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Journal

Journal of Geophysical Research: Atmospheres, 121(18)

ISSN

2169-897X

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Publication Date

2016-09-27

DOI

10.1002/2016jd025327

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Peer reviewed

RESEARCH ARTICLE

10.1002/2016JD025327

Key Points:

- Unexpectedly high benzene mixing ratios were observed in Colorado's Wattenburg Gas Field in July and August 2014
- Oil and natural gas extraction activities are implicated as the primary source for the high benzene observations
- Gas field measurements of VOCs put a spatial constraint on the location of the gas field benzene source

Supporting Information:

- Supporting Information S1

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Citation:

Halliday, H. S., A. M. Thompson, A. Wisthaler, D. R. Blake, R. S. Hornbrook, T. Mikoviny, M. Müller, P. Eichler, E. C. Apel, and A. J. Hills (2016), Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014, *J. Geophys. Res. Atmos.*, 121, 11,055–11,074, doi:10.1002/2016JD025327.

Received 11 MAY 2016

Accepted 6 AUG 2016

Accepted article online 13 AUG 2016

Published online 20 SEP 2016

Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014

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Abstract High time resolution measurements of volatile organic compounds (VOCs) were collected using a proton-transfer-reaction quadrupole mass spectrometry (PTR-QMS) instrument at the Platteville Atmospheric Observatory (PAO) in Colorado to investigate how oil and natural gas (O&NG) development impacts air quality within the Wattenburg Gas Field (WGF) in the Denver-Julesburg Basin. The measurements were carried out in July and August 2014 as part of NASA's "Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality" (DISCOVER-AQ) field campaign. The PTR-QMS data were supported by pressurized whole air canister samples and airborne vertical and horizontal surveys of VOCs. Unexpectedly high benzene mixing ratios were observed at PAO at ground level (mean benzene = 0.53 ppbv, maximum benzene = 29.3 ppbv), primarily at night (mean nighttime benzene = 0.73 ppbv). These high benzene levels were associated with southwesterly winds. The airborne measurements indicate that benzene originated from within the WGF, and typical source signatures detected in the canister samples implicate emissions from O&NG activities rather than urban vehicular emissions as primary benzene source. This conclusion is backed by a regional toluene-to-benzene ratio analysis which associated southerly flow with vehicular emissions from the Denver area. Weak benzene-to-CO correlations confirmed that traffic emissions were not responsible for the observed high benzene levels. Previous measurements at the Boulder Atmospheric Observatory (BAO) and our data obtained at PAO allow us to locate the source of benzene enhancements between the two atmospheric observatories. Fugitive emissions of benzene from O&NG operations in the Platteville area are discussed as the most likely causes of enhanced benzene levels at PAO.

1. Introduction

Oil and natural gas (O&NG) extraction has been rapidly expanding in the Denver-Julesburg Basin (DJB) in NE Colorado. In 2014, Colorado was ranked as the fifth highest state in number of gas wells, with 7.4% of the nation's wells and 5.2% of the total U.S. NG production over all active O&NG extraction regions in the state [Energy Information Administration, 2015]. The DJB is one of the active O&NG regions in Colorado, with the highest well density in the Wattenburg Gas Field (WGF) in Weld County which has more than 25,000 active gas wells within its boundary (Colorado Oil and Gas Conservation Commission (COGCC), <http://cogcc.state.co.us/>). Increased extraction of O&NG from shale deposits has been shown to have an adverse effect on air quality in areas with heavy O&NG development [McKenzie et al., 2012] and is a concern for public health [Colborn et al., 2011].

The air quality impact of unconventional O&NG production has received considerable attention from researchers and air quality managers because the Denver Metropolitan Area and Northern Front Range were categorized as noncompliant with National Ambient Air Quality Standards (NAAQS) for ozone pollution in 2007 [Colorado Air Quality Control Commission, 2008]. The region has remained in marginal nonattainment through 2015 [Allison, 2015]. Ozone is a secondary pollutant that is produced from reactions involving reactive nitrogen ($\text{NO} + \text{NO}_2 = \text{NO}_x$) and volatile organic compounds (VOCs) under sunlight. Increased mixing ratios of volatile organic compounds (VOCs) have been attributed to O&NG activity, and these increased

VOCs have been hypothesized to increased ozone levels [Katzenstein *et al.*, 2003; Kemball-Cook *et al.*, 2010; Pétron *et al.*, 2012; Gilman *et al.*, 2013; Moore *et al.*, 2014; Warneke *et al.*, 2014; Ahmadov *et al.*, 2015; Pacsi *et al.*, 2015; Prenni *et al.*, 2016]. The O&NG contribution to VOCs in the Front Range is significant; the 2011 Environmental Protection Agency (EPA) National Emissions Inventory (<http://www.epa.gov/air-emissions-inventories/national-emissions-inventory>) attributes 64% of the total point source VOC emissions in Colorado to O&NG extraction activities, while in Weld County the O&NG contributions account for 90% of the total point source VOC emissions. Several studies conducted within the DJB since 2011 have found a clear O&NG signature in atmospheric VOCs, with enhancement in the alkanes and aromatics without corresponding increases in combustion tracers [Pétron *et al.*, 2012; Gilman *et al.*, 2013; LaFranchi *et al.*, 2013; Swarthout *et al.*, 2013; Thompson *et al.*, 2014]. O&NG-related VOC sources include leaks from infrastructure and transport, fugitive emissions, and deliberate venting and flaring [Adgate *et al.*, 2014; Vinciguerra *et al.*, 2015]. Increased concentrations of methane, light alkanes, and aromatics in the DJB have been connected to O&NG development [Pétron *et al.*, 2012; Gilman *et al.*, 2013; LaFranchi *et al.*, 2013; Thompson *et al.*, 2014; Eisele *et al.*, 2016].

In addition to degrading air quality, high VOC concentrations are also a concern from a public health perspective. Exposure to aromatic VOCs has been linked to cancer, respiratory effects, and endocrine disruption [World Health Organization, 2000; McKenzie *et al.*, 2012; Bolden *et al.*, 2015]. Benzene, the simplest aromatic VOC, has an atmospheric lifetime of approximately 10 days, with OH radicals reactions as the primary atmospheric sink. Benzene is classified as an air toxic under the USA Clean Air Act in section 112, and is a known human carcinogen (IARC Group 1). Health effects associated with benzene exposure include leukemia, anemia and other blood disorders and cancers, immune system impairment, decreased respiratory function, and neural tube defects in newborn babies [Bolden *et al.*, 2015; McKenzie *et al.*, 2012]. The effects of benzene on human health have been well documented in the literature, and exposure standards and guidelines have been set. The California Air Resources Board (CARB), for example, sets a 2 ppbv limit for an 8 h exposure. However, there is no safe threshold value for benzene exposure, and the EPA Integrated Risk Information System (IRIS) puts the excess carcinogenic risk from chronic exposure to benzene at 1 in 100,000 for a chronic exposure of 0.41 to 1.41 ppbv. Since there are uncertainties in the carcinogenic risk from benzene, the mean value of 0.877 ppbv benzene for this excess risk factor is used.

Benzene is thought to have a small number of well-characterized sources. Sixty-eight percent of the benzene emissions in the EPA's 2011 National Air Toxics Assessment estimates are attributed to mobile sources, mostly on road. The remaining national benzene emissions are attributed to the evaporation of fuels at service stations, solvent use, and O&NG operations and processing [Wallace, 1989; Bolden *et al.*, 2015]. Densely populated urban areas are the primary regional sources of benzene due to traffic and industry emissions. Urban outflow studies have used benzene as a tracer for urban influence in the rural environment [Roberts *et al.*, 1984; Bravo *et al.*, 2002; Seigneur *et al.*, 2003; de Gouw *et al.*, 2005; Warneke *et al.*, 2007; Apel *et al.*, 2010]. Benzene mixing ratios have been dropping nationally [Fortin *et al.*, 2005], in part because of mandated gasoline formulation requirements and in part due to better overall vehicle pollution controls, but there is some evidence that benzene concentrations have been increasing outside of the urban centers due to increasing O&NG production [Thompson *et al.*, 2014]. These gas field aromatic emissions have not been well characterized and quantified. In Colorado, a top-down estimate of benzene over the WGF found that the official inventories were low by a factor of 7 and that the O&NG emissions of benzene were on the same order as the vehicle emissions for the region [Pétron *et al.*, 2014].

