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Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado

Chelsea R. Thompson[1]* • Jacques Hueber[1] • Detlev Helmig[1]

[1]Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado, United States
*chelsea.r.thompson@colorado.edu

Abstract

The Northern Front Range (NFR) region of Colorado has experienced rapid expansion of oil and gas extraction from shale and tight sands reservoirs in recent years due to advances in hydraulic fracturing technology, with over 25,000 wells currently in operation. This region has also been designated as a federal ozone non-attainment area by the U.S. EPA. High ozone levels are a significant health concern, as are potential health impacts from chronic exposure to primary emissions of non-methane hydrocarbons (NMHC) for residents living near wells. From measurements of ambient atmospheric NMHC present in residential areas located in close proximity to wells in Erie, Colorado, we find that mean mole fractions of the C2–C5 alkanes are enhanced by a factor of 18–77 relative to the regional background, and present at higher levels than typically found in large urban centers. When combined with NMHC observations from downtown Denver and Platteville, it is apparent that these compounds are elevated across the NFR, with highest levels within the Greater Wattenberg Gas Field. This represents a large area source for ozone precursors in the NFR. The BTEX aromatic compounds in Erie were comparable to (e.g., benzene) or lower than (e.g., toluene, ethylbenzene, xylene) in large urban centers, however, benzene was significantly higher in Platteville, and within the range of chronic health-based exposure levels. An initial look at comparisons with data sets from previous years reveal that ambient levels for oil and gas-related NMHC in Erie, as well as further downwind in Boulder, have not decreased, but appear to have been increasing, despite tightening of emissions standards for the oil and gas industries in 2008.

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1. Introduction

The Northern Front Range (NFR) region of Colorado has experienced rapid development of oil and gas drilling operations in recent years. The Denver-Julesburg Basin (DJB) is one of the most intensively drilled fields in the United States, and is currently home to over 25,000 active wells, ~24,000 of which are located in Weld County located north of the city of Denver and northeast of Boulder (Pétron et al., 2014), near and within the highly populated NFR (see Figure 1). Gas production has been increasing since 1990, and oil production has been increasing since 1999, with this growth primarily attributable to the Greater Wattenberg Field, a rich natural gas field of approximately 2530 km^2 located in the DJB. As of 2012, Colorado ranked as the 6th highest state in the U.S. in number of natural gas wells, with 32,000 total, and dry natural gas production accounting for 6.8% of total U.S. production (EIA, 2014). Increases in oil and gas production in the DJB are primarily the result of horizontal drilling and hydraulic fracturing ("fracking") technologies.

The rapidly expanding use of fracking in Colorado, and other shale formations in the United States, has led to growing environmental and public health concerns, primarily relating to air and water quality. A growing body of scientific research is finding that emissions of non-methane hydrocarbons (NMHC) from oil and gas drilling and related activities are leading to poorer air quality (Katzenstein et al., 2003), contributing to high

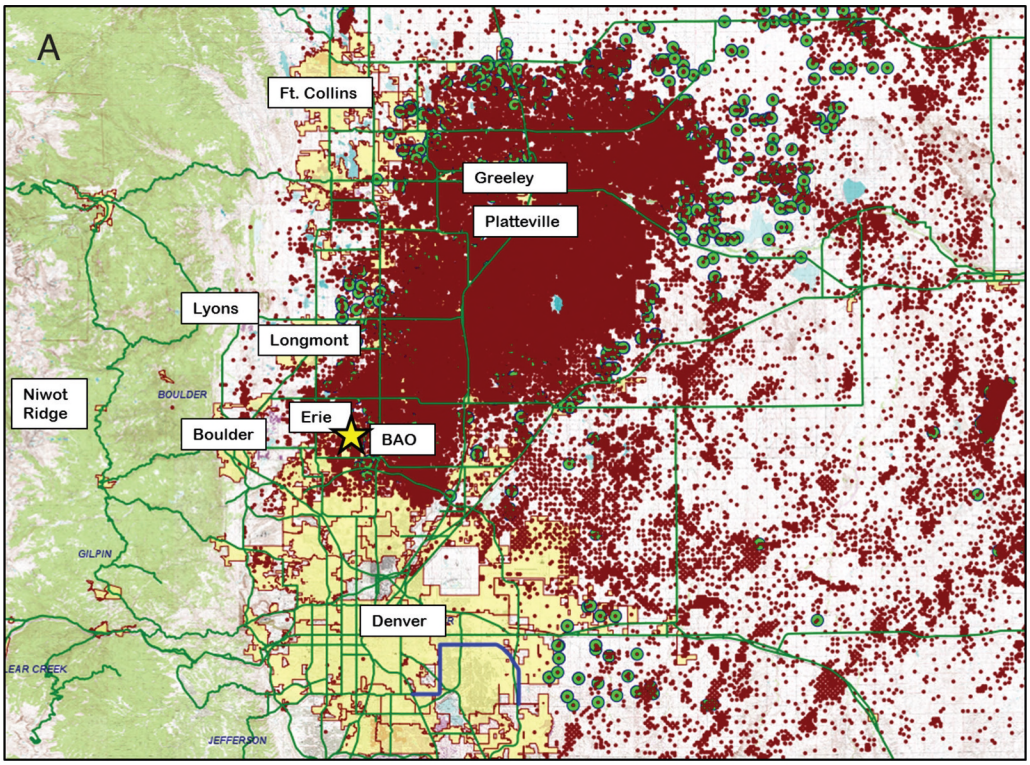

Figure 1

Map of oil and gas wells in the Colorado Northern Front Range.

Map of active (red) and proposed (green) oil and gas wells in the Colorado Northern Front Range (map from Colorado Oil and Gas Conservation Commission cogcc.state.co.us/home/gismain.cfm). The Boulder Atmospheric Observatory (BAO) is notated by the yellow star.

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ozone episodes (Edwards et al., 2013; Kemball-Cook et al., 2010; Oltmans et al., 2014; Schnell et al., 2009), and causing health concerns (Colborn et al., 2011; 2014; McKenzie et al., 2012). Elevated levels of NMHC can lead to diminished air quality as they are precursors to photochemical ozone formation and secondary organic aerosols. A large fraction of the NFR, encompassing both the Denver metropolitan area and Weld County, has been designated as a Federal Non-Attainment Area since 2007 for violation of the National Ambient Air Quality Standard for 8-hr ozone, currently set at 75 ppbv, with violations primarily occurring in the summer months (CDPHE, 2013). In an effort to mitigate the ozone production, the Colorado Department of Public Health and Environment (CDPHE) implemented stricter VOC (volatile organic compounds) emissions controls on oil and natural gas (O&NG) operations in 2008 to achieve a 90% reduction in VOC emissions during the summer months, including a mandatory VOC emissions reduction of 95% from condensate tanks, in conjunction with an already on-going statewide mandatory automotive emissions inspection program. Further tightening of O&NG VOC emissions, and new controls on methane, have recently been implemented by the Air Quality Control Commission in 2014 (CDPHE, 2014).

Recent studies focusing on the NFR (Pétron et al., 2012; Gilman et al., 2013; Swarthout et al., 2013) have revealed enhanced atmospheric methane and NMHC from operations in the Greater Wattenberg Field. In February–March, 2011, as part of the NACHTT experiment, continuous, in-situ measurements of NMHC were made from the Boulder Atmospheric Observatory Tall Tower located in Erie. Gilman et al. (2013) observed high NMHC levels that were well correlated with propane, indicating the dominant oil and gas source of these emissions. Additionally, this study found that NMHC attributable to O&NG operations, primarily short-chain alkanes, accounted for 55% of the OH reactivity, or ozone production potential, in the region. This conclusion was independently verified by Swarthout et al. (2013) during the same campaign from whole-air canister samples. From vertical profiles and wind back-trajectory analyses, Swarthout et al. (2013) determined that the dominant source of the alkanes was from the Greater Wattenberg Field. Most recently, Pétron et al. (2014) implemented a top-down approach via aircraft for calculation of NMHC emissions over the DJB and concluded that the state inventory for total O&NG-related NMHC emissions is at least a factor of two too low, while emissions of benzene alone were approximately seven times larger than the state inventory.

