RESEARCH ARTICLE

Spatial distribution of atmospheric oil and natural gas volatile organic compounds in the Northern Colorado Front Range

Samuel Rossabi1, Jacques Hueber1, Wei Wang1, Pam Milmoe2, and Detlev Helmig1,3,*

Methane and nonmethane volatile organic compounds (VOCs) were monitored near Boulder in the Northern Colorado Front Range to investigate their spatial distribution and sources as a part of the Front Range Air Pollution and Photochemistry Experiment (FRAPPE) and the Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) campaign, in summer 2014. A particular emphasis was the study of the contribution of emissions from oil and natural gas (O&NG) operations on the regional air quality. One network extended along an elevation gradient from the City of Boulder (elevation ≈1,600 m) to the University of Colorado Mountain Research Station (≈2,900 m) on the eastern slopes of the Rocky Mountains. Light alkane petroleum hydrocarbons had the highest mole fraction of the VOCs that could be analyzed with the applied techniques. The longer lived VOCs ethane and propane decreased with increasing elevation, suggesting that Boulder and the surrounding plains were a source of these anthropogenic compounds. VOC diurnal time series showed a few events with elevated mole fractions at the mountain sites, which were likely the result of the upslope transport of plumes with elevated VOCs from the plains. Within the other site network, which extended into suburban East Boulder County (EBC), VOCs were monitored at 5 sites increasingly close to O&NG development in the Denver Julesburg Basin. Mean mole fractions and variability of primarily O&NG-associated VOCs (ethane, propane, butane isomers) increased by a factor of 2.4–5.2 with closer proximity to the O&NG producing region. Median mole fractions of C2–C5 n-alkanes and of much-butane at the EBC sites were higher than those previously reported from 28 larger urban areas in the United States. Among the VOCs that could be quantified with the gas chromatography methods, VOCs most clearly associated to O&NG-related emissions (C2–C5 alkanes) accounted for 52%–79% of the VOC hydroxyl radical reactivity (OHR). The horizontal gradient in OHR of the considered VOCs, with ≈3 times higher values at the furthest eastern sites, points toward higher chemical reactivity and ozone production potential from these ozone precursors in the eastern area of the county than within the City of Boulder.

Keywords: Methane, Volatile organic compounds, Oil and natural gas emissions

1. Introduction
The city of Boulder, CO, is located in the Northern Colorado Front Range (NCFR) east of the Rocky Mountains. Local wind patterns expose Boulder to air plumes from many directions. Relatively clean air reaches Boulder from over the mountains to the west. This downslope flow occurs mostly at night, when cooler air from the mountains descends and flows to the east (Johnson and Toth, 1982). Upslope flow that causes air flow from east to west is especially dominant during daytime in summer. This flow regime can transport polluted air from the plains up the mountain slope from midmorning to late afternoon. This is reflected in diurnal cycles of pollutants in data from elevation sites exhibiting distinctly increasing concentrations during midday to late afternoon. The onset of the increase is becoming later in the day with increasing elevation, reflecting the east-to-west and upward (in elevation) progression of the polluted air masses (Brodin et al., 2010; Benedict et al., 2018; Darby et al., 2021). There have been a few reported cases that demonstrated that this flow can make it all across the high mountain tops of the Continental Divide and descend into the Frazier Valley to the west of the Divide (Pfister et al., 2017b; Flocke et al., 2020). Midday to afternoon concentration increases resulting from upslope flow have been observed both for primary emissions (i.e., volatile organic compounds (VOCs; Benedict et al., 2019), oxidized nitrogen compounds (Benedict et al., 2018; Benedict et al., 2019), and secondary
The Front Range Air Pollution and Photochemistry Experiment (FRAPPE) and the Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) study took place in parallel in the wider NCFR during the summer of 2014 (Flocke et al., 2020). The research reported here contributed to these campaigns. The emphasis of our study was the investigation of spatial surface gradients of VOCs within and in the area surrounding Boulder, in particular of O&NG-related VOCs and their relation to O&NG well locations.

2. Methods

VOC and methane data were collected from 2 networks of sites. One network followed an elevation gradient from Boulder (≈1,600 m above sea level [asl]) to the University of Colorado Research Station (≈2,900 m asl) near Ward, CO. The other network included 5 sites in the eastern portion of Boulder County (EBC).

2.1. Elevation gradient measurements

Locations, elevations, site abbreviations, and sampling methods used at sites in the elevation gradient network are available in Table 1; locations are also marked on the map in Figure 1. Stainless steel (Summa) canisters were deployed to each site for whole air sample collection on 8 days in July and August 2014. A programmable flask package (PFPs) was deployed at the Lost Angels (LA) site on 4 days in July and August 2014. Continuous ozone observations from these sites during June–August, 2014, are reported by Oltmans et al. (2019).

