providing a representative data set for assessing annual and seasonal changes. Flask samples were analyzed in accordance with protocols used in the NOAA GML (2021b) global sampling network.

Reported methane mole fractions are tied to WMO international standards maintained by NOAA/GML (Dlugokencky et al., 2005, 2019). BAO NMHCs measured at the site (benzene, propane, i-pentane, n-pentane, i-butane, n-butane, and acetylene) and reported on here (propane, i-pentane, n-pentane and acetylene) are linked to NOAA/ GML laboratory prepared standards, and with the exception of acetylene, have been compared with standards from NIST and other laboratories (Rhoderick et al., 2014).

In order to isolate regional influences on long-term changes of methane at BAO, flask samples obtained by NOAA/GML at the Niwot Ridge (NWR) high elevation (40.053°N, 105.586°W, 3,523 masl) sampling location in the Rocky Mountains, approximately 45 km to the west of the BAO site (see **Figure 1**), were compared to the BAO data. NWR is a site that is minimally impacted by O&NG emissions transported from the NCFR based on the low mole fractions of the O&NG constituent propane (Figure S1) measured at this site. At NWR, <5% of propane results exceeded 2 ppb, with almost all of these during warm-month, upslope flow. During July, these upslope samples led to a somewhat elevated median mole fractions that likely overestimate the background concentration. Comparison of the BAO samples with those from NWR provided a unique opportunity to assess impacts of NCFR sources, especially O&NG emissions, on local air composition at BAO.

Meteorological data and back trajectory/footprint model
Continuous measurements of temperature, humidity, wind direction, and wind speed were obtained at three levels (10 m, 100 m, and 300 m) on the BAO tower every 30 s averaged to 1-h intervals. Flask sample analysis results (methane, propane, i-pentane, n-pentane, and acetylene) were matched with local wind direction measured at the 300 m level for filtering data based on the air transport sector at the time of the sampling.

Source footprints were assessed by Potential Source Contribution Function (PSCF) modeling for constituents measured at BAO based on 6-h back trajectories at the 300 m agl receptor height from the Hybrid Single-Particle Lagrangian Integrated Trajectory model using the North American Mesoscale (2021) Forecast System 12 km resolution forecast data. Calculations are performed on a longitude–latitude grid which covers the spatial domain of interest. It is assumed that a species emitted within a grid cell is swept into the air parcel and transported to the receptor site without loss through diffusion, chemical transformation, or atmospheric scavenging. The PSCF uses the trajLevel function in R package openair (Carslaw and Ropkins, 2012) to calculate the probability that a source is located at latitude i and longitude j (Pekney et al., 2006). The basis of PSCF is that if a source is located at (i, j), an air parcel back trajectory passing through that location indicates that material from the source can be collected and transported along the trajectory to the receptor site (Malm et al., 1986). PSCF solves $PSCF = m\{ij\} / n\{ij\}$, where $n\{ij\}$ is the number of times that the trajectories passed through the cell (i, j), and $m\{ij\}$ is the number of times that a source

concentration was high when the trajectories passed through the cell (i, j). High values in the spatial distribution of PSCF will pinpoint geographical regions that are likely to produce high concentration values at the receptor site if crossed by a trajectory. Cells with few data have a weighting factor applied to reduce their effect. A limitation of the PSCF method is that grid cells can have the same PSCF value when sample concentrations are either only slightly higher or much higher than the chosen criterion (median). As a result, it can be difficult to distinguish moderate sources from stronger ones. The PSCF analysis shows the probability of having methane and VOC concentrations at BAO higher than the median from a grid cell over the 2007–2016 period. For each compound, n gives the number of data used for the PSCF analysis.

Results

Footprint analysis of sources of air at BAO

In this section, PSCFs were used to identify the spatial distribution of potential sources for constituents measured in flasks collected at the 300 m level of the BAO tower. Methane, the primary constituent of natural gas, has a strong PSCF source to the NE of BAO but also has contributions to the southeast (SE; **Figure 2**). Methane measured at BAO may have contributions from sources including wastewater treatment facilities, landfills, and cattle feedlots (Pétron et al., 2012; Pétron et al., 2014). However, previous work concluded that O&NG emissions dominate (approximately 75%) over other methane emission sources in Weld county (Pétron et al., 2014; Peischl et al., 2018). Propane mole fractions above background in the NCFR have been attributed almost exclusively to

O&NG-related emissions (Pétron, et al., 2012; Gilman et al., 2013; Swarthout et al., 2013). Propane mole fractions greater than the median value show a strong pattern of potential source strength to the NE of BAO (**Figure 3**), corresponding to the primary area of O&NG operations in Weld County (**Figure 1**). This spatial pattern is nearly identical to that seen in the ratio of i-pentane to n-pentane for values when this ratio is <1 (Figure S2), another marker of O&NG NMHC emissions (Gilman et al., 2013; Pétron et al., 2014).

On the other hand, acetylene (ethyne) has emissions associated primarily with combustion sources, including motor vehicle engine emissions and a relatively minor contribution from O&NG-related emissions (Gilman et al., 2013; Swarthout et al., 2013; Abeleira et al. 2017). Acetylene PSCF results show a pattern concentrated on the Interstate 25 corridor both north and particularly south and southeast of BAO and to the west of BAO toward Boulder (**Figures 1** and **4**). The linkage of the strongest PSCF contributions from the primary O&NG region with the constituents most strongly associated with O&NG activity lends strong support for relating changes in methane, propane, and other O&NG-related constituents observed at BAO to emissions from the Weld County O&NG region.