While oil and gas development has traditionally been conducted in rural areas, this dynamic has been changing in recent years, with an increasing number of wells being drilled in residential and municipal locations, posing new questions related to health impacts of oil and gas emissions. In Colorado, community groups have successfully lobbied for, and passed, drilling moratoriums in several communities across the NFR citing the need for further scientific research. Health impact studies relating to oil and gas operations are sparse, and challenging due to the chronic nature of such exposures; however, a recent study by McKenzie et al. (2012) conducted in Garfield County found that residents living within 1/2 mile of wells were at a greater risk of health impacts relating to NMHC exposure, such as to benzene, a known carcinogen. An air sampling study

conducted at a private residence in the same region by Colborn et al. (2014) identified numerous chemical species that have the potential to cause detrimental health effects, such as endocrine disruptors, and detected levels of poly-aromatic hyrocarbons (PAHs) high enough to lead to diminished mental development in children who suffered prenatal exposure. Conversely, Bunch et al. (2014) reported that ambient levels of NMHC air toxics in the Barnett Shale (e.g., benzene, toluene) were not present at levels that would constitute a health concern based upon both acute and chronic exposure limits, as defined by the Texas Commission on Environmental Quality (TCEQ). It should be noted, however, that exposure limits are typically determined upon exposure to individual chemicals, and do not account for effects from interactions amongst multiple chemicals, nor do they include impacts on prenatal development, such as is the case with endocrine disruptors (Colborn et al., 2014). Apart from concerns related to primary NMHC emissions, ozone is also a health concern, as elevated levels of ground-level ozone can lead to severe respiratory distress (Koren et al., 1989; Tager et al., 2005; Triche et al., 2006). Unlike the NMHC emissions, ozone is a secondary pollutant that can often be formed far from the source of precursor compounds, and thus becomes a regional problem.

Although several recently published studies have focused on O&NG-related NMHC in the NFR, none have yet specifically addressed ambient NMHC levels within primarily residential areas to investigate exposure by the general population. Here, we present results from an air sampling study conducted in 2013, in which we collected a series of ambient air samples from private residences in and near Erie, Colorado. This sampling effort was specifically motivated by a pilot health study conducted by a local doctor that found elevated levels of certain NMHC (i.e., ethylbenzene and xylenes) in the blood of a group of Erie residents. We were approached with the request of conducting air sampling near the homes of these patients to investigate if residents in this area are exposed to unusual levels of NMHC from nearby oil and gas operations. Using these data, as well as NMHC measurements from several other datasets in the region, we investigate the spatial distribution and temporal changes of common NMHC in the region, and show that elevated mole fractions of O&NG-related NMHC are widespread in the NFR, and that ambient levels of these compounds have been increasing in recent years both within and downwind of DJB operations.

2. Measurement sites and methods

2.1. 2013 Erie/Longmont air sampling

This was a limited study consisting of a total of thirty whole air samples divided amongst seven residences within the town of Erie, and north of Erie, in rural farmland approximately halfway between Erie and the town of Longmont. Erie (population ~19,000) and Longmont (population ~89,000) are located on the eastern edge of Boulder County, and straddle the county line into Weld County. This also marks the southwestern edge of the Greater Wattenberg Gas Field.

In Erie, as with other towns in this region, there are a significant number of gas wells located in close proximity to homes, residential neighborhoods, schools, and community centers (Figure 2). The well setback requirements as of 2012 require a 350 foot (107 m) setback from outdoor activity areas and 500 foot (152 m) setback from building units, however, this does not apply to existing or previous well locations (COGCC, 2012). In Erie, some gas wells are located as close as 15 feet (4.6 m) from residential structures. The sampling sites for this study included five homes located within the town of Erie in large residential neighborhoods, three of which were located in Boulder County and two in Weld County. For these five homes, the nearest wells were located 105, 125, 165, 206, and 424 m away. The remaining two sampling sites were small farms located north of Erie, between Erie and the town of Longmont. These properties are considered rural, with their closest wells located 206 and 335 m away. All samples were collected outside in backyards or adjacent open space to avoid close proximity with neighborhood streets or driveways. For the purposes of this work, we have grouped the sampling sites into three general regions, East Erie (Weld County side), West Erie (Boulder side), and Longmont, as shown in Figure 3. To respect the privacy and anonymity of the residents, the exact location of their homes is not disclosed.

Whole air samples were collected between March–June 2013 into evacuated 6-L stainless steel Summa canisters (Restek Corp., Bellefonte, Pennsylvania). Veriflo flow controllers (Restek Corp.), consisting of a pressure sensor and critical orifice, were used to restrict the air-flow into the canister to allow for 24-hour and 3-hour integrated samples. Flow controllers were tested for flow rate consistency prior to deployment and were found to have stable flow until the last 5% of canister vacuum. Ozone was scrubbed from the air entering the canister using an inline AcroDisc 50 mm diameter glass fiber filter (Pall Corp., Port Washington, NY) impregnated with sodium thiosulfate (Pollmann et al., 2005). Nineteen 24-hour samples and six 3-hour samples were collected over the course of the study; additionally, five fast collection "grab samples" were collected using a needle valve to restrict air flow such that the sampling time was ~ 5 minutes. Supplementary Table 1 lists sampling time, duration, and location for the 30 samples collected.

Prior to and between samples, canisters were cleaned and conditioned according to Section 11 of EPA Method TO-14 (EPA, 1999). Canisters were analyzed in the laboratory at INSTAAR (University of Colorado

Figure 2

Wells near homes in Erie, Colorado.

Photograph showing an example of a typical residential neighborhood in Erie with an active natural gas well pad and condensate tanks in very close proximity. (Photo credit: C. Thompson)

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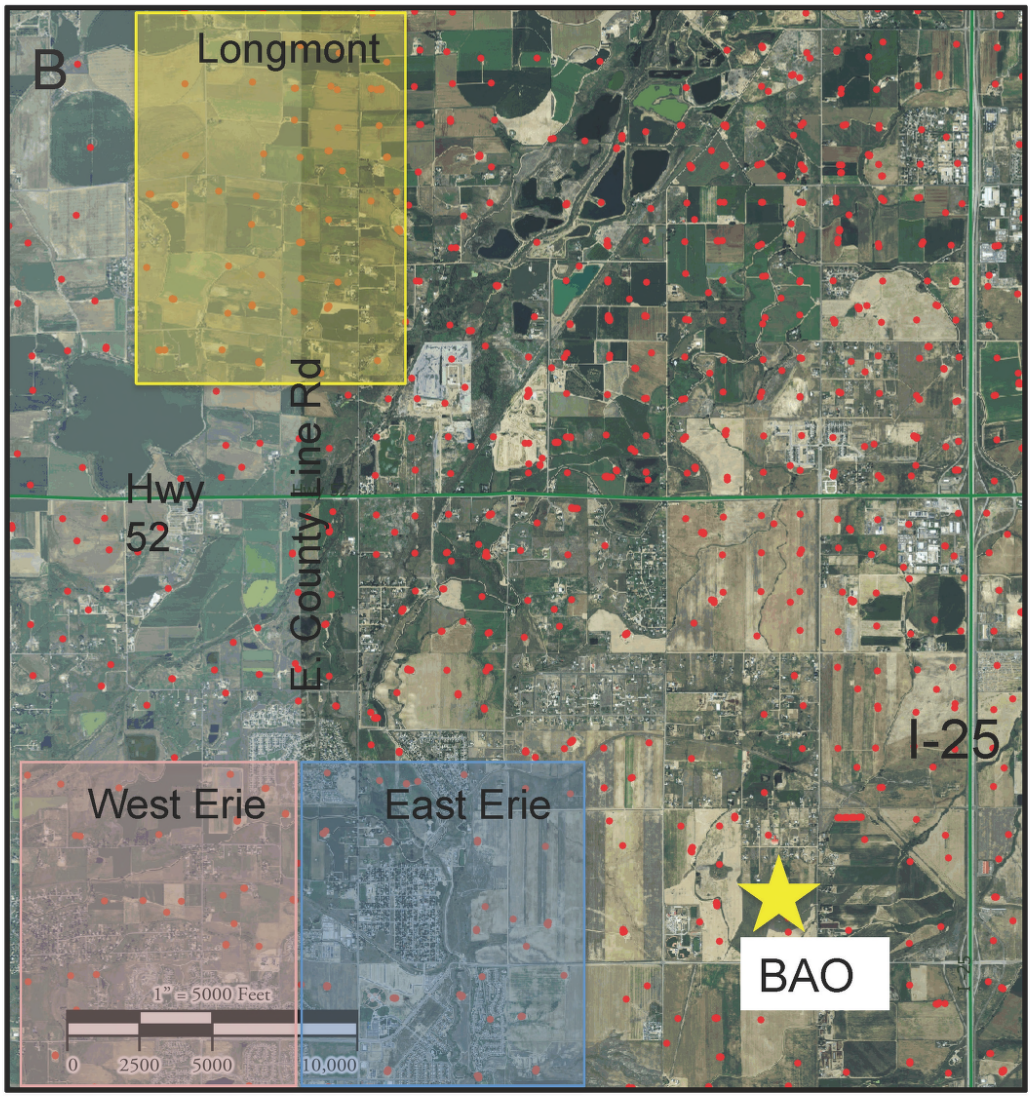

Figure 3

Map of sampling areas in Erie/Longmont.

Close-up map of the sampling areas for the 2013 Erie/Longmont study, classified as Longmont, East Erie, and West Erie. The Boulder Atmospheric Observatory (BAO) is the site of the previous NOAA study.