The 6-L Summa canisters (part #27405, Restek, Bellefonte, PA, USA) were sampled at the elevation gradient sites for 3-h periods on 8 days when FRAPPE/DISCOVER-AQ aircraft missions took place. The canisters were conditioned prior to deployment by 3 cycles of filling with humidified zero air and evacuation to a final pressure of ≈1–2 in Hg. Canisters were placed within temperature-controlled buildings, and air was sampled from the outside via 0.64 cm o.d. sampling lines with an in-line ozone scrubber (glass fiber filter soaked in sodium thiosulfate solution [preparation details available in Helmig, 1997]) from inlets that were mounted 3–5 m above the surface. The sampling line was purged continuously by a pump at 1.2 L min⁻¹. Collection of air into the canister was through a tee in the sampling line and controlled by a programmable timer and Veriflo passive flow devices (part #24232, Restek) that maintained a constant flow of ≈25 ml min⁻¹ into the canister. The sampling was conducted over the 3-h period from noon to 3 PM. The final pressure in the canisters was ≈19 in Hg. Canister samples were analyzed via gas chromatography (GC) within 1–3 days of sampling.
**Figure 1.** Map displaying sites where VOC samples and methane measurements were collected. Blue stars indicate the elevation gradient sites, red stars the east Boulder County (EBC) sites, and purple dots indicate the locations of O&NG wells, respectively. The map with O&G well locations was obtained from the Colorado Oil and Gas Commission website (COGCC, 2016). DOI: https://doi.org/10.1525/elementa.2019.00036.f1

**Table 1.** Monitoring sites with site name abbreviation, location, elevation, and sampling methods. DOI: https://doi.org/10.1525/elementa.2019.00036.t1

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Site Abbr.</th>
<th>Lat.</th>
<th>Lon.</th>
<th>Elevation (m)</th>
<th>Sampling Methods Employed</th>
<th>Distance to Center of O&amp;NG Region (km)</th>
<th>Population Density (km⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soddie Lab (MRS)</td>
<td>SO</td>
<td>40° 2' 52'' N</td>
<td>105° 34' 15'' W</td>
<td>3,345</td>
<td>3-h canisters</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Coughlin</td>
<td>CO</td>
<td>40° 0' 13'' N</td>
<td>105° 28' 43'' W</td>
<td>2,523</td>
<td>3-h canisters</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Lost Angels Road</td>
<td>LA</td>
<td>40° 1' 8'' N</td>
<td>105° 24' 18'' W</td>
<td>2,392</td>
<td>PFP, 3-h canisters</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sugarloaf Road</td>
<td>SL</td>
<td>40° 1' 1'' N</td>
<td>105° 21' 28'' W</td>
<td>1,978</td>
<td>PFP, 3-h canisters</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>INSTAAR, CU-Boulder</td>
<td>BO</td>
<td>40° 0' 48''</td>
<td>105° 15' 11'' W</td>
<td>1,607</td>
<td>in situ GC</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Boulder County Public Health</td>
<td>BCPH</td>
<td>40° 2' 14'' N</td>
<td>105° 16' 53'' W</td>
<td>1,569</td>
<td>3-day canisters</td>
<td>48</td>
<td>1,568</td>
</tr>
<tr>
<td>Lafayette Fire Department</td>
<td>LFD</td>
<td>40° 0' 6'' N</td>
<td>105° 5' 40'' W</td>
<td>1,600</td>
<td>3-day canisters</td>
<td>44</td>
<td>1,095</td>
</tr>
<tr>
<td>Dawson School</td>
<td>DAW</td>
<td>40° 3' 50'' N</td>
<td>105° 6' 37'' W</td>
<td>1,562</td>
<td>3-day canisters</td>
<td>39</td>
<td>77</td>
</tr>
<tr>
<td>St. Luke’s Church</td>
<td>SLC</td>
<td>40° 1' 56'' N</td>
<td>105° 3' 24'' W</td>
<td>1,550</td>
<td>3-day canisters</td>
<td>38</td>
<td>427</td>
</tr>
<tr>
<td>Stephen Day Park</td>
<td>SDP</td>
<td>40° 10' 57''</td>
<td>105° 3' 49'' W</td>
<td>1,522</td>
<td>3-day canisters</td>
<td>30</td>
<td>1,210</td>
</tr>
</tbody>
</table>

MRS stands for University of Colorado’s Mountain Research Station. Distances to the O&NG producing region are included for East Boulder County (EBC) sites. These were determined using the distance function in Google Earth from each of the sites to the center of Weld County. Population density data were found at Bureau (2010) and Population (2016). EBC sites are listed in order of decreasing distance to the center of Weld County. GC = gas chromatography.
with the column flow split for compound identification by mass spectrometry (MS) and quantification by flame ionization detection (FID; more detail on the analysis method is provided in Section 2.4).

The PFP (Atmospheric Observing Systems, INC., Boulder, CO, USA) was deployed at the Lost Angels Road fire station site (LA) to investigate diurnal cycles of VOCs. The PFP contains twelve ≈0.8 L whole air sampling glass flasks, a set of shutoff valves, and an external compressor, to allow purging and then pressurizing the flasks sequentially with ambient air. Air was collected through an inlet line equipped with a sodium thiosulfate-coated inlet filter mounted at 2 m height outside of the building. Air samples were collected at 2-h intervals during 5 deployments (July 23, July 31, August 1, August 3–4, August 10–11), yielding a total of 42 samples. These samples were analyzed with the same analytical system as the canisters. The analysis procedure is detailed in Section 2.4.