Selection of samples using wind data

Based on the PSCF results for propane, which showed a strong contribution from the northeast (NE) quadrant, a subset of samples was selected when wind directions were 0–90° and wind speeds less than 10 m/s at the 300 m level at the time of the flask sample collection. The wind speed/direction analysis shows that samples with the highest mole fractions of propane came from the
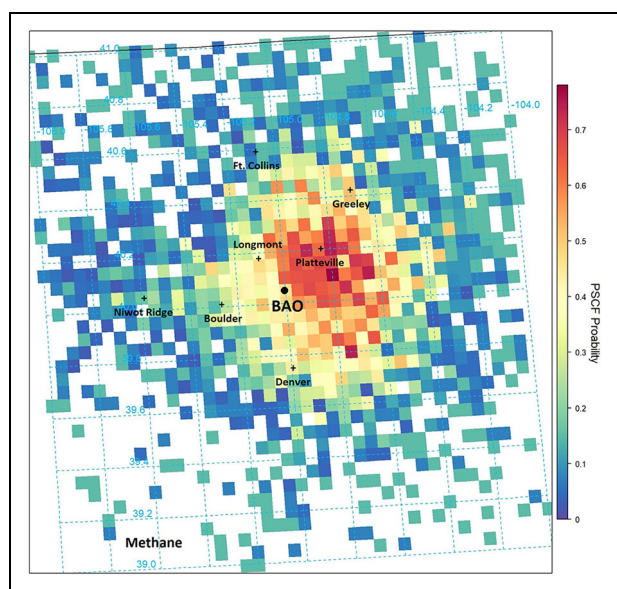

Figure 2. Potential Source Contribution Function results for methane greater than the median for 2007–2016 (data for all seasons; $n = 2{,}728$) in flasks collected during daytime hours at Boulder Atmospheric Observatory (black dot). DOI: https://doi.org/10.1525/elementa.2020.00136.f2
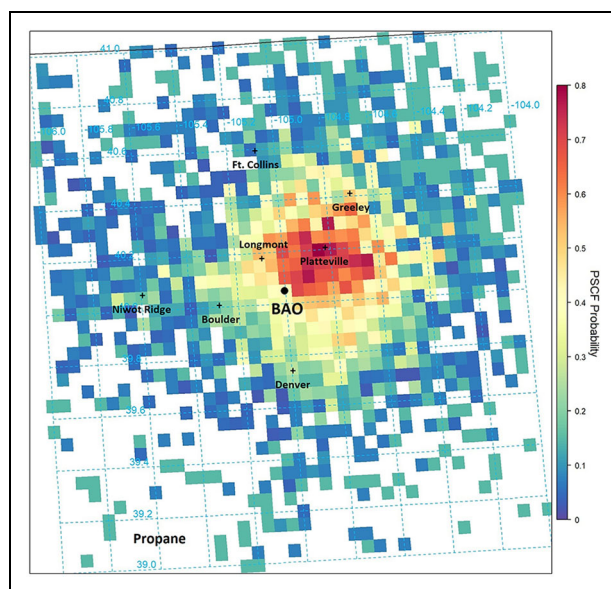

Figure 3. Potential Source Contribution Function results for propane greater than the median for 2007–2016 (data for all seasons; $n = 2{,}520$) in flasks collected during daytime hours at Boulder Atmospheric Observatory (black dot). DOI: https://doi.org/10.1525/elementa.2020.00136.f3
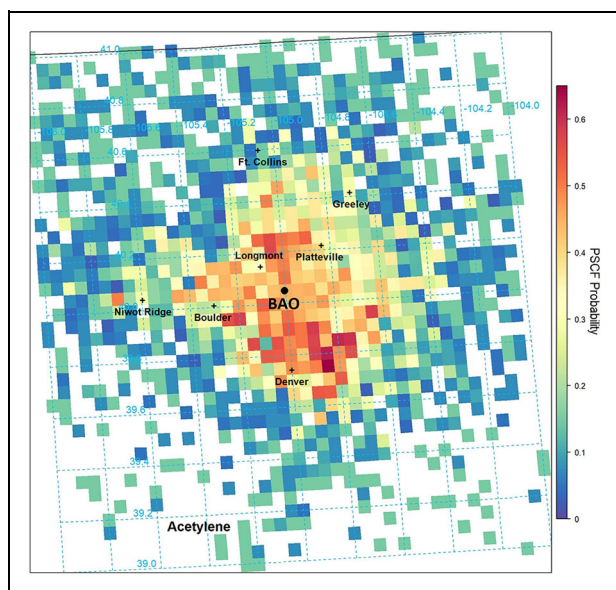
Figure 4. Potential Source Contribution Function results for acetylene greater than the median for 2007–2016 (data for all seasons; $n = 2{,}447$) in flasks collected during daytime hours at Boulder Atmospheric Observatory (black dot). DOI: https://doi.org/10.1525/elementa.2020.00136.f4

region with the highest level of O&NG-related activity (**Figure 5**). Similarly, the dependency for methane (**Figure 5**) shows that the highest levels of methane are associated with wind directions from the NE quadrant. For acetylene, on the other hand, the same analysis (**Figure 5**) shows the highest mole fractions with winds from the south. The percentage of samples from the northeast (0–90°) quadrant ranged from 38% (2009 and 2015) to 25% (2011) of all the samples collected during a year. South sector samples (90–270°) ranged from 52% (2012) to 23% (2015) collected in a year.

Average and seasonal variability at BAO and comparison with NWR

Data from the daytime individual flask samples were used to investigate seasonal patterns and annual and photochemical season (May–September) behavior for methane, propane, acetylene, and the ratio of i-pentane to n-pentane, as an indicator of the relative contribution of O&NG versus other VOC sources (Gilman et al., 2013). Monthly averages were calculated from all daytime samples for individual months, and annual averages were then computed from the monthly averages. In addition, a subset of samples associated with wind direction measured at the 300 m height at the BAO tower from the NE quadrant were used to better characterize changes that were most likely to be influenced by air parcels associated with O&NG activity, while samples with directions from the south were used to represent cases where emissions from the Denver Metropolitan Area were likely to dominate.