The present investigation, part of the 2014 NASA "Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality" (DISCOVER-AQ) field campaign in July and August 2014 DISCOVER-AQ Science Team [2012], presents the first detailed analysis of benzene measurements made continuously at a sampling site in the midst of O&NG activities in the WGF. The benzene data were measured along with other VOCs by a proton-transfer-reaction quadrupole mass spectrometry (PTR-QMS) instrument at the Platteville Atmospheric Observatory (PAO), one of six instrumented ground stations in DISCOVER-AQ. Vertical benzene measurements were made using an airborne PTR-ToF-MS instrument installed on the NASA P-3B aircraft which conducted regular spirals over Platteville and five other ground sites in Colorado. Additional VOC measurements were collected concurrently during the Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) on the NSF/NCAR (National Center for Atmospheric Research) C-130. We observed high, potentially harmful, benzene levels at PAO, especially under nighttime conditions. In the following sections, we present the PAO and aircraft benzene observations in detail to more

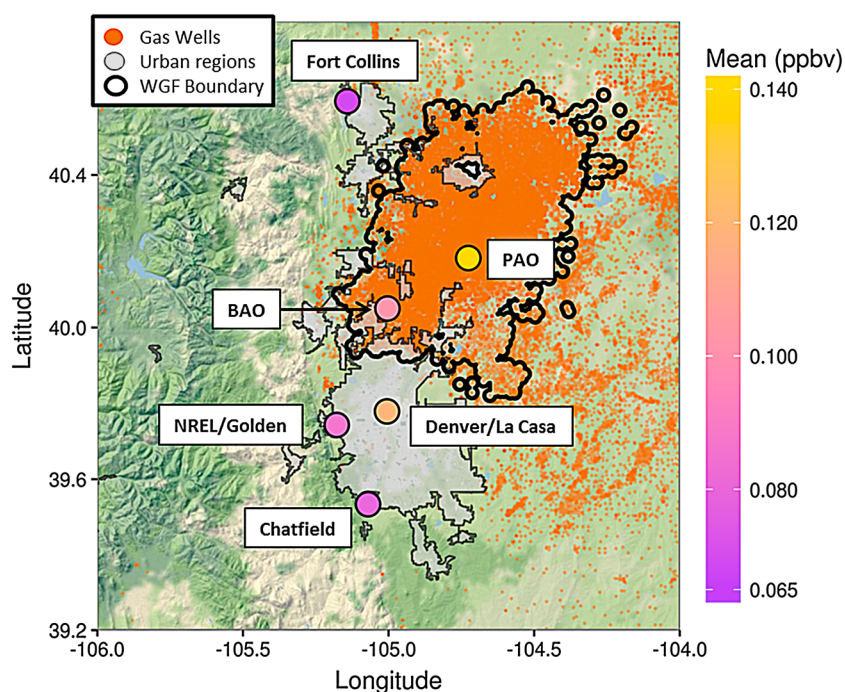


Figure 1. Map of the 2014 DISCOVER-AQ study area. The urban areas are shown in grey (data courtesy of the United States Census Bureau, <http://www.census.gov/geo/maps-data/data/tiger.html>). The boundary of the WGF is shown in black along with the gas wells (brown points) (data courtesy of the Colorado Oil and Gas Conservation Commission, <http://cogcc.state.co.us/>). The DISCOVER-AQ ground sites are plotted and colored using the mean benzene volume mixing ratio measured during the aircraft spirals over each site. Benzene statistics were calculated using data from the bottom 1 km agl for each site.

completely understand emissions from O&NG activities in the WGF. We address two main points in this study. First, we examine benzene variability, which is characterized by comparison of aircraft data across the FRAPPÉ study region, over DISCOVER-AQ sampling sites, and at the Platteville surface site. Second, we investigate potential benzene sources at the Platteville ground station, using benzene data measured in canister samples and by the PTR-QMS. Tracer correlations with benzene and wind direction-benzene relationships measured at the site are used to identify general source locations and likely O&NG activities contributing to the elevated benzene.

2. Methods

2.1. Site Description

NASA's DISCOVER-AQ field campaign was conducted from mid-July to mid-August of 2014 in the Colorado Front Range region. The measurements encompassed the Denver urban area and the nonurban gas field environment to the north of the Denver urban region bounded by Fort Collins, CO and PAO. A map of the study area is shown in Figure 1. The campaign measurements included six instrumented ground sites and two instrumented NASA aircraft. This study primarily analyzes a subset of these measurements collected at PAO (40.1815°N, 104.7268°W) which was selected as a study site due to its central location in the WGF.

The site is located 9 km SE of the City of Platteville (Lat: 40.214°N, Long: 104.823°W) and 25 km S of Greeley, CO (40.422°N, 104.709°W). The site elevation is 1520 m above mean sea level (asl). PAO is situated in a primarily rural location, surrounded by a mix of agricultural and grazing lands. There were active wells in close proximity to the NW, SW, and S of the site, and collection tanks located 0.5 km to the SW of PAO. Truck traffic was active in the area to service the O&NG infrastructure around PAO, and US 85 runs N to S 8 km to the W of PAO.

Air quality relevant trace gas sampling was made with a common inlet 4 m above ground level (agl) within the Nittany Atmospheric Trailer and Integrated Validation Experiment (NATIVE) mobile air quality research station (see *Martins et al.* [2012], for a full description). The NATIVE instrument package provides 1 min

averaged in situ measurements of ozone, NO/NO₂/NO_x, total reactive nitrogen (NO_y), sulfur dioxide (SO₂), carbon monoxide (CO), carbon dioxide (CO₂), and methane (CH₄). Additionally, 1 min averaged meteorological data were also collected, including wind speed and direction, temperature, relative humidity, pressure, and NO₂ photolysis rates.

2.2. PTR-QMS Benzene Measurements

A conventional proton-transfer-reaction quadrupole mass spectrometry (PTR-QMS) instrument (Ionicon Analytik, Innsbruck, Austria) was used for VOC measurements at the PAO site. The measurement principle and technical details of this instrument have been reviewed in great detail elsewhere [*de Gouw and Warneke, 2007*]. Routine operating parameters and procedures were applied in this study. The drift tube was operated at a pressure of 2.25 mbar, an electric field strength of 57 V/cm and a temperature of 50°C. The QMS was run in the multiple ion detection (MID) mode. It sequentially measured 51 *m/z* signals over the course of 1 min. Benzene was detected as protonated benzene (*m/z* 79) with a 1 s signal integration time during the 1 min measurement cycle. The ethylbenzene interference with benzene measurements was minimized (~25% fragmentation on *m/z* 79). The interference from acetic acid (*m/z* 79 from hydrated protonated acetic acid) was found to be negligible.

A dynamically diluted certified multicomponent gas mixture (Apel Riemer Environmental Inc., Broomfield, CO, USA) containing 1 ppmv of benzene was used for calibration. The instrumental background was determined by supplying catalytically (Pt/Pd at 325°C) cleaned air to the instrument. The accuracy of the reported benzene volume mixing ratios is ±5.2%.