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Table 1. Quantitative results and statistics for the samples collected in this study, with comparison to the mean values reported in Gilman et al. (2013) and Swarthout et al. (2013) where available

Compound	Range	Median	Mean	Std Dev	Mean *Gilman et al. (2013)*	Mean *Swarthout et al. (2013)*
Ethane	1.80 – 84.1	18.8	27.0	19.8	35	22.1
Ethene	0.09 – 0.87	0.45	0.45	0.25		0.43
Ethyne	0.11 – 1.09	0.38	0.48	0.26		0.63
Propane	0.64 – 65.8	14.3	18.5	16.2	27	15.9
Propene	0.04 – 0.73	0.33	0.32	0.16		0.104
Propyne	0.01 – 0.44	0.03	0.06	0.09		
i-Butane	0.15 – 13.1	2.51	3.49	3.17	6	2.89
n-Butane	0.35 – 30.9	5.54	8.09	7.41	14	7.06
1-Butene	0.01 – 0.34	0.15	0.14	0.09		0.015
Trans-2-butene	0.02 – 0.10	0.04	0.05	0.02		0.014
i-Butene	0.03 – 5.86	1.32	1.49	1.37		
i-Pentane	0.24 – 8.89	1.88	2.58	2.06	4.2	1.99
n-Pentane	0.20 – 9.09	1.97	2.55	2.12	4.7	2.01
Cyclopentane	0.01 – 0.55	0.12	0.14	0.12		0.117
1-Pentene	0.01 – 0.25	0.12	0.11	0.07		0.008
Cyclohexane	0.02 – 0.79	0.17	0.21	0.17		0.143
Hexane	0.36 – 3.24	0.79	1.12	0.82	1.1	0.528
Methylcyclo-hexane	0.04 – 1.51	0.36	0.48	0.35	0.28	0.143
Heptane	0.03 – 0.73	0.17	0.23	0.17	0.32	0.150
Octane	0.02 – 0.33	0.08	0.10	0.07		0.052
Benzene	0.17 – 0.96	0.57	0.57	0.22	0.29	0.186
Toluene	0.11 – 0.84	0.44	0.43	0.19	0.30	0.190
Ethylbenzene	0.02 – 0.10	0.05	0.05	0.03		0.017
m and p Xylene	0.03 – 0.41	0.15	0.17	0.11	0.11	0.074
o-Xylene	0.01 – 0.14	0.04	0.06	0.04	0.03	0.023

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at Boulder) using a cryogen-free preconcentration system (Pollmann et al., 2006) followed by separation on a Gas-Pro column (Agilent Technologies) with an automated gas chromatograph-mass spectrometer/flame ionization detection instrument (GC-MS/FID). Blanks and calibration standards were analyzed prior to and immediately after each set of seven canisters, and canister analysis results were blank-subtracted. Blanks were performed both by injecting laboratory-scrubbed zero-air directly into the GC-MS system, and by filling canisters with zero-air followed by standard analysis on the GC-MS. Calibrations were performed using two different gravimetrically prepared NMHC standards. Our laboratory NMHC calibration scale has been cross-referenced against other national and international laboratories, including two audits by the World Calibration Centre for Volatile Organic Compounds. Due to known benzene contamination issues with SUMMA canisters and with the absorbent traps used in the pre-concentration system, as well as a slight overlap with a neighboring peak in the chromatogram that required peak separation in signal processing software, the reported benzene uncertainty value is greater than the other NMHC analyzed. Measurement uncertainties for the C2–C6 alkanes are between 2–5%, acetylene is 9%, and benzene is estimated at 25%.

2.2. Additional datasets

Several other NMHC datasets collected by different groups are also used in this work for spatial and temporal comparison purposes. We utilize data collected during the 2007 Boulder County Air Toxics Study, as well as from the Colorado Department of Public Health and Environment (CDPHE) and the National Oceanic and Atmospheric Administration (NOAA). The Boulder County Air Toxics Study investigated temporal and spatial behavior of non-methane hydrocarbons and carbonyls throughout Boulder County (Eisele et al., 2009). Measurements were conducted from March 2007 – February 2008 at five sites: Niwot Ridge, Lyons, South Boulder, downtown Boulder and Longmont (see Figure 1 for map of the NFR). Whole air samples

were collected on a 1-in-6 day sampling schedule. A total of 46, 47, 47, 45, and 50 24-hour samples were collected from each of the five sites, respectively. NMHC were analyzed in our laboratory at INSTAAR. System calibrations, sample analyses, and conditioning of the canisters followed the same protocol as described above, with the exception that a DB1 (Agilent Technologies) column was used for chromatographic separation.

The CDPHE Air Pollution Control Division operates monitoring sites in downtown Denver (2105 Broadway St.) near the center of the city (population ~2.2 million in the core metropolitan area) and in downtown Platteville (at South Valley Middle School), a small town of ~2,600 residents located in Weld County. The town of Platteville is situated in the heart of the Greater Wattenberg Field (see Figure 1), in contrast to Denver, which has relatively few oil or gas wells located within the city footprint. From January through December 2013, 3-hr integrated whole air canister samples were collected at each site on a 1-in-6 day sampling schedule from 6:00 – 9:00 MST during their 2013 Ozone Precursor Study. Canisters collected by the CDPHE are analyzed by a contracted analytical laboratory, ERG (Eastern Research Group), using an ATEC 2200–2 air toxics analyzer following EPA Method TO-11a for carbonyl analyses and EPA TO-12 for speciated non-methane organic compounds (SNMOC) analyses. These data were made available by request and permission by the CDPHE Air Pollution Control Division, and are used here for spatial comparisons with our 2013 Erie/Longmont data. Supplementary Table S2 lists the NMHC quantified in these data.

In February of 1991, researchers from the NOAA Boulder Laboratory conducted continuous GC-FID monitoring of NMHC from the Table Mesa site located approximately 1 km west of Boulder's main north-south artery (Goldan et al., 1995). These data are used for temporal comparison with our 2007 measurements from Boulder.

The NMHC measurements used herein are also compared to regional background NMHC values determined using data collected from the NOAA/INSTAAR Global Greenhouse Gas Reference Network for global monitoring of greenhouse gases and NMHC. This project is part of the Global VOC Monitoring Program of the World Meteorological Organization (WMO) Global Atmospheric Watch (Helmig et al., 2009; WMO, 2007). This program centers on the analysis of whole air samples collected on a bi-weekly basis from 42 global background monitoring sites. Regional background values used here are calculated by extracting the NMHC values for 40°N, the latitude of Boulder, Colorado, from a spatial interpolation model (Dlugokencky et al., 1994) and averaging over the years 2005 – 2011 for yearly and Spring (March – May) background values.

3. Results and discussion

3.1. Ambient NMHC at residences in Erie/Longmont

Quantitative results and statistics of the primary compounds measured from the 2013 Erie/Longmont samples are presented in Table 1. Carbonyls and other oxygenated or halogenated NMHC were not measured in this study, however, other recent, more comprehensive, studies in this area have determined that the alkanes constitute the largest fraction of ambient NMHC (Gilman et al., 2013; Swarthout et al., 2013). The primary focus of this work is to investigate spatial and temporal variability of common NMHC, and does not attempt to determine the ozone production potential of the total NMHC burden in the region; therefore, the exclusion of these functionalized NMHC does not hinder this analysis.

Many of the NMHC measured, particularly the short-chain alkanes, were much enhanced relative to regional background values, and were found to have the highest atmospheric mole fractions. Ethane and propane, for example, have maximum measured values of 84.1 and 65.8 ppbv, respectively. For comparison, the regional backgrounds for ethane and propane in the Spring were found to be 1.51 and 0.37, ppbv, respectively. The mean values determined in this study represent enhancements of 17.9, 49.4, 61.2, 80.9, 53.9, and 77.3 times above regional background levels for ethane, propane, i-butane, n-butane, i-pentane and n-pentane, respectively (Table 2). These light alkanes are sourced predominantly from oil and gas operations and related industries, and do not constitute a large fraction of urban or vehicle emissions. These compounds accounted for the largest fraction of total carbon (in ppbC), averaging 84% across all samples, regardless of absolute mole fractions. The alkenes and aromatics, which have primarily urban vehicular sources, were consistently a minor fraction of the NMHC composition, averaging 4.5% and 3.8%, respectively, although these two classes of NMHC at times accounted for up to 20% of total carbon in individual samples. This observation is in general agreement with Swarthout et al. (2013), who found the alkanes to account for an average of 69% of total measured NMHC mixing ratio in the region, and Gilman et al. (2013) who identified the alkanes as the dominant NMHC type in this region, even though these studies quantified a greater number of individual compounds, including oxygenated and halogenated NMHC.