Propane

In the absence of influence from O&NG activity, atmospheric propane values are generally below 1 ppb (Gilman et al., 2013). At BAO, for all samples, even at the 25th percentile, propane mole fractions were >1 ppb, with median values during all months ≥3 ppb. For samples from the NE quadrant (**Figure 6**, left panel) the overall median value was 6.2 ppb, and the overall 75th percentile result was 10.6 ppb (see **Table 1** for numerical values). Values at the 25th percentile and higher reflect the influence of O&NG. Therefore, changes at median and greater levels of propane should be indicative of changes in O&NG impacts at BAO. Mole fractions for samples with winds from the south (**Figure 6**, right panel) were much lower than those with winds from the NE quadrant, but still considerably higher than those at NWR, where median values were 0.6 ppb or less for all months of the year (Figure S1 and Table S2). Somewhat elevated propane concentrations would be expected in the south sector samples relative to those at NWR based on the presence of O&NG wells located to the SE of BAO (**Figure 1**). There was a tendency toward higher mole fractions during cooler months at and above the 75th percentile, likely related to reduced vertical mixing in the lower atmosphere during winter. In winter 2009 and to a somewhat lesser extent in 2010, there were episodes where propane concentrations exceeded 50 ppb that led to very large
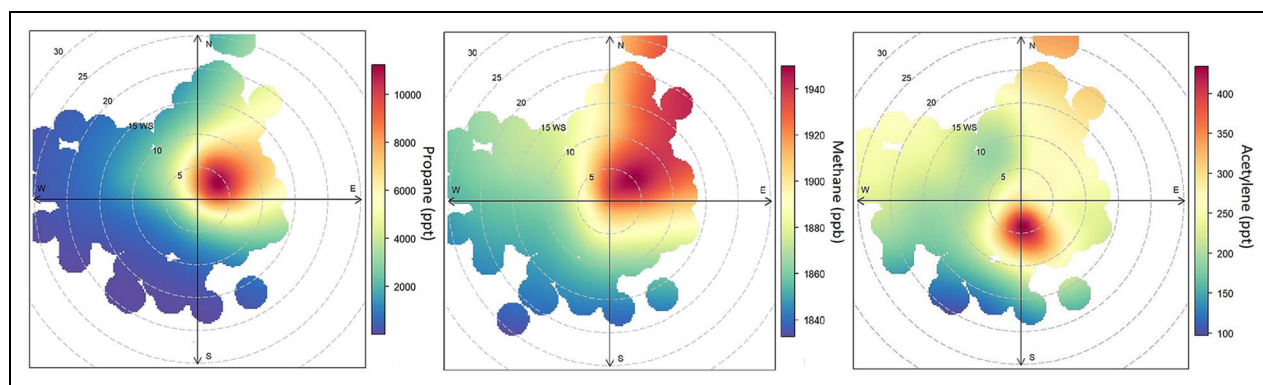

Figure 5. Wind speed/direction dependency for propane (left panel), methane (middle panel), and acetylene (right panel) for winds at the 300 m level of the Boulder Atmospheric Observatory tower. Wind speeds (WS) in m/s. Samples are for daytime observations (10:00 AM to 6:00 PM MDT). DOI: https://doi.org/10.1525/elementa.2020.00136.f5
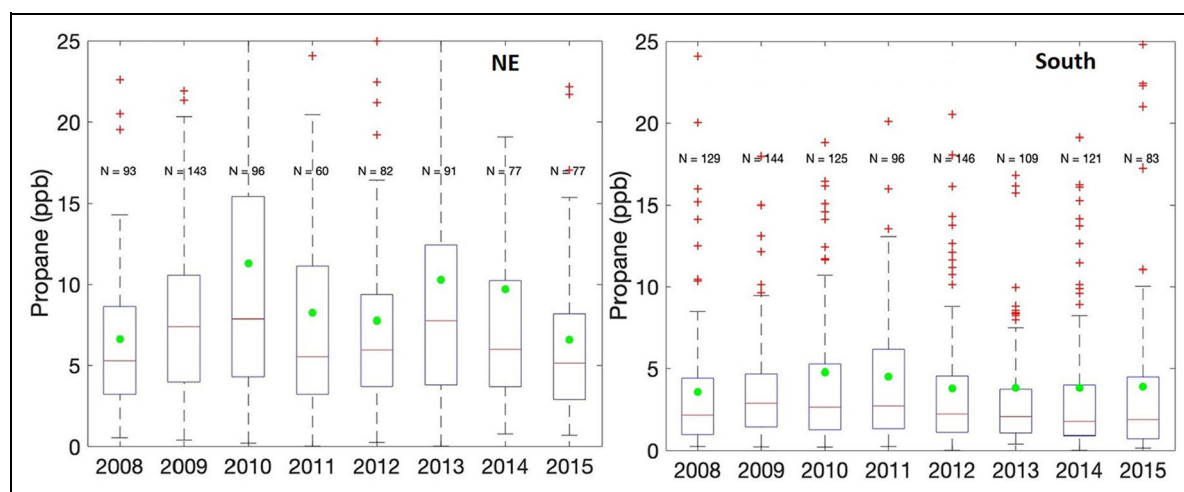
Figure 6. Annual distribution of propane mole fractions at Boulder Atmospheric Observatory for each year for daytime samples collected when winds at the tower were from the northeast (NE) quadrant (left panel) and for daytime samples collected when winds at the tower were from the south (right panel). The horizontal red line in each box is the median, the box bottom and top are the 25th and 75th percentiles, the vertical bars indicate the 5th and 95th percentiles, the red pluses values >95th percentile, and the green dots are the mean (in 2009, the mean was above the upper limit of the y-axis; very high individual samples for the NE quadrant are not encompassed within the 25 ppb y-axis limit where samples exceeded 50 ppb [highest value >100 ppb]). Annual statistics were calculated using daytime individual flask samples (N) including all 12 months of the year. DOI: https://doi.org/10.1525/elementa.2020.00136.f6

Table 1. Trend statistics for propane mole fractions at Boulder Atmospheric Observatory for 2008–2015 using daytime samples with wind directions from the northeast quadrant. DOI: https://doi.org/10.1525/elementa.2020.00136.t1

Propane	Full Year				Photochemical Season (May–September)			
	Value (ppb)	Slope (ppb yr^{-1})	2 σ Standard Deviation (ppb yr^{-1})	P-Value	Value (ppb)	Slope (ppb yr^{-1})	2 σ Standard Deviation (ppb yr^{-1})	P-Value
Mean	12.78	−1.200	6.452	0.333	7.318	−0.182	0.901	0.296
Median	6.241	−0.094	1.046	0.628	5.632	−0.084	0.587	0.447
5th %ile	1.392	0.056	0.291	0.319	1.609	0.086	0.344	0.207
25th %ile	3.578	−0.052	0.406	0.492	3.455	−0.032	0.422	0.682
75th %ile	10.59	−0.186	2.161	0.643	9.107	−0.309	1.250	0.212
95th %ile	25.63	0.389	6.090	0.730	18.21	−0.821	4.612	0.353

annual mean values. It is unclear why the values were more extreme during these years than in other years or if they were associated with poorer control of drilling and extraction processes or stronger nearby sources.