2.2. East Boulder measurements

These samples were collected to investigate the influence of the nearby O&NG drilling region on the surface horizontal gradients of atmospheric methane and VOCs in the plains. The 5 sampling sites locations, elevations, sampling methods, and distances from the center of Weld County are listed in Table 1. Figure 1 shows the locations of these sites in relation to locations of O&NG wells.

The Boulder County Public Health (BCPH) building was chosen as the “urban reference” site for contrasting the sites in EBC. The BCPH site is located in the City of Boulder and is subjected to typical urban emission profiles emanating from mobile and industrial sources and is the furthest of the 5 sites from Boulder County’s border with Weld County (≈25 km), which marks the southwest corner of the region of concentrated O&NG operations. The population densities displayed in Table 1 were calculated based on the population and area of the nearest city, town, or incorporated settlement to the monitoring site (Bureau, 2010; Population, 2016).

Samples at the EBC sites were also collected in 6 L-Summa stainless steel canisters (Restek #27420, Bellefonte, PA). Canisters were deployed on 12 occasions for 3-day periods from mid-May to late August. Because these samples were collected over multi-day timescales, they are more representative of average conditions at a given site than shorter sampling techniques such as grab or aircraft sampling. The sampling schedule is provided in Figure S1. An example of the sampling setup is presented in Figure S2. In total, 36 days of canister sampling were conducted at each site. Consequently, the data obtained from this sampling represent the average of a total of 36 sampling days spread over the summer of 2014. To minimize temperature variations during the sampling, canisters were placed in ≈45 L insulated ice chest boxes with ≈6 L of water contained in plastic bottles. The sampling line, made of 0.16 cm o.d. silcosteel tubing (part #29191, Restek, Bellefonte, PA, USA), was fed through a hole in the box, and the inlet was fit with an ozone scrubber (same as described above). Effective sampling heights were ≈3 m above ground level. Canister sampling was controlled using VeriFlo passive flow devices (part #24232, Restek) that maintained a constant flow of ≈1 mL min⁻¹ into the canister over the 3-day sampling window. At the end of the sampling period, the final pressures in the canisters were ≈19 in Hg. Canisters were capped and transported to the lab for analysis (details in Section 2.4). Air samples were analyzed for methane and C₂–C₄ VOCs (including benzene, toluene, ethylbenzene, and xylenes [BTEX compounds]) using GC-FID/MS (Section 2.4).

2.3. Continuous GC data

Air was sampled from an inlet outside a second-story window at the former INSTAAR building (Rose Litman Laboratory 1) on the University of Colorado’s east campus (BO site, Figure 1). The sample preconcentration and injection system was similar in its configuration as the instrument described in Tanner et al. (2006) using an SRI 310 GC/FID (SRI Instruments #0310-6003, Torrance, CA) with a 0.32 mm i.d., 30 m length GasPro PLOT column (Agilent Technologies #113-4332, Santa Clara, CA). Ethane was not quantified because the GC ethane peak was not adequately separated. VOCs were analyzed on FRAPPE/DISCOVER-AQ flight days continuously at 2-h time resolution.

2.4. Canister and PFP sample analysis

First, methane was analyzed by drawing sample from the canisters (or PFPs) through a 3 mL sample loop at a flow rate of 50 mL min⁻¹ for 3 min. The loop content was then injected onto a Porapak Q packed column (0.31 cm, 0.21 cm i.D., 3.6 m long; Agilent Technologies #113-4362, Santa Clara, CA). GC separation was isothermal (at 50°C) with FID. The FID was calibrated using a whole air standard made of compressed air (breathing air); its methane mole fraction of 1.89873 ppb was determined by reference analysis against the NOAA Global Monitoring Division methane scale. The methane standard was run before and after each set of samples (no more than 7 samples analyzed at a time).

Following methane analysis, VOC sample volumes of 500 mL were first scrubbed of water by passing through a cryogenic trap (–30°C). VOCs were then preconcentrated on a Peltier-cooled micro-adsorbent trap (–30°C, Pollmann et al., 2006) and then injected into a GC-FID/MS equipped with a 60 m, 0.32 mm i.d., 30 m length GasPro PLOT column (Agilent Technologies #80468-800, Santa Clara, CA), with the column flow split between a second FID (i.e., in addition to the FID used for methane analysis) and an MS. The GC oven temperature began at 50°C for 2 min, was then ramped at a rate of 8°C min⁻¹, and held at 225°C for 15 min.

Blanks and calibration standards were analyzed prior to and immediately after each set of 7 canisters, and canister analysis results were blank-subtracted. Blank sample air was prepared by a custom zero-air generator that used a heated PO catalyst to remove hydrocarbons. Blank experiments were conducted by direct injection of zero air into the GC-MS system and by retrieving zero air from canisters after filling them with the blank air. Calibrations were performed using a series of gravimetrically prepared
3. Results and discussion

3.1. Elevation gradient data

Figure 2 shows VOC mole fractions from the canister measurements along the elevation gradient, with sites arranged by decreasing elevation from left to right. Ethane mole fractions and the variability in the data increase as elevation decreases. For all sites but Soddie (SO), the ethane mean mole fraction is at least 2 ppb higher than the median, indicating that means are biased upward by selected occurrences of high mole fractions. Propane shows a similar behavior, except that mole fractions are highest and most variable at the Lost Angels (LA) site. Mountain homes in the area are primarily fueled by propane gas with storage tanks that are located on the premises. This accounts to a high number of potential point sources within the area that may explain why observations at LA deviate from the elevation gradient seen for ethane.