The PTR-QMS instrument was housed at the PAO site in a separate trailer located 5 m from the NATIVE trailer. Ambient air was sampled at a height of 5.6 m above ground (2.4 m above trailer roof) from a mast attached to the trailer. The inlet line was a 6.25 mm outer diameter, 4.3 m long Teflon PFA tube that was capped with a 5–6 μm pore size Teflon PTFE filter. The tube was heated to 40°C inside the air-conditioned trailer to prevent condensation. The flow rate through this main inlet line was 7 standard liters per minute (slpm). The PTR-QMS instrument subsampled from this flow.

A proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) instrument was used for airborne benzene measurements aboard the NASA P-3B. This instrument and its operating procedures have been described in great detail by *Müller et al.* [2014].

2.3. TOGA VOC Collection

The NCAR Trace Organic Gas Analyzer (TOGA), a fast online gas chromatograph/mass spectrometer (GC/MS), was installed on the NSF/NCAR C-130 for the FRAPPÉ field study and made continuous measurements of over 70 VOCs including benzene and toluene during the study. Integrated air samples, 35 s in duration, were taken every 2 min and analyzed by TOGA in flight. For a detailed description of TOGA, see *Apel et al.* [2015]. The reported TOGA benzene and toluene data have an overall uncertainty of ±15%, with detection limits of 0.5 pptv and 1 pptv for benzene and toluene, respectively.

2.4. Canister Whole Air Sample VOC Collection

The whole air canister samples were collected at PAO and analyzed within the University of California at Irvine (UCI) VOC canister collection program. Modules of 12 stainless steel 0.9 L canisters connected in series were deployed. The fill time was ~30 s and the evacuated canisters reached final pressures of ~10 psig. After the canisters were filled, the modules were shipped to the UCI laboratory where they underwent GC analysis for ~30 halogenated hydrocarbons and alkylnitrates and ~50 C₂–C₁₀ nonmethane hydrocarbons (NMHCs). The limit of detection was 3 pptv for all NMHCs. For more details, see *Colman et al.* [2001].

2.5. Ozonesonde Boundary Height Calculations

Planetary boundary layer height (PBLH) calculations were made from ozonesonde profiles that were collected at the PAO site. One to three ozonesonde-radiosonde profile pairs were launched each day for a total of 42 total profiles. PBLH was calculated from these profiles using the method outlined in *Martins et al.* [2012]. The profiles are smoothed by averaging the vertical data in to 50 m bins, and the potential temperature (θ) lapse rate ($\Delta\theta/\Delta z$) calculated between height bins. The PBLH at the inversion where the lapse rate is greater than or equal to 5 K km⁻¹, and the relative humidity does not change between height bins. If multiple

Table 1. Mixing Ratio Statistics for Benzene Measured From the NASA P-3B Over the Six DISCOVER-AQ Observation Sites From 1 km AGL and Below^a

	Fort Collins	Chatfield	NREL/Golden	BAO	Denver/La Casa	PAO
Mean	0.068	0.080	0.087	0.102	0.119	0.140
Median	0.064	0.071	0.085	0.095	0.110	0.115
25th	0.036	0.038	0.045	0.053	0.067	0.062
75th	0.095	0.110	0.122	0.139	0.166	0.190
Max	0.269	0.284	0.260	0.674	0.466	1.004

^aUnits are in ppbv.

possible PBLH values were obtained with these metrics, we used the lowest realistic value obtained by visual inspection, selecting the best fit inversion that was closest to the ground.

3. Results

3.1. Spatial Distribution of Benzene

The vertical distribution of benzene was obtained from spiral maneuvers over the six DISCOVER-AQ 2014 ground sites; each measurement location had two to three spirals per flight day over 15 total flight days. All flights were done during the daytime. To determine differences in benzene between the various sites within the PBL, we used measurements in the bottom 1 km agl over each site to calculate benzene statistics for the entire campaign. Confining the statistical calculations to a single vertical kilometer for each site allows us to assume that we are comparing measurements that were primarily collected within the planetary boundary layer.

Figure 1 shows the mean benzene mixing ratios calculated for each site in the context of the study area and the boundaries of the WGF. PAO shows the highest benzene mixing ratios averaged over all spirals (0.140 ppbv), followed by Denver (0.119 ppbv) and the Boulder Atmospheric Observatory (BAO) (0.102 ppbv). PAO and BAO are both gas field sites, while the spiral over Denver was in the urban core. In comparison, the three sites closest to the mountains (Fort Collins, Golden, and Chatfield) have low average values relative to the gas field and urban sites. Fort Collins has the lowest mean value during the campaign (0.068 ppbv) while the two sites expected to be most influenced by the Denver plume, Chatfield (0.080 ppbv) and Golden (0.087 ppbv), are slightly elevated relative to Fort Collins but still low compared to Denver.

Table 1 shows the aggregate statistics for the six measurement sites, which gives context on the mean values. Comparing the statistics of the sites, the mean values are relatively uniform, with Denver and PAO, in particular, having close values despite the difference in environment. The two locations with the highest observed values, BAO and PAO, are both gas field sites and are within the boundary of the WGF. Benzene is expected to be high in the city center where vehicular emissions are high. The elevated benzene values over the gas field sites are unexpected and indicate a nontraffic source of benzene.

3.2. Benzene Observations at PAO

The time series of ground site benzene measured by PTR-QMS during the DISCOVER-AQ 2014 campaign is shown in Figure 2a. The PTR-QMS measurements were in excellent agreement with the canister-based measurements. A regression plot (Figure S1) returned a correlation slope of 1.007 and an R^2 value is 0.921 with an intercept of 0.012 ppbv. A potential positive bias in the PTR-QMS measurements can thus be excluded as it is very small.

Figure 2b shows daily benzene statistics, calculated from midnight to midnight local time (MDT). The diurnal cycle and its variability are shown in Figure 2c, and a strong daytime-nighttime difference becomes immediately evident. The high nighttime benzene levels increase the mean and median values of the entire campaign (Table 2). The diurnal split for the statistics is based on the Sun's zenith angle: the Sun above the horizon was defined as daytime, and below the horizon was defined as nighttime. During daytime, benzene mixing ratios are reduced and less variable, while nighttime benzene shows much higher variability and the largest mixing ratios observed during the campaign. Beyond the day-night differences, Figure 2b also shows that nighttime benzene levels were highest during the later third of the campaign from 31 July to the end of the observations on 8 August.