Methane

Comparison of the monthly methane mole fractions at BAO and NWR showed overall higher and more variable data at BAO (**Figure 7**) but a similar seasonal pattern (Figure S3). The vertical gradient of methane mole fractions below 5 km in the absence of a local surface source is relatively small (<10 ppb) based on vertical profile measurements off the west coast of North America (Groot Zwaaftink, et al., 2018). The vertical gradient between BAO and NWR could thus be mostly attributed to sources at the BAO location. Median methane mole fractions at BAO in

air samples most likely to be influenced by O&NG emissions (wind directions from the NE quadrant) were 1,924 ppb (Table S4b), while at NWR, the median was 1,859 ppb (Table S3). For wind directions from the NE quadrant, at the 75th percentile, BAO had mole fractions 93 ppb greater than NWR, and even at the 25th percentile, BAO mole fractions exceeded the 75th percentile mole fractions at NWR.

Enhancements in methane over the background for BAO samples were calculated by subtracting the monthly median methane mole fraction at NWR for a given month corresponding to the samples at BAO for the month. Based on the strong correlation (**Figure 8** and Figure S4) between the methane residual and propane at BAO ($r^2 = 0.79$), and the source footprint results from the PSCF, the methane enhancements at BAO likely reflect the
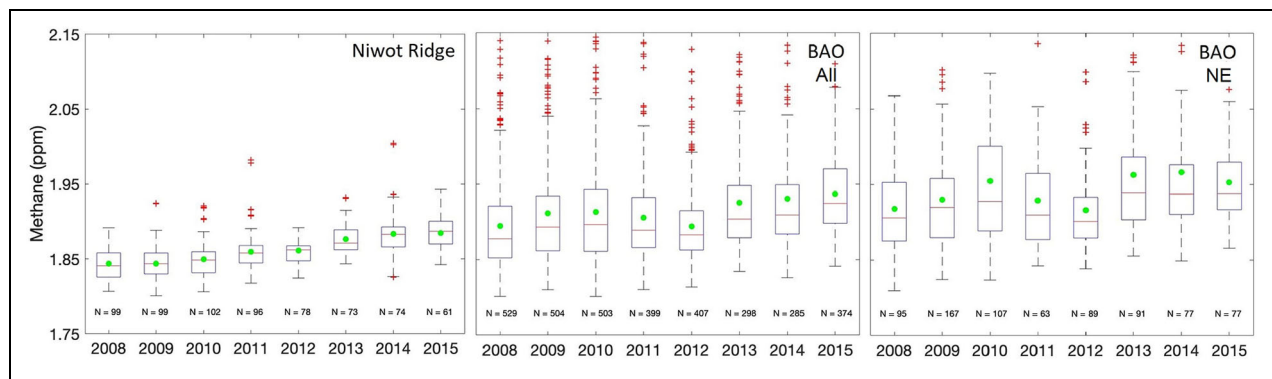
Figure 7. Annual distribution of methane at Niwot Ridge and Boulder Atmospheric Observatory (BAO) for 2008−2015. The middle graph includes BAO data for all wind directions (All), the rightmost panel is for samples at BAO exclusively collected for wind directions from the northeast quadrant. The box whisker format is as in **Figure 6**. Annual statistics were calculated using daytime individual flask samples (N) including all 12 months of the year. DOI: https://doi.org/10.1525/elementa.2020.00136.f7
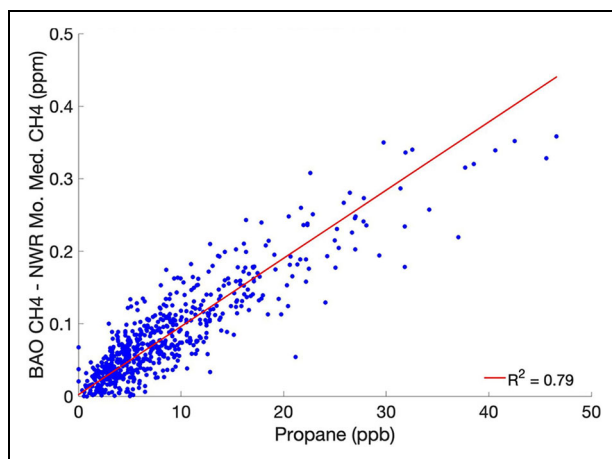

Figure 8. Correlation between Boulder Atmospheric Observatory methane residuals (ppm) and propane (ppb) for 2008−2015 daytime samples with wind directions from the northeast quadrant. DOI: https://doi.org/10.1525/elementa.2020.00136.f8

influence of O&NG emissions. This is consistent with the value of 75% found by Pétron et al. (2014), and 77% determined by Peischl et al. (2018), of methane emissions in the DJB attributable to O&NG, and points to O&NG emissions as the primary source of enhanced methane mole fractions at BAO. The molar propane/methane ratio deduced from the regression line is 0.12, which compares well (within approximately 20%) with earlier reported propane/methane emission ratio data reported from ground surveying in the DJB (Pétron et al., 2014). The proportion of methane in BAO samples attributable to O&NG emissions remained essentially unchanged over the study period (Figure S4).

Acetylene
Annual median acetylene mole fractions (**Figure 9**) were similar in the south sector samples to those from the NE quadrant (median: 0.25 ppb vs. 0.23 ppb), while higher percentiles (75th: 0.41 vs. 0.35 and 95th: 0.88 vs. 0.59)

and extreme values were more noticeably enhanced in the south sector consistent with a traffic source that would be much stronger in the more heavily urban influenced south sector than in the NE quadrant.

Longer term changes
Longer term changes (trends) were determined using the linear model in the routine "fitim" in MatLab. Changes were investigated for methane for the full set of daytime samples at NWR and BAO and for samples at BAO wind directions from the NE quadrant and for the NMHC samples at BAO for NE quadrant and south sector samples. Both year-round and photochemical season trends were determined.

Propane
The trend analyses at BAO for samples with wind directions from the NE quadrant (**Table 1**) and from the south sector (Table S2) did not reveal any statistically significant changes. Interannual variability was particularly large in samples from the NE quadrant as was the variation within a year. For example, while annual median mole fractions for 2015 were less than those in 2013 for NE quadrant samples, this does not represent the overall change over the 8-year record.