For the Coughlin (CO) site, 2 samples showed anomalously high (more than 10 times higher than the median of other data) mole fractions for VOCs > C3. This mostly concerned gasoline-type compounds. Those samples also showed an i/n-pentane ratio that was larger than 1.5, which is characteristic for gasoline and urban emissions, while data from the other, further eastern sites, had lower i/n-pentane ratios. We suspect that these sample values resulted from a nearby petroleum source, possibly a gasoline leak from a nearby residence. It is possible that the mole fractions observed at the CO site are exacerbated by the site's location in a valley defined by Bald Mountain, Klondike Mountain, and Hurricane Hill. Those data were therefore excluded from further consideration.

For the other samples, mole fractions for >C3 compounds also generally increase as elevation decreases, but higher median mole fractions are observed at LA than at the lower elevation Sugarloaf (SL) site for i-butane, the pentane isomers, hexane, benzene, and toluene. It is noteworthy that overall, the concentration gradient is most evident for the natural gas VOCs (i.e., ethane, propane, butane isomers) and becomes less pronounced with increasing molecular weight of the hydrocarbon. Scatterplots that show individual canister measurements as a function of elevation are available in Figure S3.

3.2. East Boulder County observations

3.2.1. Methane

Figure 3 shows box whisker plots of the statistical distribution of methane values at sites in the EBC network. The regional background level of methane (estimated from the 10th percentile value from NOAA monitoring at the Mountain Research Station Niwot Ridge site in the summer of 2014) is shown as a red horizontal line in the figure. Methane was lowest at the BCPH site and increased toward the east of the county; the overall highest levels were observed at Stephen Day Park (SDP) in Longmont. The methane enhancement (values above background) at SDP was approximately twice that seen in Boulder. There was a noticeable increase in variability with increasing absolute levels, indicated by the wider spread of the data at the more easterly EBC monitoring sites. These 2 features (higher absolute levels as well as higher variability) are a clear indication of higher abundance and stronger strength of methane sources in the eastern part of the county.

Methane is emitted from a variety of sources. Correlations of methane with characteristic VOCs can provide insight into the contributing local sources. Pearson correlation coefficients (PCC) and the statistical significance (P-values) of orthogonal linear regressions of mole
fractions of methane and VOCs in all data combined are reported in Table 2. Figure 4 visualizes these relationships. Data points are color coded by site; PCC are available in the title of each plot.

The C2-C5 alkanes have statistically significant correlations with methane at >95% confidence (Table 2), with ethane and propane having the highest correlations (PCC = 0.75 and 0.54, respectively). The butane and pentane isomers have correlations with methane that range from PCC = 0.37 to 0.46. Poorer correlations were found for other compounds. Controlled and fugitive emissions, and incomplete flaring of natural gas is the globally dominant source of atmospheric ethane (Tzompa-Sosa et al., 2017). Secondary sources are biofuels and biomass burning. These 2 latter source categories were of negligible importance for the NCFR during the summer of 2014; therefore, it is highly likely that emissions from natural gas extraction industry are the dominant regional source of ethane. The tight correlation between methane and ethane in our data indicates that a major portion of methane and the light n-alkanes (especially ethane and propane) resulted from common sources. This has been pointed out previously: Pétron et al. (2014) estimated from their 2012 experiment that 75%; Peischl et al. (2018) estimated that during a campaign in 2014, 75 ± 37%; and Kille et al. (2019) estimated that in 2015, 63 ± 17% of observed methane emissions in the DJB were attributable to O&NG sources. Our mean ethane/methane ratio (EMR) result for the linear regression analysis (9.12% molar) for all 4 site data is /C25 50% lower than mean slope values reported by Peischl et al. (2018) and Kille et al. (2019; that span a range of 13%–16%), which can possibly be attributed to a relatively lower O&NG influence in our sample population compared to these 2 comparison studies (i.e., methane contributions from non-O&NG methane sources will pull the EMR to lower values) that relied more heavily on sampling within the central region of the DJB. Similarly, our propane/methane molar ratio of 4.6% is smaller than a ratio of 15% that was found from mobile lab and stationary surface sampling in the central DJB by Pétron et al. (2014). The fact that VOC/methane correlations become weaker for the heavier VOCs (i.e., toluene and ethylbenzene) is likely due to 2 reasons: (1) The atmospheric lifetimes of VOCs from reaction with OH become

![Figure 2. VOC mole fractions from canister measurements along the elevation gradient. Sites on the x-axis are in order of decreasing elevation. Boxes show the range of 25th–75th percentile data. The middle line represents the median. The diamond represents the mean. Whiskers show 10th and 90th percentile ranges. DOI: https://doi.org/10.1525/elementa.2019.00036.f2](image-url)
alkanes. None of the compounds in EBC (Pe´tron et al., 2012; Pe´tron et al., 2014; Thompson et al., 2014) are indicative of O&NG emission being a strong regional emission source for these VOCs. The spatial gradient becomes weaker with increasing alkane molecular weight. Other VOC, for example BTEX compounds, show more similar mole fractions and variability across all sites. This suggests that multiple sources are contributing to their emissions, which is consistent with findings from other previous NCFR studies (Pétron et al., 2012; Pétron et al., 2014).