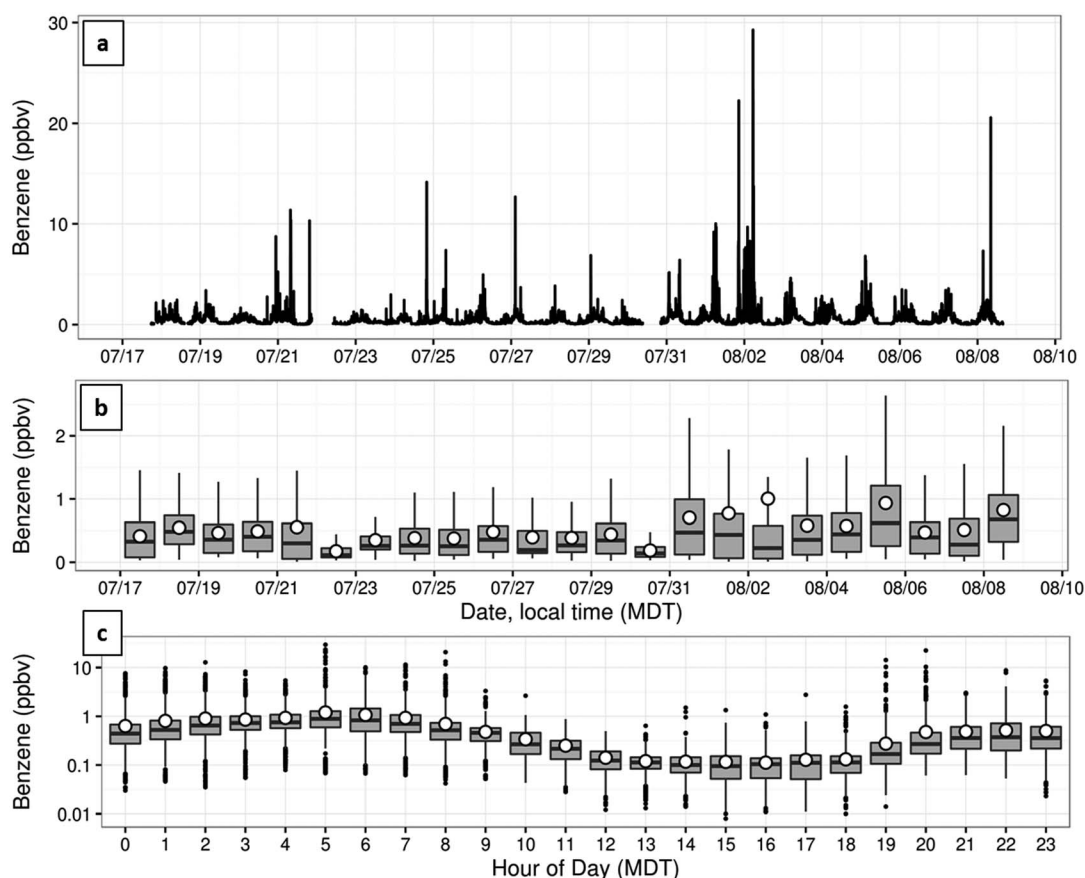


Figure 2. PTR-QMS benzene data collected at PAO during the DISCOVER-AQ 2014 campaign. (a) Ground level benzene time series for the entire campaign. (b) Box and whisker benzene mixing ratios organized by day, midnight to midnight MDT. Outlier points are not shown. Open points are the daily means, and these mean values are calculated from all data. The boxes indicate the locations of the 25th, 50th, and 75th quartiles. The whiskers encompass any data points within 1.5 times the interquartile range; observations outside of this range are considered outliers. (c) The diurnal cycle of benzene plotted in log scale with the outlier points shown in black. The open points are the hourly mean values. All dates and times are in local time (MDT).

The benzene levels measured at PAO were higher than expected for this region. Canister samples collected in the nearby City of Platteville in 2013 had peak benzene mixing ratios of 0.96 ppbv [Thompson *et al.*, 2014], well below the levels observed in this study. This disparity may be explained by the fact that the samples in Thompson *et al.* [2014] were 3 h integrated samples collected between 0600 and 0900 MST, missing high nighttime benzene levels. The fact that high benzene mixing ratios mostly occurred at night, i.e., when canister samples are not routinely collected in this region, implies that previous studies in the WGF did not capture the full range of the benzene mixing ratios. Based on previous studies of the region [Pétron *et al.*, 2012; Gilman *et al.*, 2013; Swarthout *et al.*, 2013; Thompson *et al.*, 2014], we expected the benzene mixing ratios to range up to 5 ppbv, so the maximum observation of 29 ppbv was an unexpected result.

Table 2. Mixing Ratio Statistics for Benzene Measured at PAO at Ground Level Using the 1 s Time Resolution PTR-QMS Data^a

	Campaign	Day	Night
Mean	0.53	0.37	0.74
Median	0.33	0.18	0.54
25th	0.14	0.10	0.30
75th	0.66	0.45	0.89
Max	29.3	20.6	29.3

^aUnits are in ppbv.

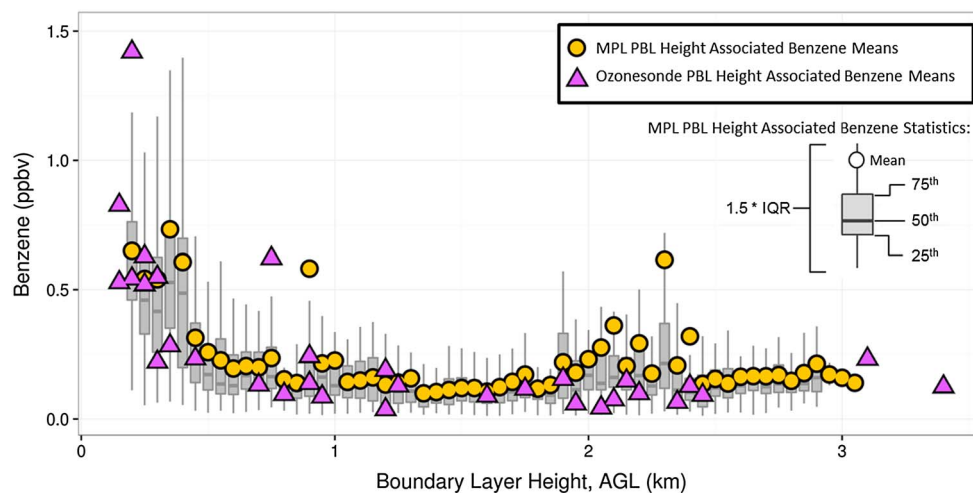


Figure 3. Benzene relationship to PBLH. The purple triangles are the PBLH depth calculated from ozonesonde data, using 15 min mean benzene data starting at balloon launch time. Gold points are mean benzene associated with PBLH derived from MPL data (binned by 50 m, collected between 0700 and 2000 MDT). Boxes and whisker plots for benzene mixing ratios associated with the MPL derived PBLH data are shown in grey. Outlier points have been excluded for clarity. All PBLH heights are calculated as km agl. The high variability between 2 and 2.5 km is due to a high benzene event on 24 July 2014 at the end of the day, and represents end of day boundary layer dynamics.

The high time resolution data should be compared to the previous canister samples with care, since *Thompson et al.* [2014] uses 3 h integrated samples compared to our 1 s data. However, while the campaign means between our work (0.53 ppbv) and *Thompson et al.* (0.57 ppbv) are very similar, the range of the benzene is much higher for our study, and the nighttime enhancement (shown in Table 2) is statistically significant. For capturing the baseline level of benzene the long canister samples are sufficient, but there are important variability data that are lost in these samples, particularly since they are not collected over night.

Figure 3 shows the benzene relationship to PBLH, calculated from both ozonesonde profiles and micropulse lidar (MPL) aerosol data (for a comparison, see Figure S2). The ozonesonde calculated boundary layer height is plotted against a mean benzene mixing ratio calculated from a 15 min window beginning at sonde launch, shown as purple triangles. The MPL PBLH heights use data collected between 0700 and 2000 to avoid including data that are not representative of a well-mixed daytime boundary layer. The MPL PBLH values are binned by 50 m and the associated benzene mixing ratios are plotted against the binned PBLH values, with the gold points showing the mean benzene for each binned PBLH, and the grey box and whisker plots show the 25th, 50th, and 75th quartiles of the benzene data for each height bin.

The surface benzene concentrations are sensitive to the PBLH, especially in the early morning and late evening when the PBLH is low but the Sun is still above the horizon. Benzene mixing ratios are enhanced when the PBLH is shallow, but as convective mixing begins and the PBLH begins to grow, the benzene mixing ratios rapidly drop off. Once the PBLH depth is greater than 0.5 km, benzene mixing ratios level off and approach the daytime median benzene value. The high variability of the benzene mixing ratios associated with the PBLH between 2.0 and 2.5 km is due to a high benzene event that occurred on 24 July at the end of the day between 1900 and 2000 MDT when the boundary layer began to collapse.

3.3. Vertical Distribution of Benzene From Aircraft Measurements

The ground observations of benzene at PAO were supported by vertical profile information obtained by a PTR-ToF-MS instrument on the NASA P3-B aircraft. Data were collected in spiral maneuvers over the site, with the aircraft starting high and ending at low altitude. Flights occurred between 0800 and 1600 MDT resulting in two to three vertical profiles over PAO on each flight day. A total of 32 full vertical profiles were completed over PAO during the DISCOVER-AQ 2014 campaign. The obtained data are shown in Figure S3 together with the time series of the ground data.