Methane
Since methane is the primary component of natural gas, and recent regulations (CDPHE, 2019) include limitations on methane emissions, changes in this constituent are of particular interest. At NWR, the 8-year methane record for both the full year (**Figure 7**) and the photochemical season (Figure S5) shows increasing methane values. The 0.007 ppm yr^{-1} ($P = 0.00$) change in the median at NWR (Table S3) is consistent with the global annual growth rate in methane (0.0075 ppm yr^{-1}) during this period reported by Nisbet et al. (2019). The change in the median at BAO of 0.005 ppm yr^{-1} ($P = 0.014$) was also statistically significant (**Figure 7** and Table S4a) when using all daytime samples. Although the trend value at the median level for samples with wind directions from the NE quadrant was
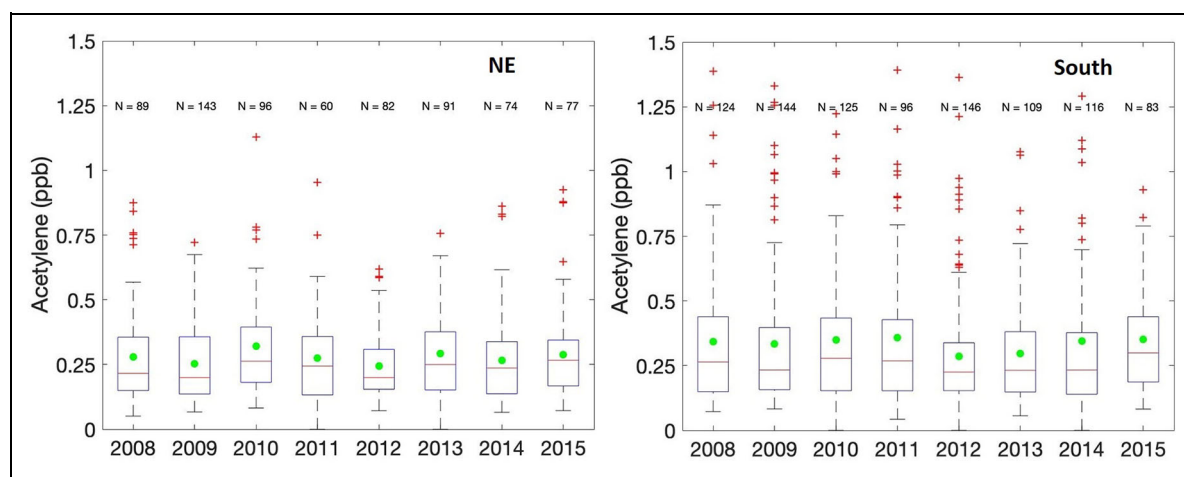
Figure 9. Annual distribution of acetylene mole fractions at Boulder Atmospheric Observatory for each year for daytime samples collected when winds at the tower were from the northeast quadrant (left panel), and from the south (right panel). The box whisker format is as in **Figure 6**. Annual statistics were calculated using daytime individual flask samples (*N*) including all 12 months of the year. DOI: https://doi.org/10.1525/elementa.2020.00136.f9
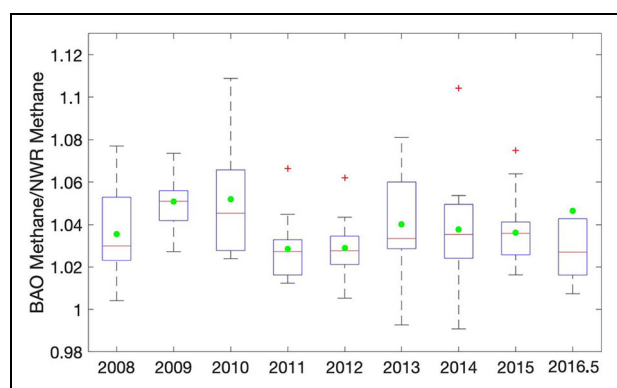

Figure 10. Ratio of the monthly median mole fractions of methane at Boulder Atmospheric Observatory (BAO)/ Niwot Ridge for 2008−2016 for BAO samples with wind directions from the northeast quadrant. For each year, there are 12 monthly values (except 2016 when only January–June had samples). The plotted box-whisker plots represent the variability of the 12 monthly values but do not include the variability of individual samples within the month. The box whisker format is as in Figure 6. DOI: https://doi.org/10.1525/elementa.2020.00136.f10

fractions at NWR represented regional background methane values minimally perturbed by local sources (Figure S1), the ratio of the BAO to NWR mole fractions can then be used as an indication of the changes in methane at BAO relative to the background (**Figure 10**), and that could be attributed to changing influences from methane emissions reaching BAO from the northeast that are dominated by O&NG emissions (**Figure 8** and Figure S5).

The 8.5-year record of the ratio BAO/NWR annual statistics for methane (**Table 2**) shows no significant change in the ratio over time for BAO samples collected with winds originating in the NE quadrant over the period of measurement. Within a given year, monthly values that make up the annual values of the ratio show large variability as evidenced by the wide range of the 25th and 75th percentiles. There is also large year-to-year variability in the ratio. When the larger set that includes all daytime samples at BAO is considered, there was also no significant change over time in the BAO/NWR ratio (Table S5). Results for measurements during the photochemical season followed the same pattern as those from year-round results; however, there was a statistically significant decrease in the 95th percentile values.

Ratio of i-pentane to n-pentane

O&NG fugitive emissions have been found to have a relatively higher fraction of the n-isomer of pentane versus the i-isomer in comparison to other pentane sources (Gilman et al., 2013). This dependency has been used to investigate the relative importance of O&NG toward total VOC sources (Rossabi and Helmig, 2018). The pentane isomer ratio has the advantage that though the individual mole fractions have significant variability, the ratio is less variable (Pollmann et al., 2016). Values <1 are indicative of the enhanced contributions of O&NG sources (Gilman et al., 2013; Thompson et al., 2014; Rossabi and Helmig, 2018). For BAO daytime samples, the mean i-/n-pentane ratio for the full year is 0.95 (**Figure 11**, left panel), and for the

the same as for all daytime samples, the change was not statistically significant (Table S4b) because of the higher variability in the data. For all samples and for samples originating from the NE quadrant (**Figure 7**), changes at the 5th and 25th percentiles were statistically significant (Table S4b) as they were mostly representing the increasing background levels (Nisbet et al., 2019).