In Table 1, we also compare the mean values from this study to those reported in Gilman et al. (2013) and Swarthout et al. (2013) where available. Both the Gilman study and the Swarthout study were stationary point studies conducted with sampling at 8 m height on the BAO tall tower during a shorter time window in winter (February 18–March 7, 2011 for Gilman et al. and February 18–March 13, 2011 for Swarthout et al.), whereas our study consisted of multiple locations over a greater area and over a longer time period

Table 2. Enhancement factors for the C2-C5 alkanes for Denver, Erie/Longmont, and Platteville in comparison to calculated regional background values for 40°N using the NOAA/INSTAAR Global Greenhouse Reference Gas flask network[a]

Compound	Year-Average Background	Spring Background (March–June)	Denver Enhancement (Year Average)	Erie/Longmont Enhancement (Spring Average)	Platteville Enhancement (Year Average)
Ethane	1.29	1.51	11.3	17.9	105
Propane	0.404	0.374	17.3	49.4	254
i-Butane	0.068	0.057	19.2	61.2	314
n-Butane	0.127	0.100	26.7	80.9	398
i-Pentane	0.061	0.048	40.2	53.8	310
n-Pentane	0.040	0.033	40.2	77.3	426

[a] Denver and Platteville values are calculated using a full year of samples in 2013; Erie values are calculated using samples collected between March-June 2013.

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(March 20–June 5). The mean values for the simple alkanes reported by both Gilman et al. and Swarthout et al. fall within one standard deviation of the mean values determined in this study for all compounds except for n-pentane. Gilman et al. found average n-pentane values slightly higher than we determined, although our values were in agreement with Swarthout et al. Our mean values for the BTEX aromatic compounds were all slightly higher than either Gilman et al. or Swarthout et al., although generally within one standard deviation of these studies.

It would not be expected that these studies would agree completely with our present study, since they were conducted in two different years, in different months of the year, and with different sampling methods. The prevalence of stable boundary layer conditions and temperature inversions in the wintertime in this region, as well as lower OH concentrations and lower solar zenith angle for photochemistry, can lead to higher ambient air mole ratios of these primary emissions during the winter months. Specifically, from measurements of NMHC conducted from the top of the BAO tower, Pétron et al. (2012) found that NMHC are enhanced by a factor of ~1.75 in the winter months over the summer months. Consequently, since the Gilman et al. (2013) study was conducted from February to March, whereas our study continued through June, the seasonal difference is a potential contributing reason for the slightly higher mean values observed in Gilman et al. for many of the NMHC. Nevertheless, the strong agreement between our study and the NACHTT studies from two years previous is quite remarkable, and provides evidence for a consistent and continuing source of NMHC in this region.

Figure 4 shows statistics for a subset of the alkanes and aromatics measured in this study, divided by sampling region as West Erie, East Erie, and Longmont (refer to map in Figure 3). The light alkanes are statistically similar between East Erie and West Erie, though East Erie has higher maximum values amongst these thirty samples. Longmont has statistically higher values for the C2–C5 alkanes than Erie, demonstrating significant spatial variability in ambient NMHC even on this relatively small scale. This is presumably due to the more rural setting of the Longmont sampling sites, and the greater number of wells, located in the proximity of these sites (see map in Figure 1). The aromatic air toxics benzene, toluene, ethylbenzene, and the xylenes were found to be statistically similar amongst all sites.

3.2. Regional spatial heterogeneity of VOC enhancements

The ozone non-attainment area in Colorado consists of nine counties within the NFR: Adams, Arapahoe, Boulder, Broomfield, Denver, Douglas, Jefferson, Larimer, and Weld. These counties contain the most populated urban center in Colorado (Denver) and the region with both the greatest O&NG and agricultural production in the state (Weld County). In contrast to other Western oil and gas basins, such as the Uintah and Green River basins, the DJB contains some highly populated areas, and thus contains a mix of ozone precursor sources. Thus, while elevated ozone is widespread throughout the region, it would be expected that spatial heterogeneity would exist for primary NMHC. In a drive-around study using a mobile laboratory by Pétron et al (2012) within Boulder and Weld Counties, several different point sources for methane and the light alkanes were identified, including wastewater treatment plants, landfills, and various types of emissions sources from O&NG activities. Here, rather than identifying specific point sources, we examine the spatial distribution of NMHC composition across a wider area, specifically focusing on populated residential areas across the NFR.

In Figure 5, we utilize our 2013 Erie/Longmont measurements described above and compare select alkanes, aromatics, and alkenes with ambient measurements from Denver and Platteville performed by the CDPHE in 2013. For the Denver and Platteville data, we use only measurements collected during the months of March, April, and May to be consistent with the study period of Erie/Longmont sampling.

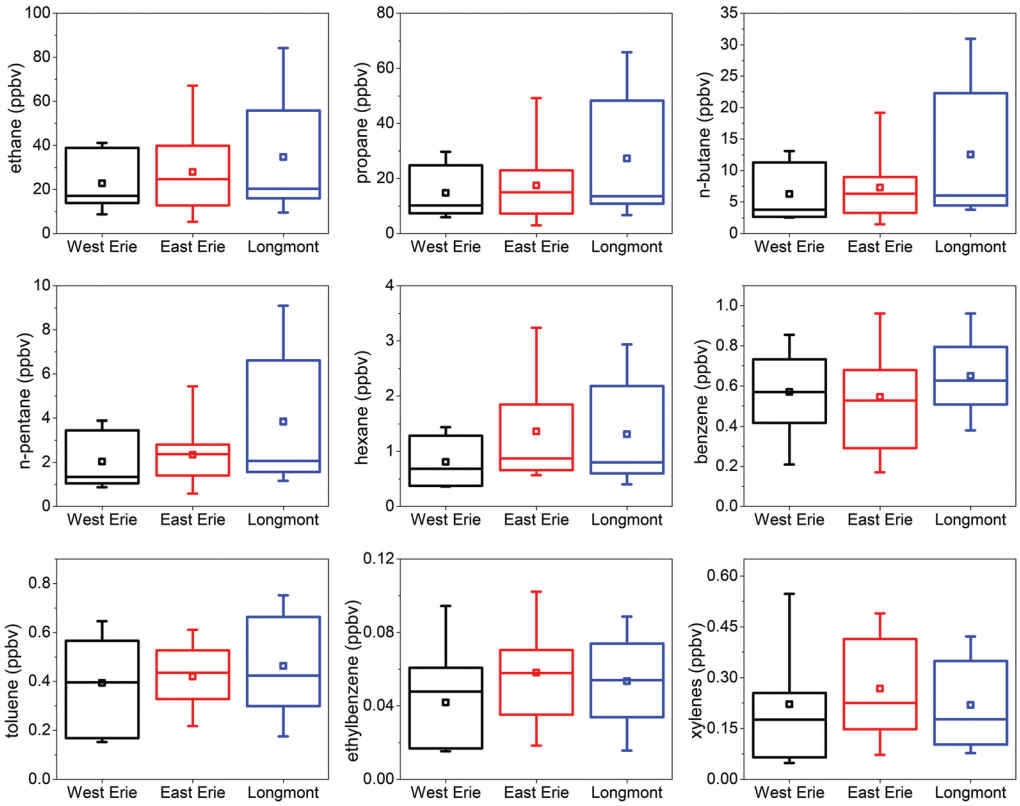

Figure 4

Statistics for select alkanes and aromatics from the 2013 Erie/Longmont study.

Results are grouped by general sampling area: West Erie, East Erie, and Longmont. In these plots, the box represents the 25th, 50th and 75th percentile values, the marker represents the mean, and the whiskers represent the minimum and maximum measured values. Xylenes represents the sum of *o*-, *m*-, and *p*- isomers.

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The light alkanes, ethane, propane, n-butane, and n-pentane, are primarily sourced from natural gas, though automobiles do emit small amounts of n-butane, n-pentane, and i-pentane, and biomass burning can also be a source of these compounds to the atmosphere (see Supplemental Table S3 for reference). In comparing the alkanes in Fig. 5A, these compounds exhibit the greatest ambient mole fractions in Platteville, in the center of the Wattenberg Gas Field, significantly lower mole fractions in Erie/Longmont on the western periphery of the densest drilling area, and the lowest levels in downtown Denver. Overall, the mean mole fractions of these alkanes in Platteville are 5–6 times greater than observed in Erie/Longmont, and 9–15 times greater than in downtown Denver. The yearly (2013) averages in Platteville are furthermore 10–30 times greater than yearly averages observed in Los Angeles (CARB air monitoring network data, 2011) or Houston (TCEQ air monitoring network data, 2013), two U.S. megacities that have historically been known for poor air quality (refer to Supplemental Figure S2). On a fractional basis, the saturated alkanes (C2–C10) account for nearly 90% of total measured ppbC (parts per billion carbon) in Platteville, 84% in Erie/Longmont, and 64% in Denver (Figure 6). Unsaturated and aromatic NMHC species account for a greater fraction of the total NMHC carbon in downtown Denver. The mean sum of total measured NMHC over the entire year of 2013 was 129 ppbC in Denver compared to 966 ppbC in Platteville.