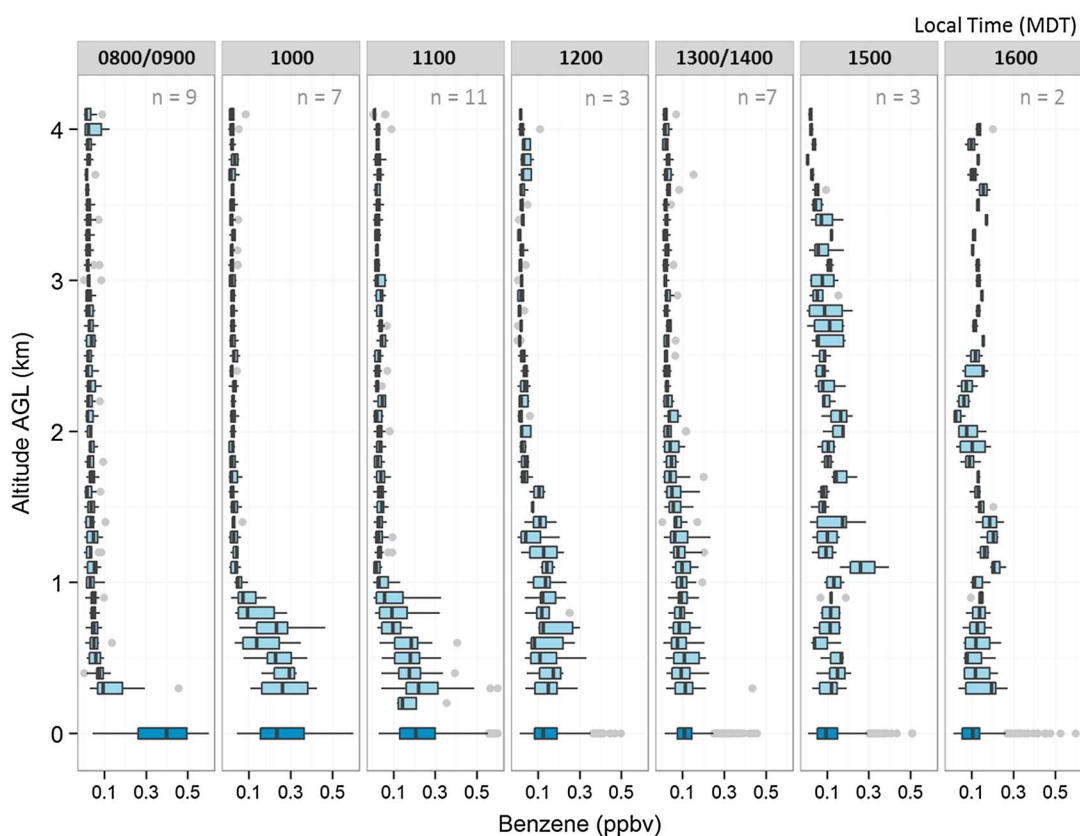


Figure 4. Vertical distribution of benzene observed over PAO as a function of time of the day (MDT). The aircraft data are binned into 50 m boxes and plotted in box-and-whisker format. Mixing ratios are cut off at 0.60 ppbv for clarity. A total of 42 profiles (full vertical and partial) have been used to construct this plot, and the number of each profile is labeled within each group (n = number of spirals).

Figure 4 summarizes the mixing ratios of benzene measured in the vertical columns and on the ground, grouped by hour of day and binned vertically by 50 m sections. In the early morning hours, benzene levels on the ground are high, with low benzene concentrations aloft. A decrease of benzene concentration with height was also observed at BAO in 2011 [Swarthout *et al.*, 2013]. As the day progresses and mixing in the boundary layer begins, two trends become evident: first, ground level benzene decreases, and second, benzene at altitude increases. The boundary layer evolution can be observed in the vertical benzene measurements throughout the morning and midday. By midafternoon the troposphere is well mixed with respect to benzene.

Similar decreases of benzene concentration with height were observed at BAO in 2011 [Swarthout *et al.*, 2013] and attributed to local emissions of gas field benzene. The overall mean vertical profile of benzene over PAO is shown in Figure S4. Our observations indicate that benzene is emitted at the surface, with the PBLH defining the mixing volume. The benzene emitted into the low boundary layer overnight is mixed into the troposphere as the boundary layer expands and mixes with the free troposphere layer above, which has lower benzene levels, resulting in the mean surface benzene mixing ratio decreasing with increasing PBL height. Advection aloft is not a significant contributor to the benzene measured in the columns.

3.4. Wind Direction Dependence of Benzene Mixing Ratios

To get more information on the geographical source location, we used a polar frequency analysis of benzene mixing ratios measured on the ground at PAO (Figure 5). The plot depicts wind speed and direction information to determine how wind regimes are associated with high benzene observations. Wind speed and direction data are binned by 10° wind direction and 0.5 m s^{-1} wind speed, and statistics on the associated benzene observations are calculated for each bin independently. The polar frequency plot shows that high

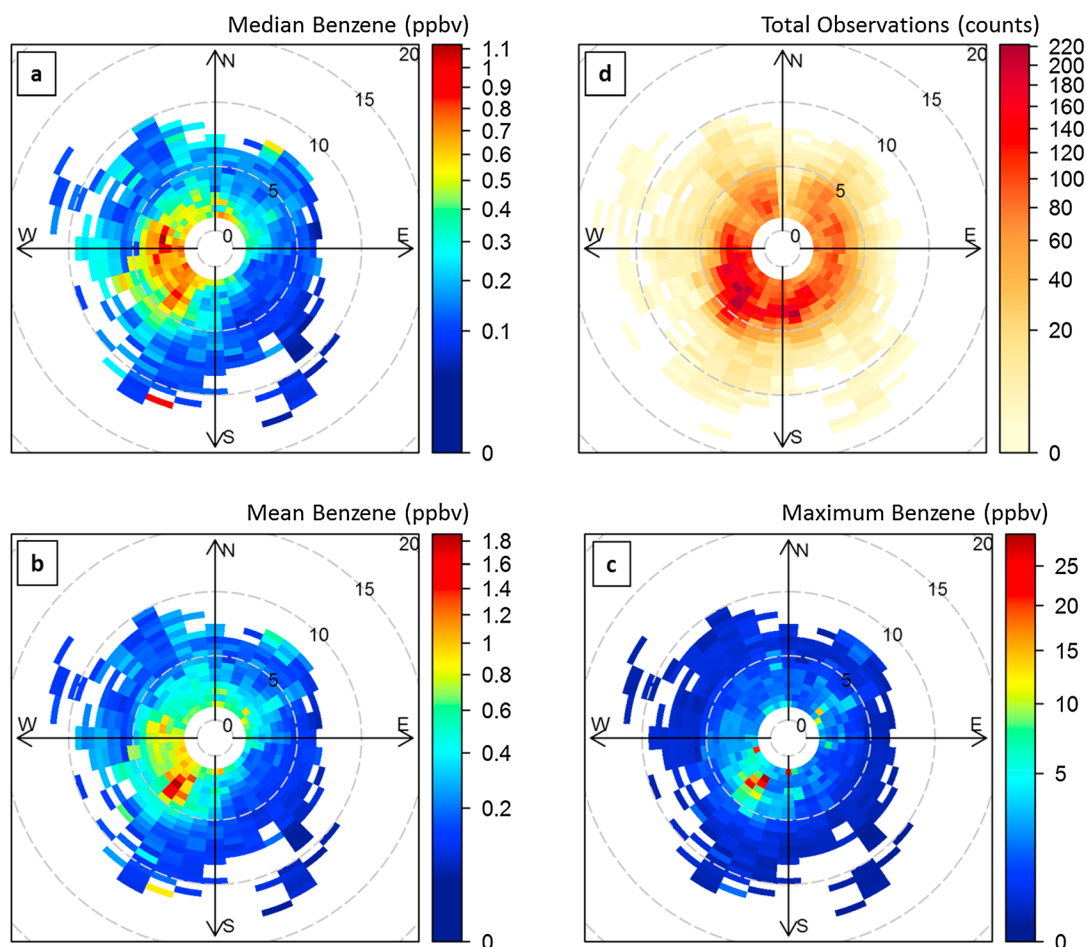


Figure 5. Polar frequency plots of benzene as measured at PAO during the DISCOVER-AQ 2014 campaign. Wind observations are binned by 10° wind direction and 0.5 m s^{-1} wind speed. Wind speed and direction bins are plotted on a polar plot and colored by mean benzene mixing ratio for each bin.

benzene is associated with westerly and southwesterly winds, with the highest mixing ratios originating from the southwest in a confined wind regime.