The observed gradients do not show an obvious correlation with population and traffic density, which is highest at the BCPH site (Table 1). As a matter of fact, median mole fractions are lowest at BCPH for all of the C2–C5 alkanes. None of the compounds in Figure 5 exhibit a gradient that correlates with population density. This behavior suggests that population and traffic density have a relatively small influence on the composition of the petroleum hydrocarbons at these sites. At all of the EBC network sites, median results for ethane and propane are all higher than those reported in data from 28 much larger urban U.S. cities (Baker et al., 2008; except for 1 case, i.e., BCPH propane compared to Los Angeles). Since petroleum hydrocarbons constitute the bulk of the overall VOC carbon, O&NG sources have a strong role in determining the regional VOC gradients. C2–C5 alkanes are the most abundantly emitted VOCs from O&NG operations (Pétron et al., 2012; Swarthout et al., 2013; Helmig et al., 2014; Pétron et al., 2014; Thompson et al., 2014); their highly elevated concentrations, and the clear gradients of these compounds as distance to the O&NG region decreases, demonstrate how selective these compounds are as O&NG emissions tracers, and how strongly these O&G industry emissions influence VOC composition and absolute levels not just in the immediate surrounding of well sites, but on large geographical scales in the NCFR.

The variability of the observed mole fractions for the C2–C5 alkanes, shown by the range of the box-whiskers in Figure 5, increased with decreasing distance to Weld County. High variability has indicated proximity to a source in other previous work (Russo et al., 2011; Sharma et al., 2016; Zheng et al., 2017). It is remarkable that this behavior is this pronounced despite that these results are from 3-day integrated sampling. Emission plumes are most compact at their source and gain volume during transport from dispersion and entrainment of the surrounding air. Their relatively small initial volume makes it more likely that factors such as wind direction will result in a nearby monitoring site “missing” the plume. For the same reason, if the center of the plume passes through the monitoring site, then high mole fractions will be observed because this portion of the plume has undergone the least mixing with surrounding air. Therefore, sampling at a site near a source will produce a dataset with a large amount of variation. The high degree of variability seen at the eastern network sites (especially at SDP) for the petroleum hydrocarbons at these sites.

The bottom right panel of Figure 5 shows the i/n-pentane isomeric ratios observed at each of the EBC sites. Gilman et al. (2013) investigated i/n-pentane isomeric ratios in different urban and O&NG influenced settings and defined an overall range of 0.9–3, with the lower end values being characteristic of air that is strongly influenced by O&NG emissions, and the higher end values being typical urban signatures. The highest i/n-pentane ratios were observed at BCPH. Median ratios of i/n-pentane at LFD, DAW, SLC, and SDP are 0.09–0.19 lower than at BCPH, and other percentile values of the i/n-pentane ratio similarly show a general trend towards smaller values from west-to-east and closer proximity to the DJB, which likely is indicative of the increasing influence of O&NG emissions on the pentanes composition along this transect.
The atmospheric photooxidation of VOCs by the hydroxyl (OH) radical fuels the diurnal ozone production. The contribution of the identified VOCs to the OH reactivity (OHR) and the spatial gradients of OHR from the identified VOCs was estimated for the C_2–C_8 alkanes, BTEX compounds, acetylene, and propyne. Please note that these calculations represent only a portion of the total OHR. There are many other atmospheric gases, that is, nitric oxide, carbon monoxide, alkenes, unsaturated biogenic VOCs, and partially oxidized VOCs (i.e., alcohols, aldehydes, ketones), that also contribute to the total OHR and that were not included in our assessment of the OH reactivity because of the lack of their observations.

OHR were determined by multiplying the mole fraction of each compound quantified during deployment periods by its OH reaction rate constants (Hatakeyama et al., 1986; Atkinson, 2003). OHRs of considered compounds were then totaled for each deployment period (\( \Sigma \text{OHRs} \)). The statistical distribution of \( \Sigma \text{OHRs} \) from all deployments at each site and the spatial gradient of the results from the 5 considered sites is shown in Figure 6. Figure 7 shows pie charts of the campaign median mole fractions by

![Figure 4. Comparison of VOC and methane mole fractions at EBC sites.](https://doi.org/10.1525/elementa.2019.00036.f4)

The atmospheric photooxidation of VOCs by the hydroxyl (OH) radical fuels the diurnal ozone production. The contribution of the identified VOCs to the OH reactivity (OHR) and the spatial gradients of OHR from the identified VOCs was estimated for the C_2–C_8 alkanes, BTEX compounds, acetylene, and propyne. Please note that these calculations represent only a portion of the total OHR. There are many other atmospheric gases, that is, nitric oxide, carbon monoxide, alkenes, unsaturated biogenic VOCs, and partially oxidized VOCs (i.e., alcohols, aldehydes, ketones), that also contribute to the total OHR and that were not included in our assessment of the OH reactivity because of the lack of their observations. Therefore, analyses and interpretations presented here reflect the relative contribution among the identified VOC species only and not of the overall reactivity of all VOCs present in ambient air.