Table 2 shows the average regional background values of the C2–C5 alkanes for 40°N extracted from the NOAA/INSTAAR Global Greenhouse Reference Network flask data calculated as both a yearly average and a Spring-only average (defined here as March–June). The calculated enhancement factors for Denver, Erie/Longmont, and Platteville are also shown in Table 2., The Erie/Longmont enhancement factors are calculated using the Spring-only regional background average, whereas Denver and Platteville enhancement factors are calculated using the yearly average. 2013 was a highly active forest fire year in Colorado, and large fires occurred south of the Denver area in late June and July, near the city of Colorado Springs. The ambient NMHC for Denver and Platteville in June and July do not reveal any indication of significant impact from these fires on the C2–C5 alkanes; all of these compounds have lower mole fractions in June-July than either the Spring-only data or the yearly average. Moreover, the June-July averages of these species are lower (by between 19–35%) in 2013 than for the same time period in 2012 (see Supplemental Tables S4 and S5 for complete statistics). Therefore, we conclude that the yearly averages for the C2–C5 compounds shown in Table 2 for Denver and Platteville are not impacted by these southerly forest fires and are appropriate for this analysis.

The results in Table 2 show that the light alkanes are greatly enhanced over background values and illustrate the widespread impact of oil and gas-sourced NMHC on air composition throughout the NFR.

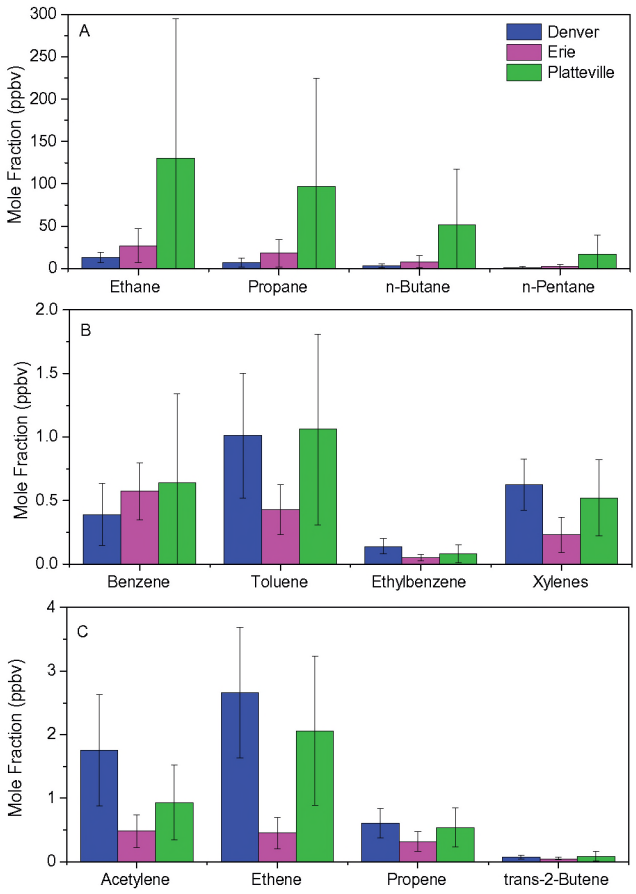

Figure 5

Mean ambient mole fractions for select NMHC in Denver, Erie/Longmont, and Platteville.

Comparison of ambient levels of select alkanes, aromatics, and alkenes using our data from Erie/Longmont 2013 and March–May measurements from Denver and Platteville in 2013 performed by CDPHE. The bars represent the mean of available data and error bars represent the 1-sigma standard deviation.

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As is expected, Platteville has the greatest enhancements, with several hundred times over background values. These enhancement factors are similar to those recently observed in the Uintah Basin, an O&NG region in northeast Utah that similarly has been found to have highly elevated atmospheric NMHC. (Helmig et al., 2014). Denver, which is removed from the primary gas field area and has relatively few wells, also has significant enhancements in the light alkanes, up to a factor of 40 for C2, relative to background values.

As mentioned above, automobiles emit small amounts of n-butane, n-pentane, and i-pentane, at 2.20, 2.40 and 9.35 percent by weight of total carbon in tailpipe emissions, respectively (Gentner et al., 2013), however, natural gas is the dominant source of these compounds. Figures 7 and 8 show a series of correlation plots for n-butane, n-pentane, and i-pentane for Denver and Platteville using the full year of measurements from 2013. The measurements from downtown Denver (Figure 7) display a high correlation between

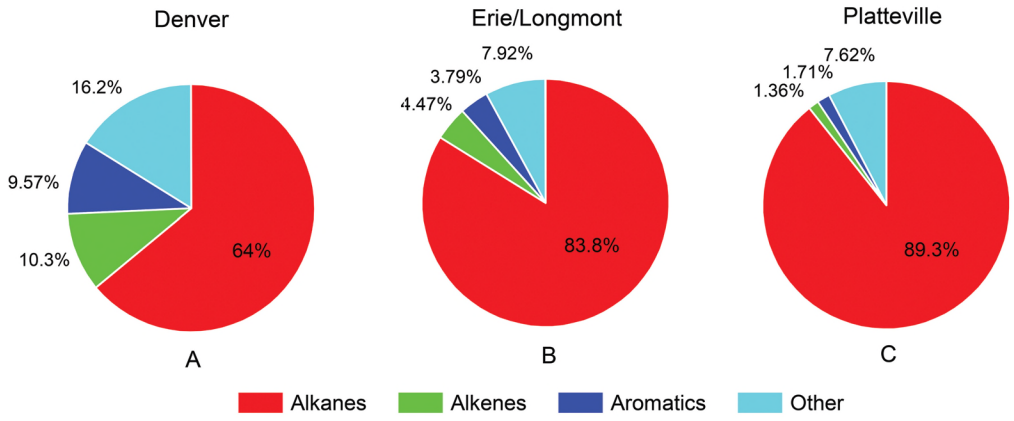

Figure 6

Fractional composition of NMHC measured in Denver, Erie/Longmont, and Platteville.

Pie charts show fractional contribution of different NMHC types to total NMHC carbon (in ppbC). Platteville and Denver data represent yearly averages for 2013. The percentage of light alkanes contribution to total NMHC increases with proximity to the gas field, from Denver, to Erie, then to Platteville.

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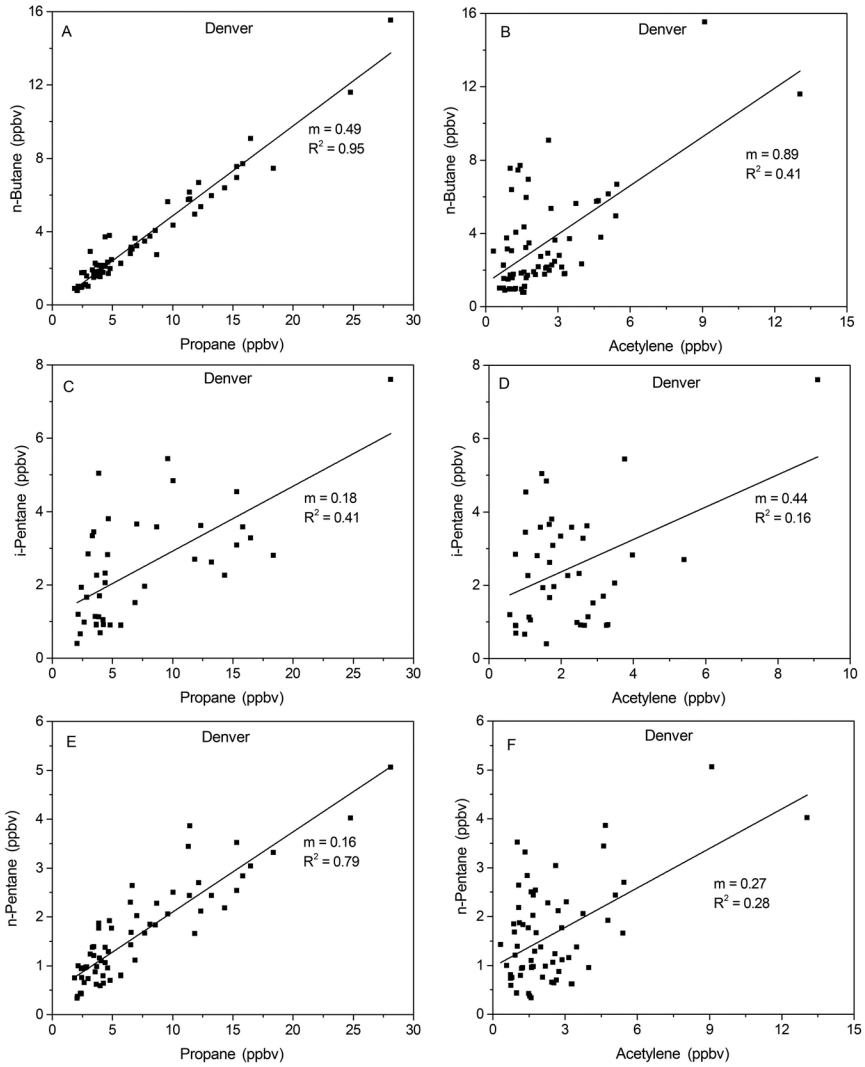

Figure 7

Correlations of select alkanes with propane and acetylene in Denver.