Separating the polar frequency plots into median, mean, and maximum associated benzene mixing ratios (Figures 5a–5c) allows us to investigate the directional dependence of the enhanced benzene at different mixing ratio levels, i.e., low and background levels through the median values, midlevel through the mean values, and the wind regimes associated with the highest benzene mixing ratios through the maximum. A diurnal analysis of these plots is shown in Figure S5. In all three plots, benzene is associated with a southwesterly flow. A westerly enhancement in the median plot is most likely due to mountain-valley circulation over the site. This circulation pattern was originally described in *Toth and Johnson* [1985] and has been connected to air pollution transport [*Reddy and Pfister*, 2016]. Upslope flow in the daytime transports air and pollutants out of the WGF, and return downwind flow overnight and in the early morning recirculates these pollutants back over the Front Range region, leading to a persistent westerly component in the low-level benzene measurements. However, the persistent enhancement to the SW in all three plots indicates a primary benzene source to the SW of PAO. Although no distinct point source is evident, the high benzene observed at PAO has a directional component; it is not simply a general elevation of mixing levels throughout the region.

3.5. Hydrocarbon Tracer Correlations From PAO VOC Canister Samples

Tracer-tracer correlations in the canister samples are used to confine the source of hydrocarbons at PAO in general and the source of benzene in particular. Propane is an O&NG tracer in the Colorado Front Range region [*Gilman et al.*, 2013; *Thompson et al.*, 2014] and acetylene is a tracer for vehicular emissions [*Whitby*

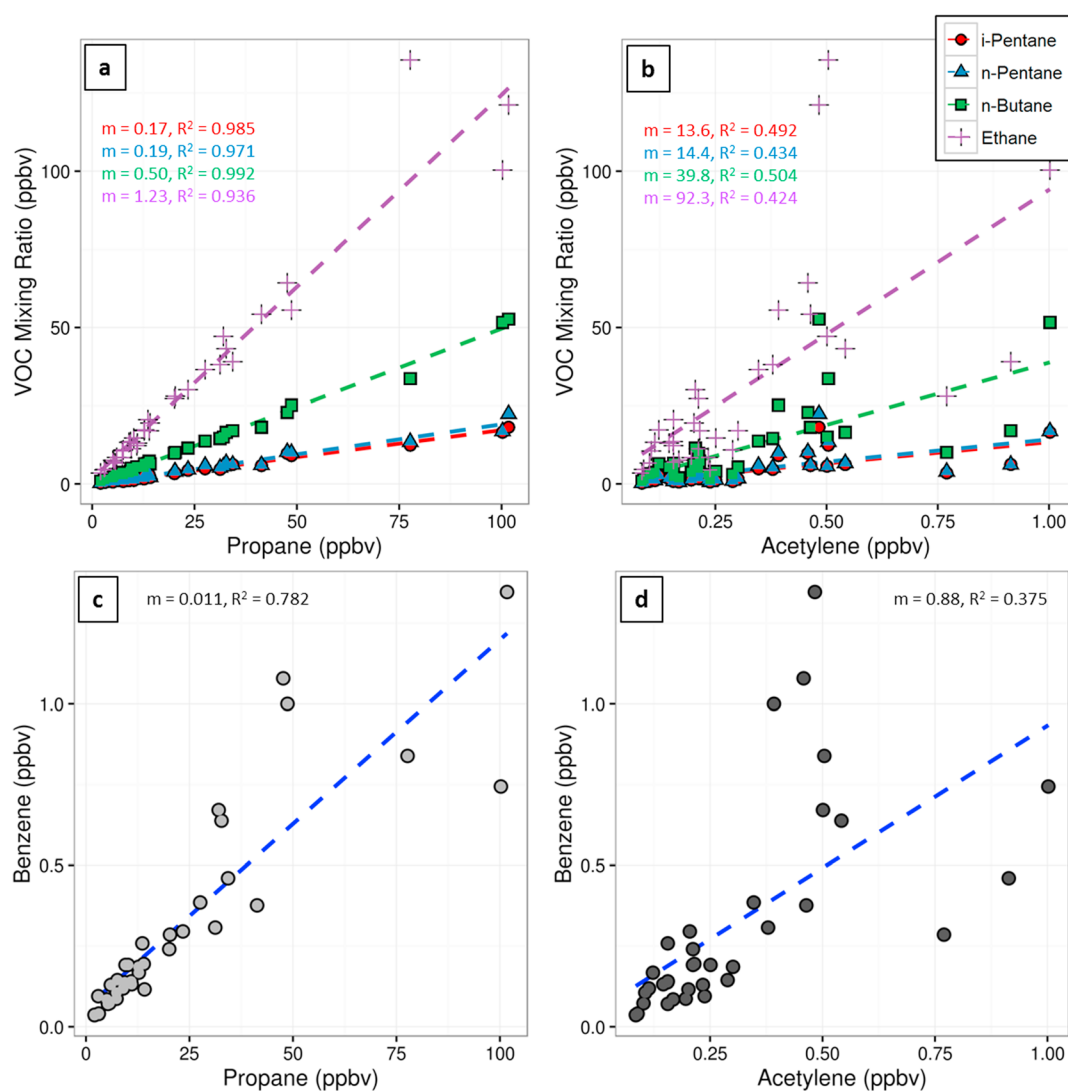


Figure 6. Regression plots of various hydrocarbons as measured in the canister samples during the DISCOVER-AQ 2014 campaign. Propane is an O&NG tracer and acetylene is a tracer for vehicular emissions. *i*-pentane, *n*-pentane, *n*-butane, ethane, and benzene, respectively, show a stronger correlation with propane than with acetylene.

and Altwicker, 1978; Xiao et al., 2007]. These tracer compounds are not measured by PTR-QMS, but pressurized canister samples collected at PAO during the P3-B spirals were analyzed for these tracers. The canister samples are confined to daylight observations but offer important source context for PAO.

The *i*-pentane, *n*-pentane, *n*-butane, and ethane are primarily emitted from NG, but can also be emitted from traffic in small amounts [Gentner et al., 2013; Thompson et al., 2014]. The correlations of these four species with propane (Figure 6a) are strong, with *i*-pentane ($R^2 = 0.985$), *n*-pentane ($R^2 = 0.971$), *n*-butane ($R^2 = 0.992$), and ethane ($R^2 = 0.936$) showing tight correlation over all 35 samples. In contrast, the correlations with acetylene (Figure 6b) are much weaker; *i*-pentane ($R^2 = 0.492$), *n*-pentane ($R^2 = 0.434$), *n*-butane ($R^2 = 0.504$), and ethane ($R^2 = 0.424$). The strong correlations with propane indicate that the hydrocarbon mix observed at PAO during the DISCOVER-AQ 2014 campaign was predominantly influenced by O&NG activities. The weak correlation with acetylene confirms that vehicular emissions are not a major source of the atmospheric tracers measured at PAO. Our observations agree well with the findings by Thompson et al. [2014] who use data collected by the Colorado Department of Public Health and Environment (CDPHE) in the City of Platteville in 2013 (Table 3). The only notable difference between the results at PAO and in Thompson et al. [2014] is that less acetylene was measured in the canister samples at PAO, which is isolated from major traffic, compared to the city of Platteville, which straddles US 85, a major N-S highway with heavy truck traffic.