OHR were determined by multiplying the mole fraction of each compound quantified during deployment periods by its OH reaction rate constants (Hatakeyama et al., 1986; Atkinson, 2003). OHRs of considered compounds were then totaled for each deployment period (\( \Sigma \text{OHRs} \)). The statistical distribution of \( \Sigma \text{OHRs} \) from all deployments at each site and the spatial gradient of the results from the 5 considered sites is shown in Figure 6. Figure 7 shows pie charts of the campaign median mole fractions by...
compound class and scaled to the number of carbons for each considered VOC (ppbC). The bottom row of graphs depicts the OHRs calculated from these median values. (Please note that the median mole fractions for each compound were not necessarily observed during the same deployment period; therefore, the sum of OHRs in the pie charts may not be exactly identical to the median value in the box plots in Figure 6).

Both analyses result in BCPH having the lowest total OHR and the lowest OHR variability. There is a general tendency of OHR variability and absolute percentile values increasing with the site being located further to the east. Figure 7 shows that the C₂–C₅ alkanes made up 72%–88% of the mole fractions of carbon (ppbC) of the quantified compounds and 52%–79% of ΣOHR at each site. The median total amount of VOC carbon of quantified species almost triples going from BCPH to SDP. Despite constituting only 4%–12% of the ppbC observed at each site, the alkenes and BTEX considered by this analysis accounted for 8%–22% of ΣOHR at the EBC sites due to the relatively fast reaction constant speeds with OH, demonstrating the reactive potential of the unsaturated VOCs to the ΣOHR.

3.3. Diurnal cycle of VOC

Figure 8 shows 7 diurnal cycles of VOCs measured by the in situ GC at INSTAAR. A striking feature is the high variability in the data and the lack of a consistent diurnal cycle. During most times, individual VOC species behave quite similarly in their dynamic behavior, suggesting that they mostly arise from common source emissions that are transported to the site. Mole fractions of some VOCs peaked during the day on 3 of the sampling dates. Propane and isomers of butane and pentane are the most frequently and most highly elevated compounds. Despite this sampling being from an inner-city site, and within ≈100 m of a very busy traffic intersection and a gas station, benzene and toluene are rarely above ≈0.2 ppb.

The high variability seen in these data suggests that these light alkane VOCs likely arise from upwind emission sources that are variable in strength and/or that transport regimes vary such that polluted air from these sources is only transported to the site with particular air flow conditions. The absence of a distinct diurnal cycle for these compounds indicates that nearby emissions (within ≈1 day of transport time distance) have a stronger influence than daily photochemical oxidation and boundary layer dynamics, which both would result in concentration minima during midday hours. During the events on July 20 and July 31, the i/n-pentane ratio rises, which suggests urban or industrial sources (Gilman et al., 2013). This is supported by HYSPLIT back trajectories (Figures S4 and S6), which show that the air parcels that reached INSTAAR at the time of the event had passed through rural and urban areas in the 8 h preceding the event. In contrast, the VOC peak seen on July 26 is accompanied by a drop in the i/n-pentane ratio. The HYSPLIT back trajectory for this event (Figure S5) shows that the air parcel had circulated northeast of the city of Boulder and had passed through the southwestern part of Weld County. East to west transport as seen on July 26 is fairly common in this region, especially during mid to afternoon hours in the summer months, as elucidated in the introduction section.

The diurnal cycle data also do not show an obvious correlation with the diurnal traffic behavior (there are no peaks in VOCs concentrations seen during traffic rush hours). With mixed boundary layer depths being the highest during midday to afternoon hours, particularly during the midsummer, the large enhancements that were seen during midday hours in this surface sampling can be deemed representative of a large atmospheric column and therefore an indication of the strength of these sources.

Diurnal cycles were collected via PFP sampling at the LA site and are available in Figure S7. A comparison of the 3-h integrated samples with the PFP results is provided in Table S3. The PFP measurements support the canister measurements (Figure 2) in that propane is often higher than ethane in these elevation samples. This also supports the conclusion that the LA site, or potentially a larger area in this mountainous region, is exposed to local propane sources, possibly related to domestic gas usage. Expected diurnal cycles, that is, minimum mole fractions during the day and maximum mole fractions at night, are not clearly present in these diurnal cycles (Figure S7), nor are any obvious pollution transport events during these sample dates. The lack of consistent behavior suggests daily transport patterns are variable, at least in this limited number of samples. As for the canister data, the i/n-pentane isomeric ratios in the PFP data are close to the O&NG signature, which shows that these high elevation sites exhibit VOC signatures that are predominately influenced by VOC sources and the upslope transport of polluted air from the plains.