Correlation plots of n-butane, i-pentane, and n-pentane with propane (O&NG tracer) and acetylene (vehicle/combustion tracer) from Denver.

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n-butane and propane (R^2 = 0.95), and a much weaker relationship with the vehicle exhaust tracer acetylene (R^2 = 0.41). The same relationship is seen between n-butane and propane in Platteville (Figure 8A), with identical n-butane:propane ratios of 0.49 in the two cities, despite the much higher absolute mole fractions in Platteville. Similarly, the n-pentane:propane ratios for Denver and Platteville are both 0.16, although the data for Denver have a weaker correlation coefficient (R^2 = 0.79) than that for Platteville (R^2 = 0.94). Of the three compounds, i-pentane has the weakest relationship with propane in Denver, likely reflecting contribution from vehicle emissions, but correlation of i-pentane with propane (R^2 = 0.41) is still greater than that with acetylene (R^2 = 0.16). These relationships provide strong evidence that ambient atmospheric levels of n-butane, n-pentane, and i-pentane are dominated by oil and gas emissions throughout the NFR, including within the urban center.

The aromatic compounds benzene, toluene, ethylbenzene and the xylene isomers (collectively known as BTEX) are emitted both from vehicle exhaust and from various industrial and O&NG activities. These compounds are of interest especially from a health perspective, as they are considered air toxics and can have detrimental health impacts; benzene in particular is a known carcinogen. These compounds are often elevated in densely populated urban mega-cities, however, recently mole fractions of up to 11.3 ppbv benzene and 14.3 ppbv toluene were observed in the Uintah Basin (Helmig et al., 2014), a primarily rural region where NMHC emissions are nearly exclusively due to O&NG activities. In the NFR, Gilman et al. (2013) used a multi-variate regression analysis to conclude that 32% of the benzene observed from the Boulder Atmospheric Observatory (BAO) tower, located near Erie, originated from oil and gas emissions. Figure 5B shows the comparison between Denver, Erie/Longmont, and Platteville for the BTEX compounds. Average atmospheric levels of benzene in Platteville are approximately twice that of either Erie/Longmont or downtown Denver. Toluene, ethylbenzene, and the xylenes have comparable levels between Denver and Platteville, whereas levels of these compounds in Erie/Longmont are approximately one-third of that observed in Denver and

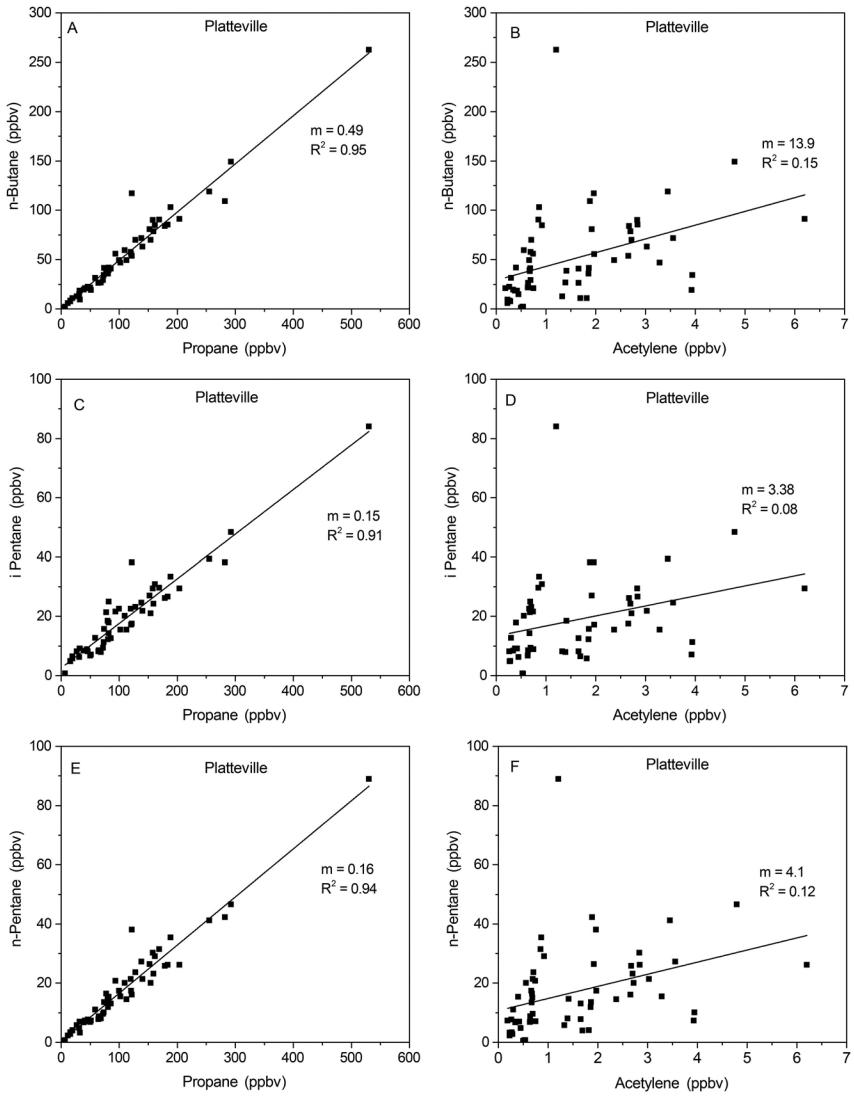

Figure 8

Correlations of select alkanes with propane and acetylene in Platteville.

Correlation plots of n-butane, i-pentane, and n-pentane with propane (O&NG tracer) and acetylene (vehicle/combustion tracer) from Platteville.

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Platteville. The mean value for benzene measured at residences in Erie/Longmont was 0.57 ppbv, which is equivalent to 2.0 μg/m^3. This falls below the chronic health-based exposure used in Bunch et al (2014), of an annual mean concentration of 4.5 μg/m^3. The 2013 yearly mean benzene in Platteville from samples collected at the middle school, 0.66 ppbv, is equivalent to 2.3 μg/m^3, with a 1-sigma concentration of 4.8 μg/m^3 and a maximum of 8.3 μg/m^3. As defined by the World Health Organization and the U.S. EPA, lifetime exposure to benzene of 1.7 μg/m^3 increases one's risk of cancer to 1 in 100,000 (EPA, 2013; WHO, 2010). Thus, the mean benzene levels in Platteville and Erie are above this threshold and therefore of a high enough concentration for the potential of detrimental health effects if chronic exposure at these levels should occur.

The comparison of the aromatic species between Denver and Platteville is of interest given that these two locations are quite different, with Denver being a highly populated urban center (population ~2.2 million) and Platteville being a rural town located within the Wattenberg Field (population ~2600). Benzene, in particular, is significantly higher in Platteville than in Denver. Figure 9 shows correlations of ambient benzene mole fractions in Denver and Platteville with propane and acetylene. In Denver, there is a significantly higher correlation between benzene and acetylene (R^2 = 0.72) than with propane (R^2 = 0.29), indicating that within the urban center, the majority of benzene is sourced from vehicle traffic or other combustion sources. In Platteville, this relationship is reversed, so that benzene has a much stronger correlation with propane (R^2 = 0.73) than with acetylene (R^2 = 0.29). Though it is apparent that both oil and gas and vehicular/urban emissions are contributing to observed ambient levels, O&NG emissions are the primary source of benzene in Platteville. A similar, though weaker, relationship is also observed for toluene (Supplemental Figure S1). This suggests that ambient aromatics in these two locations primarily arise from distinctly different sources.

Figure 5C compares average ambient levels of select unsaturated hydrocarbons in Denver, Erie/Longmont, and Platteville. Primary emissions of these compounds are dominated by vehicle exhaust and other, mostly

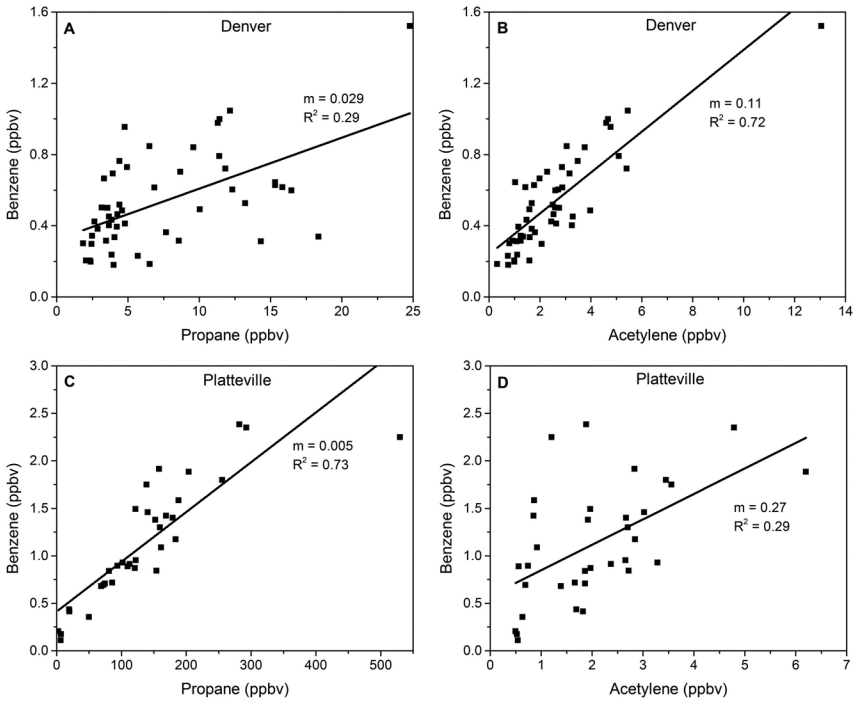

Figure 9

Correlations of benzene with propane and acetylene.