Table 3. Coefficient of Determination (R^2) Between Various VOCs as Measured in the Canister Samples Taken at PAO (This Work) and During a Previous Study in Platteville, CO

	Propane		Acetylene	
	<i>Thompson et al.</i> [2014]	This work	<i>Thompson et al.</i> [2014]	This work
<i>n</i> -butane	0.95	0.99	0.15	0.50
<i>i</i> -pentane	0.91	0.99	0.08	0.49
<i>n</i> -pentane	0.94	0.97	0.12	0.43
Benzene	0.73	0.70	0.29	0.27

Figures 6c and 6d are the regression plots of benzene versus propane and acetylene, respectively. Benzene was correlated with propane ($R^2 = 0.782$), indicating a common source. The benzene to propane ratio for this study (0.011 ppbv benzene/ppbv propane) is similar to the benzene to propane ratio in *Pétron et al.* [2012] (0.010 ppbv benzene/ppbv propane). In contrast, the correlation with acetylene was very weak ($R^2 = 0.375$). Again, our observations agree well with the study by *Thompson et al.* [2014] who found that benzene correlated with propane ($R^2 = 0.73$) much more strongly than with acetylene ($R^2 = 0.29$). The high benzene measured at PAO coupled with the vertical diurnal profile, Figure 4, and the directional dependence, Figure 5, indicates that benzene originates from some sources or emissions from the SW of PAO. The common propane-benzene source indicated by these tracer correlations provides strong evidence that we were primarily observing benzene from O&NG sources.

The isomers of pentane, *i*-pentane and *n*-pentane, can be used as additional tracers for distinguishing traffic contributions from O&NG sources [*Gilman et al.*, 2013; *Swarthout et al.*, 2015]. Tail pipe emissions enhance *i*-pentane, and high *i*-pentane-to-*n*-pentane ratios are typical for traffic sources. These tracers are affected equally by atmospheric mixing, dilution, and photochemical processing, so the source ratios remain constant in the atmosphere [*Gilman et al.*, 2013]. Figure 7 shows that the canisters collected at PAO in July and August 2014 having an *i*-pentane-to-*n*-pentane ratio of 0.888 ($R^2 = 0.988$), a value that is very close to the ratio of 0.86 reported for raw NG produced in the WGF [COGCC, 2007]. Previous studies in NE Colorado have found similar ratios: 0.885 at the BAO in 2011 [*Gilman et al.*, 2013], 0.965 in Longmont, CO [*Thompson et al.*, 2014], and 1.00 at BAO [*Swarthout et al.*, 2013]. In contrast, fresh vehicle emissions have an *i*-pentane-to-*n*-pentane ratio of 2.96 [*Broderick and Marnane*, 2002]. Measurements taken in Denver, CO, and Boulder, CO, found an *i*-pentane-to-*n*-pentane ratios of 1.87 [*Baker*, 2008] and 1.10 [*Gilman et al.*, 2013], respectively. Our observations indicate a

strong O&NG source of hydrocarbons at PAO (Figure 8).

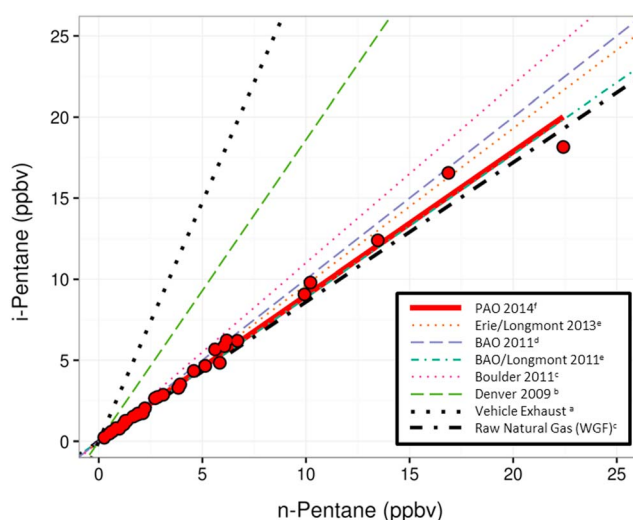


Figure 7. Regression plot of *i*-pentane versus *n*-pentane as measured in the canister samples during the DISCOVER-AQ 2014 campaign and during previous studies in NE Colorado. (a) *Broderick and Marnane* [2002]; (b) *Baker et al.* [2008]; (c) *Gilman et al.* [2013]; (d) *Swarthout et al.* [2013]; (e) *Thompson et al.* [2014]; and (f) This work [2016].

The spatial pattern of the *i*-pentane-to-*n*-pentane ratio and its correspondence to benzene can be investigated for the region using the TOGA data collected on the NSF/NCAR C-130 during the FRAPPÉ study (27 July 2014 to 18 August 2014). Only data collected from an altitude of 2.5 km asl or less (1 km agl at PAO) are used in this plot. The higher pentane ratios (≥ 1.0) are associated with the Denver metro region, while air sampled above the WGF and associated urban regions have the lower pentane ratios we associate with O&NG sources. This is notable in the W of the WGF and E of Greeley where the largest benzene mixing ratios are observed and suggests

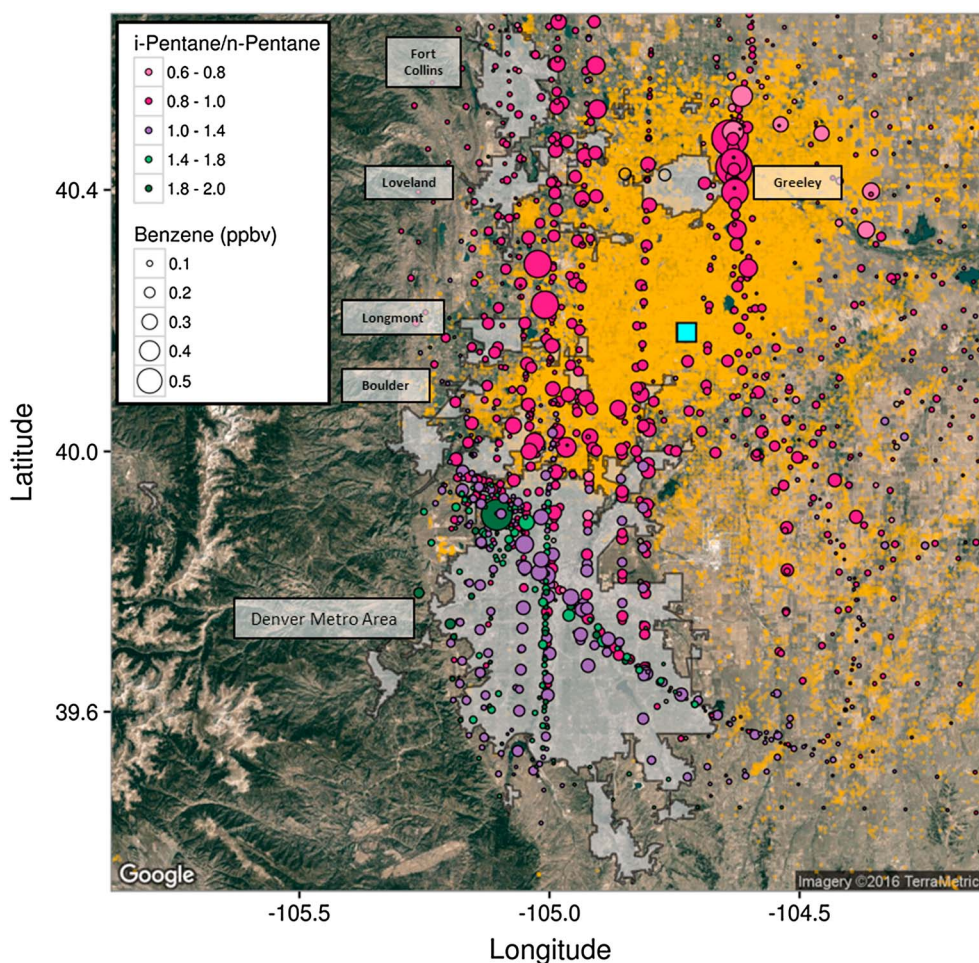


Figure 8. The *i*-pentane-to-*n*-pentane ratios as measured from the NCAR C-130 during the FRAPPÉ campaign for all measurements collected below 2.5 km asl (1 km agl for PAO, cyan square). Data points are colored by the *i*-pentane-to-*n*-pentane ratio, and all observations are sized by the measured benzene mixing ratio. The pentane ratio is separated into five ranges, with the larger ratios more indicative of vehicle emissions and lower ratios more indicative of O&NG emissions.

that these high benzene mixing ratios are more closely associated with O&NG extraction than with vehicle emissions.