4. Summary and conclusions

Observations from 2 monitoring networks showed clear elevation gradients for VOCs and spatial gradients of
methane and VOCs in the plains between the City of Boulder and the eastern Boulder County line. Mole fractions of C₂–C₅ alkanes decreased with increasing elevation and increased with decreasing distance to the O&NG producing areas in Weld County to the east. The increase in absolute mole fractions was paralleled by an increase in the variability of mole fractions. Among the identified VOCs, the total VOC carbon was dominated by light alkane hydrocarbons throughout the networks. C₂–C₈ alkanes made up 88%–95% of the total VOCs carbon (ppbC) that was quantified by this study. This high contribution of O&NG petroleum hydrocarbons to total VOCs indicates that O&NG VOCs are abundant throughout the plains east of the Front Range and not only in the areas immediately surrounding O&NG development. This conclusion is further supported by the i/n-pentane ratios seen in the data.

Medians of i/n-pentane ratios at the EBC sites ranged from 1.01 to 1.20, which is characteristic of O&NG influence. These ratios confirm the previously reported ratios of 1.1 at observation sites in Erie, CO, and Longmont, CO (Gilman et al., 2013; Thompson et al., 2014).

The spatial gradients, with increasingly elevated VOC toward the center of Weld County, as well as the predominance of petroleum hydrocarbons in the VOCs spectrum, are in accord with other previous VOC monitoring results. Unusually high levels of VOCs have been reported in measurements taken at the Boulder Atmospheric Observatory (BAO), which was located near the town of Erie in the southwest corner of Weld County (Petron et al., 2012; Brown et al., 2013; Gilman et al., 2013; Swarthout et al., 2013; Oltmans et al., 2021). VOCs associated to O&NG sector emissions were the single largest VOC-reactivity

Figure 5. Box whisker plots of VOCs quantified in canister samples from the City of Boulder (BCPH) and the 4 Eastern Boulder County sites. The bottom right panel shows the (i/n) pentane ratio of the data. DOI: https://doi.org/10.1525/elementa.2019.00036.f5
contributing sector (40%–60% of total; with others being traffic, background, and secondary chemical production) throughout the morning hours (a biogenic factor also became important during 2–10 PM; Abeleira et al., 2017). Thompson et al. (2014) reported that O&NG petroleum hydrocarbon $C_2$–$C_5$ alkanes were enhanced by a factor of 18–77 relative to the regional background at residences in southwest Weld County. Unexpectedly high benzene mole fractions were reported in measurements taken near Platteville, approximately 28 km to the northeast of BAO, and further toward the center of the DJB (Halliday et al., 2016). The maximum observed value was 29.3 ppb. The authors implicated emissions from O&NG facilities to the southwest of the site. Surface automobile transects data collected inside Weld County showed tight $n$-alkane-methane and alkane-alkane correlations in the proximity of O&NG facilities (Pétron et al., 2014). These geographic patterns are not only present at the surface but also in the mixed boundary layer, as seen in aircraft measurements: Mixed boundary layer mole fractions of methane and the O&NG tracer ethane were highest within and downwind of the DJB (Pétron et al., 2014; Richter et al., 2015; Peischl et al., 2018; Flocke et al., 2020). The data and analyses presented here are consistent with this larger body of research that shows that the DJB O&NG operations constitute a strong source of atmospheric petroleum hydrocarbons that may dominate the VOCs spectrum and total carbon fraction from VOCs.

The higher time resolved data from the in situ monitoring within the City of Boulder showed evidence for pollution transport from the center of the O&NG basin into Boulder County to the west. Elevated values of the O&NG tracer ethane, low $i/n$-pentane values, and back trajectory analyses associated an event with the most

Figure 6. Box whisker plots of the sum of OH reactivity (OHR) of the quantified VOCs in the EBC network. Considered compounds were $C_2$–$C_8$ alkanes, BTEX, acetylene, and propyne. DOI: https://doi.org/10.1525/elementa.2019.00036.f6

Figure 7. VOC classes and their OH reactivity at EBC network sites. Top row: Contribution of measured compounds classified into $C_2$–$C_5$ alkanes, $C_6$–$C_{10}$ alkanes, BTEX, and alkenes + alkynes to the total, with each individual VOCs mole fraction multiplied by its number of carbons (ppbC) at the EBC sites. The sum of all compound class mole fractions (in ppbC) is given underneath the pie graphs. Bottom row: Median OH reactivity (OHR) of the same VOCs classes as in the upper row (OHR, lower row [s$^{-1}$]). DOI: https://doi.org/10.1525/elementa.2019.00036.f7
enhanced levels of VOCs to O&NG emissions transported from the DJB. The observations presented here further demonstrate that the O&NG influence extends at the surface well beyond the boundaries of Weld County toward adjacent counties and into the eastern foothills of the Rocky Mountains. The influence of VOC emissions and transport was evident at the CO site, some 1,000 m in elevation above, and ≈20 km to the west of Boulder, demonstrating that the spatial and vertical extent of pollution transport from the NCFR plains extends into the foothills on the eastern flanks of the Rocky Mountains.