Correlations of ambient benzene mole fractions with propane (and O&NG tracer) and acetylene (a vehicle/combustion tracer) for Denver and Platteville. These plots reveal a stronger correlation of benzene with acetylene in Denver, and with propane in Platteville, suggesting different primary sources in these two areas.

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urban, combustion sources. Acetylene, in particular, is considered a vehicle exhaust/urban tracer compound. Given the strong vehicular source of acetylene and ethene (8–9% and 11–14% by weight of exhaust, respectively (Nelson and Quigley, 1984; Broderick and Marnane, 2002; Gentner et al., 2013) it is not surprising that downtown Denver has the highest ambient mole fractions of these compounds. Average mole fractions of these compounds are significantly lower in Erie/Longmont compared to Denver or Platteville, and are highest in Denver, though Platteville does have elevated mole fractions, as well. Population does not explain this difference, as the population of Erie (at about 19,000) is greater than that of Platteville (~2600). The proximity of Platteville to Highway 85, a well-traveled north-south corridor between north Denver and Greeley, may explain some of the enhancement in these compounds observed at the Platteville site. Additionally, industrial activities in support of the oil and gas industry may also contribute, including emissions from generators, compressors, or diesel engines used during the drilling phase, and high volumes of heavy truck traffic, especially during the hydraulic fracturing phase.

In 2007, the Boulder Air Toxics study was undertaken to investigate ambient levels of NMHC in five communities in Boulder County, with a primary focus on heavier NMHC compounds, aromatics and carbonyls. The full details of this study can be found in Eisele et al. (2009). Sampling was conducted in Longmont, Boulder, South Boulder, Lyons, and Niwot Ridge. Although this study was conducted six years previously, and, as will be discussed, ambient mole fractions of many NMHC appear to have increased in the NFR since that time, the multiple measurement sites used in this study are valuable for investigating the spatial distribution of NMHC in other NFR residential communities.

Figure 10 illustrates the spatial heterogeneity for a representative alkane (n-butane) and aromatic (toluene) compound. High uncertainties associated with the benzene measurements for this particular study precluded its use in this analysis. The n-butane results show the greatest mole fractions at the Longmont site, a rural location closest to the Wattenberg Field, followed by Boulder. Lyons, a small community of 2,100 residents located at the base of the Front Range foothills north of Boulder, and South Boulder, a rural location along the South Boulder Creek, have nearly equal levels of n-butane that are significantly less than downtown Boulder or Longmont. The lowest values were observed at Niwot Ridge, a remote mountain location that is part of the University of Colorado Mountain Research Station.

In contrast to n-butane, which, as discussed above is primarily sourced from oil and gas, the toluene measurements reveal highest mean values in downtown Boulder that are a factor of 3.3 greater than in Longmont. The downtown Boulder site was located near the intersection of Arapahoe Rd. and 30th St., one of the busiest traffic junctions in the city; therefore, vehicle exhaust is likely the primary contributor to the toluene levels observed here, as toluene accounts for 6–10% by weight of vehicle emissions (Nelson and Quigley, 1984; Gentner et al., 2013). The Longmont site is primarily rural, located south of the Longmont city limits;

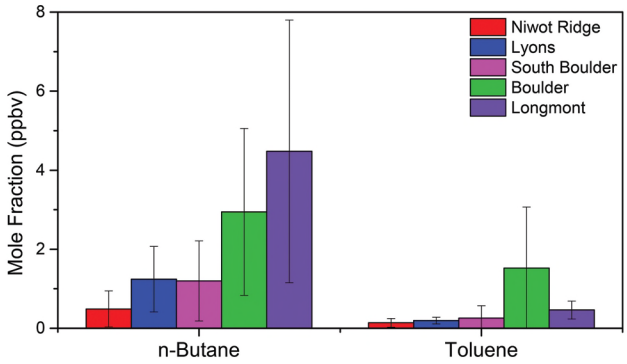

Figure 10

Comparison of mean ambient n-butane and toluene mole fractions from the Boulder Air Toxics Study.

Results are shown for the five sampling sites used in this study. Error bars represent the 1-sigma standard deviation. See Methods for study details.

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however, it is in relatively close proximity to East County Line Rd., which may account for some of the toluene observed at this site. Again, Niwot Ridge has the lowest observed ambient mole fractions of the five sites.

3.3. Temporal changes in NMHC

Since the establishment of the ozone NAA in the NFR, several ozone and ozone precursor studies have been undertaken to investigate NMHC. A valuable benefit of these numerous, though admittedly sporadic, studies is that they have provided some data that we can begin to analyze for emerging temporal trends in ambient NMHC. In Figure 11, we make use of data from the 2007 Boulder Air Toxics Study and the 2013 Erie/Longmont study, as well as measurements conducted by NOAA in February 1991 from Boulder. A weakness in this comparison is that the sites are not co-located over the years; it would be preferable to have consistent, long-term NMHC monitoring to establish statistically sound trends. However, as a first look, these datasets can be useful for beginning to understand air quality changes in the region.

Figure 11A shows changes in n-butane, n-pentane, benzene, and toluene from 1991 to 2007 in Boulder. These compounds were chosen to examine both alkanes and aromatics, and were compounds for which measurements were available from all three studies. The 1991 data from Goldan et al. (1995) were filtered for only daytime observations (9:00–20:00 local time) to capture predominately up-sloping wind conditions when the Table Mesa site would be positioned downwind of the city, whereas the 2007 data represent 24-hour integrated samples collected within the city itself closer to traffic emissions. Although both of these sites are impacted by fresh emissions from the city, the difference in location between these two studies may impart some influence from spatial heterogeneity in this comparison, which is likely to be more significant for the aromatics.

The alkanes, n-butane and n-pentane, show increasing mole fractions in Boulder in the 16 years between 1991 and 2007 of 89% and 141%, respectively. Observations of benzene and toluene in 2007 were greater than in 1991 by 69% and 134%, respectively, though high time-resolution measurements of NMHC in Boulder would be required to determine what fraction of these compounds are due to O&NG versus vehicular emissions. Figure 11B shows a comparison of these same species in Erie/Longmont between 2007 and 2013 (note the difference in y-axis scales between 11A and 11B). The increase in ambient alkane mole fractions in Erie/Longmont is remarkable (data are from March–July for both studies), with average n-butane and n-pentane

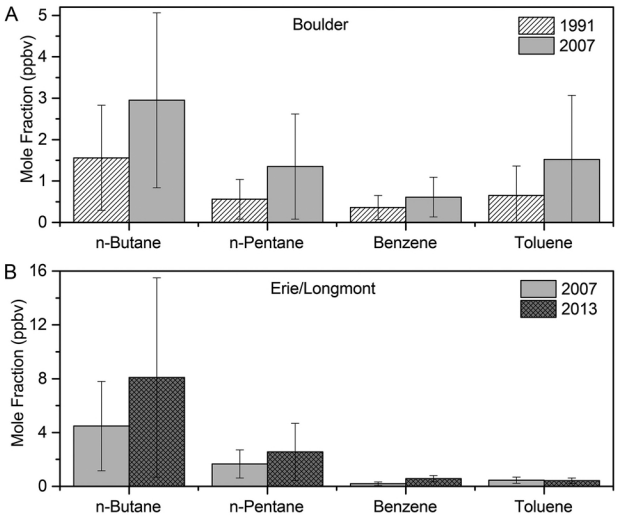

Figure 11

Temporal changes in mean ambient mole fractions in Boulder and Erie/Longmont.

A) Comparison of n-butane, n-pentane, benzene and toluene mean mole fractions in Boulder in 1991 (Goldan et al., 1995) and 2007 (this work). Errors bars represent the 1-sigma standard deviation about the mean. B) Same as above, comparing mean mole fractions in Erie/Longmont in 2007 and 2013 (this work). See Methods for study details.