To focus on the longer term variability and changes in methane at BAO not associated with the seasonal cycle or multiyear background trend, the changes at BAO were investigated by computing the ratio of individual sample values at BAO to the monthly median value for the corresponding month at NWR (Figure S6). Assuming the mole

Table 2. Trend statistics for the annual ratios of Boulder Atmospheric Observatory (BAO)/Niwot Ridge (NWR) methane mole fractions for 2008−2016 using individual BAO samples with wind directions from the northeast quadrant and corresponding NWR monthly medians for each individual month. DOI: https://doi.org/10.1525/elementa.2020.00136.t2

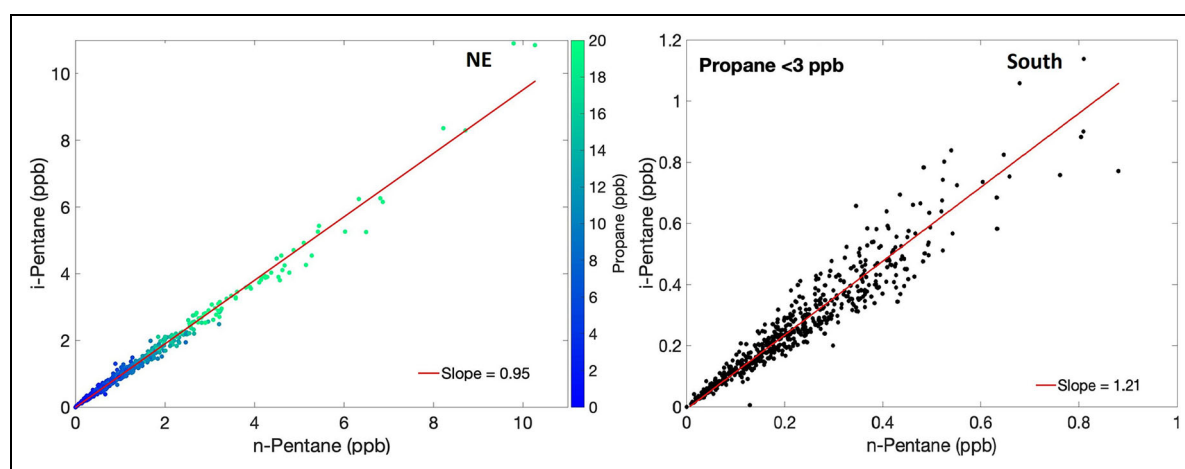| Methane	Full Year			Photochemical Season (May−September)		
	Slope (yr^{-1})	2 σ Standard Deviation (yr^{-1})	P-Value	Slope (yr^{-1})	2 σ Standard Deviation (yr^{-1})	P-Value
Mean	−0.001	0.006	0.279	−0.001	0.005	0.097
Median	−0.001	0.005	0.175	0.000	0.004	0.813
5th %ile	−0.001	0.003	0.155	−0.001	0.004	0.498
25th %ile	−0.001	0.004	0.206	0.000	0.005	0.644
75th %ile	−0.002	0.008	0.163	−0.002	0.006	0.070
95th %ile	−0.002	0.021	0.598	−0.005	0.014	0.085

Figure 11. Left: i-pentane as a function of n-pentane at Boulder Atmospheric Observatory (BAO) for daytime samples with wind directions from the northeast quadrant. Data are color-coded for the concurrent propane mole fraction sample. Right: i-pentane as a function of n-pentane at BAO for samples with wind directions from the south and for propane mole fractions less than 3 ppb. DOI: https://doi.org/10.1525/elementa.2020.00136.f11

photochemical season, it is 0.92 (Figure S7) for samples with wind directions from the NE quadrant. South sector samples for the i/n-pentane ratio, on the other hand, have a slope >1.2 (**Figure 11**, right panel) for samples with propane values less than the overall median of 3 ppb, consistent with an urban signature.

For both the full year and photochemical season, annual values of the i-/n- pentane ratio for samples with wind directions from the NE quadrant decline significantly at all percentile levels, with the median and mean ratio declining by 10% over the course of the 8-year record (**Figure 12** and **Table 3**). The change in the pentane isomer ratio was similarly pronounced during the summer photochemical season (**Table 3**). This is in contrast to the subset of samples with an urban signature: Samples associated with wind directions from the south sector and filtered for propane mole fractions <3 ppb show smaller changes in the i-/n- pentane ratio (**Figure 12** and Table S6) that were generally not significant except at the 25th percentile where the changes in the two sectors were similar. These results suggest that the relative influence

of O&NG on the VOCs composition at BAO has increased overall, particularly, in air transported from the DJB over the period of observations, while during the same time window, the urban signature has remained about the same.