The OHR contribution from petroleum hydrocarbons generally increased with decreasing distance to the DJB.
C2–C5 alkanes contributed 0.36–1.36 s−1, or 52%–79% to the OHR of the compounds that were quantified at the EBC sites. This is a sizable contribution given the relatively slow OH rate constants for these compounds. OHR from petroleum hydrocarbons was lowest at the urban/most densely populated City of Boulder site (BCPH). Our results for C2–C8 alkane mole fractions are within the range of the alkane portion of OHR determined by McDuffie et al. (2016), who found that petroleum alkanes were responsible for 50% of the OHR at the BAO. Using atmospheric modeling, these authors went a step further and estimated that these alkanes contributed ~20% to the regional photochemical ozone production. The horizontal gradient in OHR with approximately 3 times higher values at the furthest eastern site points toward faster and more chemical reactivity and ozone production from these VOC species in the area represented by the eastern network sites than in the City of Boulder.

VOCs from industrial and mobile sources have decreased in most areas in the United States and Europe (Warneke et al., 2012; Monks et al., 2015; Rossabi and Helmig, 2018). Reductions in automobile VOCs emission have made a major contribution to these trends (Von Schneidemesser et al., 2010; Warneke et al., 2012). Declining automobile-related emissions have caused other emission categories, such as household and personal care products, to increase in their relative importance (Coggon et al., 2018; McDonald et al., 2018). Stricter regulations targeting O&NG emissions appear to have been successful in reducing average emissions per well unit; however, these reductions have likely been offset by the increase in the number of wells, with the overall result being only a modest overall decline in emissions (Peischl et al., 2018). A recent trend analysis of 8 years of BAO data concluded that actual total emission reductions are likely approximately only 1 quarter of regulatory inventory projections (Oltmans et al., 2021).

The results from our and these referenced research studies show that O&NG VOC emissions in the NCFR are a strong source of total VOC carbon and may contribute as much as half of the OHR. The VOC mixture in the NCFR contains a higher fraction and abundance of alkanes from O&NG sources compared to other urban regions (Zaragoza et al., 2017). These O&NG VOC emissions contribute to photochemical ozone production, and their atmospheric oxidation appears to be particularly crucial in the occurrences of peak ozone events in the NCFR (Zaragoza et al., 2017), contributing 30%–40% to the regional ozone production (Pfister et al., 2017a; Oltmans et al., 2019; Flocke et al., 2020). Cheadle et al. (2017) estimated that O&NG emissions contribute locally up to 30 ppb on high ozone days. While improvements in surface ozone have been achieved in many regions of the United States (Chang et al., 2017), surface ozone in the NCFR thus far has not shown clear signs of improvement (Bien and Helmig, 2018) despite notable reductions in nitrogen oxides emissions (Abelaira and Farmer, 2017; Bien and Helmig, 2018). Nine counties within the NCFR remain in nonattainment for the ozone NAAQS. Flocke et al. (2020), in their campaign overview publication, conclude about O&NG emissions that, “This emission sector is also identified as carrying the largest uncertainties in currently available emission inventories, both with regard to magnitude and emission factors.” The findings of our study illustrate another complexity to this evaluation: Ambient air concentrations of methane and VOCs show spatial gradients that reflect the distribution and heterogeneity of the location of emissions from the O&NG extraction operations and their transport under the diverse surface flow and meteorological conditions in the NCFR. This and other FRAPPE and DISCOVER-AQ studies reemphasize that O&NG sector emissions exert an important influence on the regional air quality not just within the DJB and Weld County but also into neighboring counties and into the Rocky Mountain Foothills.

**Data accessibility statement**

The data from the surface sites monitoring are available in the FRAPPE/DISCOVER-AQ data archive (https://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq.co-2014?GROUND-BOULDER=1).

**Supplemental files**

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

- Figures S1–S7.
- Tables S1–S4.
- Docx.

**Acknowledgments**

Assistance from these INSTAAR/University of Colorado colleagues is acknowledged: John Ortega helped with the sampler installation and Brendan Blanchard with code development for data processing. Katie Smith and Reed Terrell assisted with the sampling and analysis work. Jana Milford and Mike Hannigan, Mechanical Engineering, University of Colorado, contributed to the planning of the study.

**Funding**

The East Boulder County sampling program and DH’s work on the manuscript were sponsored through contracts from Boulder County Public Health. The State of Colorado Department of Public Health and Environment (CDPHE) provided funding for the elevation gradient project. The National Science Foundation (NSF) funded the facilities and research at the Mountain Research Station site/Niwot Ridge under the Long-term Ecological Research program (award # DEB 1027341). FRAPPE was funded through a federal–state partnership between CDPHE and the National Science Foundation. DISCOVER-AQ was a NASA-led and funded campaign.

**Competing interests**

DH is the Editor-in-Chief of the Atmospheric Science domain of *Elementa*. He was not involved in any aspects of the editorial review process and evaluation of this manuscript.

**Author contributions**

Analyzed data, interpreted data, prepared graphics, and the manuscript: SR.
Prepared sampling equipment, collected and analyzed samples, and performed data quality control: JH.

Contributed to the design of the study: PM.

Set up GC system at INSTAAR, analyzed data, and contributed to the manuscript preparation: WW.

Contributed to the planning, design, sites selection, and execution of the study; analyzed data, prepared, and revised the manuscript: DH.

References