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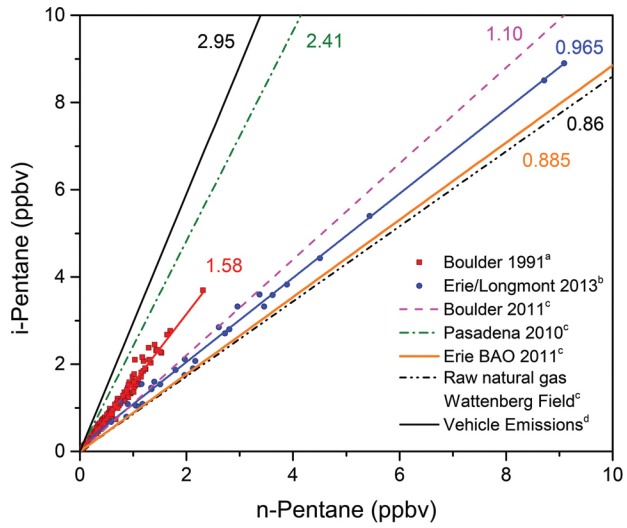

Figure 12

Emission ratios of i-pentane to n-pentane from several studies in the NFR.

Emission ratios of i-pentane to n-pentane from several studies in the NFR: Boulder 1991, Erie/Longmont 2013 (this study), and Boulder and Erie 2011, compared to the ratio for Pasadena, CA, a site with predominantly urban emissions, the raw natural gas signature from the Greater Wattenberg Field, and the vehicle emissions source signature.

[a]Goldan et al., 1995

[b]This work

[c]Gilman et al., 2013

[d]Broderick and Marnane., 2002

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approximately 2 and 1.5 times greater over the course of only five years. In that same time, benzene increased by a factor of 3, however, toluene showed no significant change.

While individual NMHC may have multiple sources, ratios of NMHC generally vary between sources and can be used to identify the importance of different source types. A useful metric for investigating the influence of urban versus oil and gas emissions sources on ambient air composition is the ratio of the pentane isomers, i-pentane/n-pentane. Vehicle tailpipe emissions are more enhanced in i-pentane, leading to a greater i-/n-pentane ratio than is produced from natural gas emissions (Hwa et al., 2002; McGaughey et al., 2004). Figure 12 compares i-/n-pentane values for several studies in the NFR to a location that is predominantly impacted by urban/vehicle emissions (Pasadena, CA), with a pentane isomer ratio of 2.41, (Gilman et al., 2013) and to the emission source signature for raw natural gas from the Greater Wattenberg Field, which has a pentane ratio of 0.86 (Gilman et al., 2013). Also included is the pentanes ratio determined directly from a busy traffic intersection (Broderick and Marnane, 2002), representative of the source signature for vehicle exhaust. The pentanes ratio from Pasadena is markedly higher than any of the NFR values, closest to the vehicle source signature of 2.95 reported by Broderick and Marnane (2002).

The pentanes ratio for the Erie/Longmont data collected in this study (blue data) is 0.965, which is within the range of the ratios of 0.885 (orange trace) determined by Gilman et al. (2013) and 1.00 by Swarthout et al. (2013) for the Erie/Longmont area, and similar to the signature of raw natural gas (difference of 12%). The red data and the pink dashed line compare ratios for Boulder from 1991 (Goldan et al., 1995) and from 2011 (Gilman et al., 2013), respectively. In twenty years, the pentanes ratio in the ambient air in Boulder has decreased from 1.58 (± 0.01, R^2 = 0.99) to 1.10 (± 0.05, R^2 = 0.91). This observation suggests that either impacts of O&NG emissions have increased in the city of Boulder, that vehicle emissions have decreased, or some combination of the above. Advancements in recent decades in catalytic converters and other emissions controls on vehicle exhaust has lead to generally decreasing trends in total vehicle hydrocarbon emissions in many major cities in the U.S., including Denver (Bishop and Stedman, 2008). There is no clear evidence to suggest, however, that the ratio of i-pentane to n-pentane in tailpipe emissions has changed significantly in this time, though there is relatively large variability between studies. Tunnel studies in the late 1980's to early 1990's report average i-/n-pentane ratios ranging from 1.97 to 3.27 (Doskey et al., 1992; Duffy and Nelson, 1996; Lonneman et al., 1986, 1991; Zweidinger et al., 1988). More recent studies report i-/n-pentane ratios from tailpipe emissions between 2.95 to 3.9 (Broderick and Marnane, 2002; Gentner et al., 2013). Given that the ambient levels of n-pentane have increased in Boulder over this time (Figure 11A), it is likely that the observed decrease in the pentane ratio is due to a combination of increased O&NG emissions and a cleaner vehicle fleet, resulting in an increasing relative contribution of O&NG sources to ambient NMHC in the city.

4. Conclusions

The findings presented here suggest that oil and gas emissions have a large-scale regional impact on ambient NMHC levels, thereby impacting a large population of NFR residents, and representing a large area source of ozone precursors. The short-chain alkanes exhibit strong correlations with propane in Erie/Longmont, Platteville, and within Denver, supporting the conclusion of widespread impact of O&NG emissions.

Significant spatial heterogeneity exists, with ambient C2–C5 NMHC levels much greater within the Greater Wattenberg Field (e.g., Platteville) than observed in Erie/Longmont, which is on the far western

edge of the field, or in Denver or Boulder, which are both further removed from the densest drilling operations. Ambient NMHC observed at residences in Erie were 18–77 times greater than regional background determined from the NOAA flask network. Modeling results presented by the CDPHE in the Colorado State Implementation Plan (CDPHE, 2008) suggest that the Wattenberg Field is indeed the primary region for ozone production in the NFR. The aromatic compounds, benzene and toluene, are also enhanced in Platteville relative to Denver, with O&NG emissions being the primary source of these compounds in the Platteville area, whereas vehicular emissions are dominant in Denver. Benzene levels in both Platteville and Erie/Longmont could be detrimental to human health if chronic lifetime exposure should occur.

Our initial look at past studies in the region suggests that the ambient NMHC mole fractions in this region have not decreased in recent years despite tightening of emissions standards in the O&NG industries and implementation of statewide vehicle emission inspections, although again we note that these past studies were not exactly co-located, and thus this comparison is not ideal. This observation, however, is highly significant for the NFR, as the State of Colorado continues to face issues related to non-attainment for ozone, and is currently pursuing a further tightening of regulations with the aim of capturing 95% of NMHC emissions. Even though the volume of emissions per well may be decreasing, the rapid and continuing increase in the number of wells may potentially negate any real improvements to the air quality situation. These findings, and the continuing development of this region, provide a strong argument for the continued atmospheric monitoring of this region in the coming years.

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Contributions

- Concept and design: CT, DH
- Acquisition of data: CT, JH
- Analysis and interpretation of data: CT, JH, DH
- Drafting the article or revising it for important intellectual content: CT, DH
- Final approval of the version to be published: CT

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Competing interests

The authors do not have any competing interests that might influence the interpretation of this manuscript.

Supplementary material

- **Table S1. Descriptions of canister samples used in this study.** doi: 10.12952/journal.elementa.000035.s001
- **Table S2. NMHC quantified according to compound class from whole air samples collected by the Colorado Department of Public Health and Environment in Denver and Platteville, 2013.** doi: 10.12952/journal.elementa.000035.s002
- **Table S3. NMHC composition of primary emissions sources impacting the NFR.** doi: 10.12952/journal.elementa.000035.s003
- **Table S4. Mean values and 1-sigma standard deviations for the entire year, March – May, and June – July of 2013 for Platteville and Denver.** doi: 10.12952/journal.elementa.000035.s004
- **Table S5. June – July means and 1-sigma standard deviations comparing 2012 and 2013 for Platteville and Denver.** doi: 10.12952/journal.elementa.000035.s005
- **Figure S1. Correlations of toluene with propane and acetylene.**

  Correlation plots of toluene with propane and acetylene for both Denver (A and B) and Platteville (C and D) demonstrating that oil and gas operations are the dominant source of toluene in Platteville, whereas vehicular/urban emissions are the dominant source of toluene in Denver. Points colored in red in panels C and D were excluded as outliers based upon panel C. doi: 10.12952/journal.elementa.000035.s006
- **Figure S2. Comparison of 2013 yearly means for Denver and Platteville with yearly means for Los Angeles (Burbank) and Houston.**

  Los Angeles NMHC data are observations from the Burbank site in 2011 from the California Air Resources Board monitoring network (http://www.arb.ca.gov/aqd/aqdcd/aqdcddld.htm). Houston NMHC data are for 2013 from the TCEQ air monitoring network Clinton site(http://www.tceq.texas.gov/cgi-bin/compliance/monops/agc_monthly_summary.pl). doi: 10.12952/journal.elementa.000035.s007

Data accessibility statement

Publicly available data used in this study from NOAA and CDPHE is available upon request from those organizations. Data available from the Dryad Digital Repository: http://doi.org/10.5061/dryad.bc24d

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