Acetylene

Annual acetylene mole fractions showed only small year-to-year changes at BAO at all percentile levels except at the most extreme values (95th and greater) for both samples with wind directions from the NE quadrant and the south sector, with no overall longer term change over the eight years of observations (Figure S9 and Table S7). VMT increased by approximately 15% in the Denver Metropolitan Area over the period of BAO observations (DRCOG, 2018). Based on the national vehicle hydrocarbon emissions profile (U.S. Department of Transportation, 2020), hydrocarbon emissions per vehicle mile declined by approximately 30%. It is not clear whether these numbers would offset each other or lead to somewhat smaller overall vehicle-related hydrocarbon emissions. The lack of
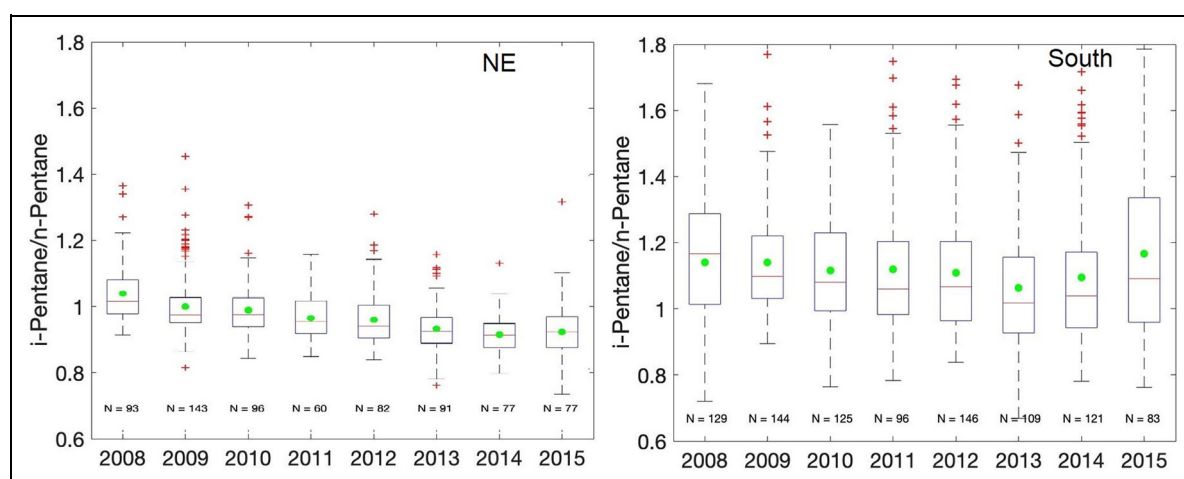
Figure 12. Ratio of the mole fractions of i-pentane to n-pentane at Boulder Atmospheric Observatory for the years 2008−2015 for samples with wind directions from the northeast quadrant (left panel) and with wind directions from the south sector (right panel) filtered for propane mole fractions <3 ppb. The box whisker format is as in **Figure 6**. Annual statistics were calculated using daytime individual flask samples (*N*) including all 12 months of the year. DOI: https://doi.org/10.1525/elementa.2020.00136.f12

Table 3. Trend statistics for the ratio of i-pentane to n-pentane at Boulder Atmospheric Observatory for 2008−2015 using daytime samples with wind directions from the northeast quadrant. DOI: https://doi.org/10.1525/elementa.2020.00136.t3

i-pentane/n-pentane	Full Year			Photochemical Season (May–September)		
	Slope (yr^{-1})	2 σ Standard Deviation (yr^{-1})	*P*-Value	Slope (yr^{-1})	2 σ Standard Deviation (yr^{-1})	*P*-Value
Mean	−0.017	0.010	0.000	−0.021	0.019	0.001
Median	−0.014	0.010	0.000	−0.016	0.014	0.001
5th %ile	−0.019	0.005	0.000	−0.020	0.037	0.023
25th %ile	−0.015	0.007	0.000	−0.017	0.016	0.001
75th %ile	−0.016	0.015	0.001	−0.019	0.024	0.005
95th %ile	−0.024	0.023	0.001	−0.038	0.047	0.004

change in acetylene concentrations, particularly in the urban-focused south sector samples, suggests that overall changes may not be large. This is an indication that non-O&NG VOC sources such as automobile and truck emissions did not change notably in the region over this time.

Discussion and conclusions

The rapid expansion of O&NG extraction activity and production in the NCFR over the past decade raises the question as to whether there has been a corresponding increase in emissions, and if so, was this reflected in representative observations of atmospheric methane and VOCs over the NCFR? The 8.5-year record of calibrated observations at the former BAO tall tower site in Erie, CO, represents one of the few (perhaps only) longer term records of consistent and high-quality observations of key gases related to O&NG activity that encompass a time of rapid growth of O&NG production in the NCFR. Constituents measured in flask samples collected between 10:00

AM and 6:00 PM MDT, taken several times a week, and obtained every month from the 300 m level of the BAO tower from January 2008 to July 2016, make a strong case for a substantial impact of O&NG-related emissions within this region of Colorado. The high mole fractions of O&NG-related constituents reaching BAO from the NE quadrant contrasted with much lower mole fractions reaching BAO from other sectors, including from the urbanized region to the south where the observed lower mole fractions are typical of those measured in other urban areas in the U.S. (Baker et al., 2008: Gilman et al., 2013; Thompson et al., 2014). Based on the PSCF calculations, observations of elevated methane and propane mole fractions and of i-pentane to n-pentane ratio values <1 (all linked to O&NG activity) were strongly associated with air reaching BAO from the NE centered in Weld County, which corresponds to the areas of highest well density and the primary area of O&NG production. This contrasted with the behavior seen in the acetylene data, a VOC that is not primarily

associated with O&NG fugitive emissions. Acetylene showed a different PSCF pattern that indicates strongest sources mostly to the south of BAO and associated with the Denver metro area transportation corridors.

Methane mole fractions at BAO were substantially elevated above those at NWR. BAO median mole fractions for daytime samples with wind directions from the NE quadrant exceeded the median at NWR by 65 ppb. The large contribution of O&NG emissions to this methane enhancement was confirmed by propane observations, where large enhancements in mole fractions above background were also observed at BAO. Nearly 80% of the variation in residual methane mole fractions (methane behavior not associated with background variations measured at the NWR site) was accounted for by the correlation with measured propane mole fractions. This indicates most of the observed methane enhancements were attributable to O&NG-related emissions. Methane mole fractions increased at BAO over the period of observations. This increase could be attributed to the increase in the methane background, as clearly seen in the methane trend at NWR. The ratio of BAO to NWR methane mole fractions, which corrects for the longer term change in the background, did not show any significant overall changes. This indicates that methane emissions within the footprint of BAO have remained relatively constant over the time window of the observations limited somewhat by the ability to determine the changes due to the large uncertainty in estimating the trend.

Propane median mole fractions at BAO for NE quadrant samples were 10 times (6.2 ppb) as large as the NWR median (0.6 ppb). By contrast, samples associated with transport from the south sector, where there was more limited O&NG-related activity, had median mole fractions of 2.3 ppb. Although propane mole fractions were highly elevated at BAO over the 8 years of observations, there was no clear evidence for overall changes in propane mole fractions during this time period in either the NE quadrant or south sector samples. Lyu et al. (2021) reported lower propane values in 2015 data compared to 2013 from Platteville, which is located more toward the center of the DJB. The high year-to-year variability demonstrated in the 8-years BAO data indicates that such short-term differences cannot be deemed representative of longer term changes.

Acetylene, used as a marker for the influence of urban emissions, did not show long-term changes in either samples from the NE quadrant or the south sector. This suggests that possible changes in urban emissions associated with increases in traffic (VMT) or reductions in vehicle hydrocarbon emissions (DOT, 2018) were not significant drivers of NMHC changes in the DJB or may have offset each other. Analysis of possible indicators of tailpipe emissions (ratios of acetylene/i-pentane and acetylene/propane) to gauge of the relative importance of increases in VMT to reductions in vehicle hydrocarbon emissions did not show any clear trends (Figure S10). While the highly variable mole fractions of individual samples of methane and propane made detection of longer term changes less clear, the more constrained ratio of i-pentane/n-pentane showed a statistically significant trend, especially during

the summer in the NE quadrant samples. This likely indicates a growing influence of the relative contribution of O&NG emissions on the VOC composition in the samples at BAO. In contrast, this ratio for south sector samples with a more urban signature did not change notably over the 8-year period of observations. A similar finding, that is, downward trends in the i/n pentane ratio, was reported for other U.S. sites in proximity to O&NG-related activity by Rossabi and Helmig (2018). High levels of VOCs along with an increasing relative contribution of O&NG VOCs to the photochemical reservoir of VOCs will likely continue to play a major role in the contribution of O&NG VOC emissions to summer ozone production and degradation of air quality (McDuffie et al., 2016).

Stricter emission control requirements have been enacted nationwide and in Colorado with the goal of reducing ozone precursor emissions (Milford, 2014; CDPHE, 2019). The BAO data show no evidence for significant changes in propane mole fractions during a time period when oil production in Weld County increased by greater than a factor of 7 and natural gas production more than tripled. This behavior indicates a possible decrease in relative leakage and/or venting rate by the industry for the average unit of operation. The most recent VOC emissions inventory for the Denver Metro/NCFR NAA that the serious ozone NAA State Implementation Plan (SIP; CDHPE- Regional Air Quality Council RAQC [2020]) relies on lists total O&NG emissions (area sources plus condensate/oil tank sources plus point sources) at 279 tons per day (tpd) for 2011, dropping to 163.3 tpd for the year 2017 and then further dropping to 119.0 tpd for 2020 (CDPHE-RAQC, 2020). This accounts to an average −18 tpd, or −6.5%, of average daily emission reductions per year using the year 2011 emissions as reference (**Figure 13**). Since more than 98% of the O&NG production in 2017 (>95% in 2011) was in Weld County, this inventory reduction would primarily apply to this area of operations. This projected reduction is based on a 64% reduction in emissions from condensate/oil tank sources (CDHPE-RAQC, 2020), while other emission sources would grow 10%–20% for an overall 45% reduction. A comparison with the ambient BAO propane data record is also included in **Figure 13**. First, the contribution of propane from regional sources was estimated by subtracting the annual 5 percentile values, reflecting the estimated background, from the observed median in the daytime northeast sector samples. These residuals were then scaled such that the linear regression result through these data for year 2011 crossed the same year inventory emissions estimate. This analysis then allows comparison of the relative changes of the two data series. The regression line through the BAO propane data has a slope of −0.097 ppb yr^{-1}, or −1.5% yr^{-1}, scaled to the 2011 value (**Figure 13**). Continuous NMHC surface measurements over a 4-year period in Boulder County show a similar trend behavior for the O&NG tracers ethane and propane (Helmig, 2020b). In conclusion, the estimated O&NG emission reductions used in the SIP are more than a factor of 4, higher than the rate of change that is seen in the
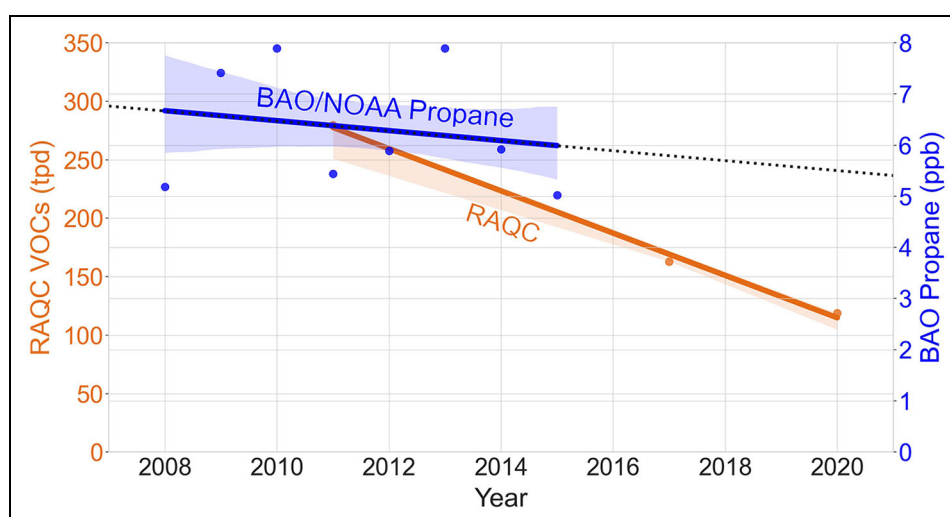
Figure 13. Comparison of the trend in the median annual propane mole fractions at Boulder Atmospheric Observatory (BAO) with projected O&NG-related VOC inventory reduction (CDHPE-RAQC, 2020). The dotted line is an extrapolation of the BAO trend beyond the period with available measurement data. Please note the different *y*-axis scales used for the two data series. Shaded areas depict the 1-σ standard deviation bounds of the regression line slope determinations. DOI: https://doi.org/10.1525/elementa.2020.00136.f13

ambient O&NG tracer data. This discrepancy poses questions about the representation of O&NG emissions in the inventory and their proper consideration in the modeling for achieving ozone NAAQS attainment.

The absence of obvious declining trends in absolute atmospheric mole fractions of methane (relative to NWR) and the O&NG tracer propane indicate that thus far there is no evident improvement in levels of O&NG VOCs and their contribution to the regional air quality. It is therefore likely that reductions in well emissions have been offset by emission increases from the overall growth in the number of wells and associated oil and gas operations in the DJB.

Data accessibility statement
Data files are included in the Supplemental Material.

Supplemental files
The supplemental files for this article can be found as follows:

Figures S1–S10. Tables S1–S7.docx.

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