The *i*-butane-to-*n*-butane ratio found in the DISCOVER-AQ 2014 canister samples was 0.405 ($R^2 = 0.993$; data not shown), again comparing well with the numbers reported by Swarthout *et al.* [2013] and Thompson *et al.* [2014], 0.41 and 0.43, respectively. Data taken by the CDPHE [Air Pollution Control Division, 2012] yield a butane isomer ratio of 0.42. These regional ratios are comparable to values observed in well-mixed urban and rural regions [Parrish *et al.*, 1998; Watson *et al.*, 2001], but lower than expected for vehicular emissions [Conner *et al.*, 1995; Jobson *et al.*, 2004]. Emissions from commercial NG have an *i*-butane-to-*n*-butane ratio of 0.60 [Fujita, 2001], but such high ratios have not been recorded in the WGF, indicating that the natural butane isomer ratio for this gas field is around 0.4.

3.6. Toluene-to-Benzene Ratio

Toluene is coemitted with benzene with source-dependent ratios. Toluene degrades more rapidly in the atmosphere than benzene, and the ratio of these two compounds can thus be used to assess the photochemical age of an air mass [e.g., Roberts *et al.*, 1984]. However, these calculations do not work reliably in areas where there are additional non-tail pipe emissions of these aromatic compounds [e.g., Gelencsér *et al.*, 1997], such as in the WGF, or where there are emissions from sources with different toluene-to-benzene ratios. The toluene-to-benzene ratio can still be useful for distinguishing O&NG and traffic emissions. Fresh traffic

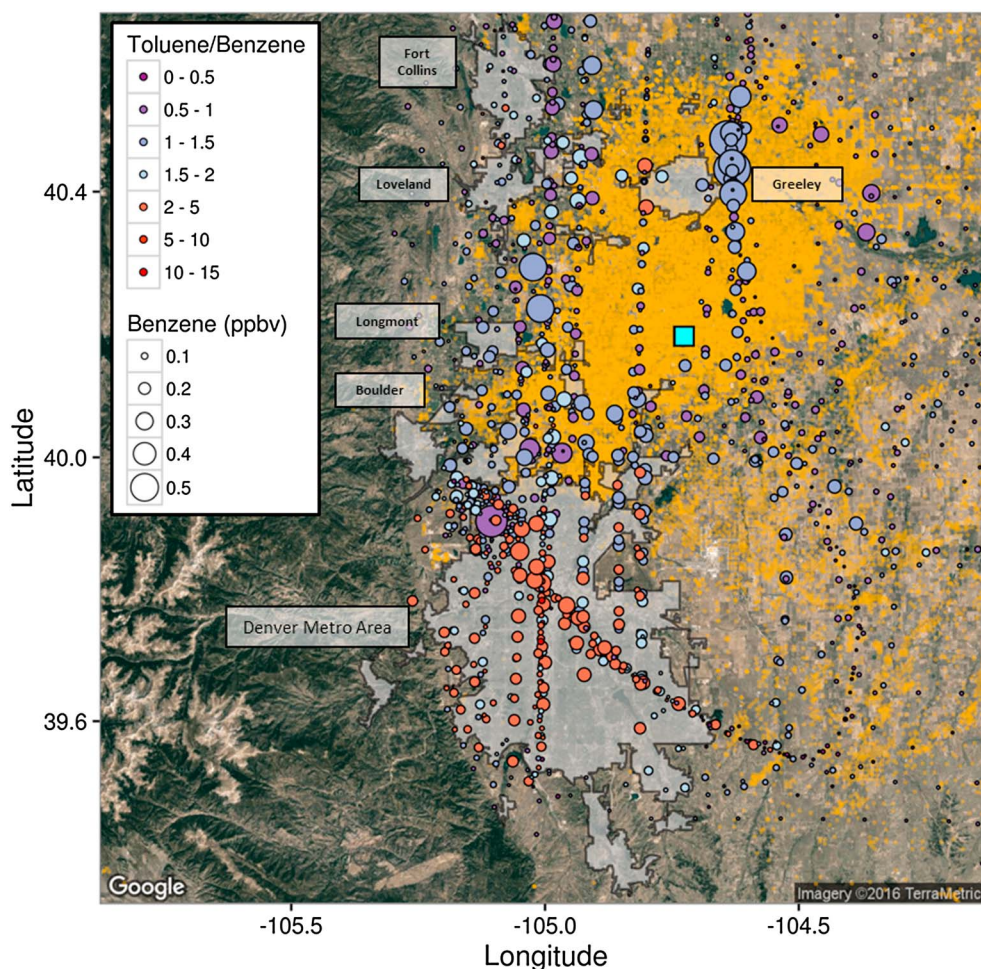


Figure 9. Toluene-to-benzene ratios as measured from the NCAR C-130 during the FRAPPÉ campaign at all altitudes. Data points are colored by the toluene-to-benzene ratio, with ratios < 2 colored cool tones, and ratios ≥ 2 presented in warm colors. All observations are sized by the measured benzene mixing ratio. High benzene levels with toluene-to-benzene ≥ 2 are only observed over the Denver urban area and close to Greeley. PAO is marked with a cyan square and had a daytime mean benzene mixing ratio of 0.37 ppbv.

emissions have a toluene-to-benzene ratio ≥ 2 [Barletta et al., 2002; Heeb et al., 2000; Bravo et al., 2002], and the mean ratio for the Denver urban region was measured as 2.1 [Baker et al., 2008].

A spatial map of toluene-to-benzene ratios calculated from the measurements made by the TOGA instrument aboard the NSF/NCAR C-130 during the FRAPPÉ study (27 July 2014 to 18 August 2014) is shown in Figure 9. A toluene-to-benzene ratio cutoff of 2 or greater appears to be appropriate for differentiating the urban from the surrounding suburban and rural environment. The data points shown are colored by the toluene-to-benzene ratio cut off value of 2, but the points are sized by the magnitude of the benzene observation for each point. The highest benzene concentrations were found within the boundary of the WGF, but these high observations occur on the E side of the Greeley urban area as well as in the SW corner of the WGF just to the N of the Denver urban boundary. The few measurements taken at or in the surroundings of PAO show comparatively low benzene values, but the airborne data provide some additional evidence for a benzene source located to the SW of PAO. Interestingly, high benzene surface observations at PAO were not associated with a flow from the NNE indicating that the site is not influenced by emissions in the Greeley area.

Figure 10a shows the regression plot of benzene versus toluene as observed by PTR-QMS at PAO during the DISCOVER-AQ 2014 campaign. The data with a toluene-to-benzene ratio ≥ 2 (traffic emissions) are colored in orange and account only for 5% of the total benzene observations. The mean toluene-to-benzene ratio

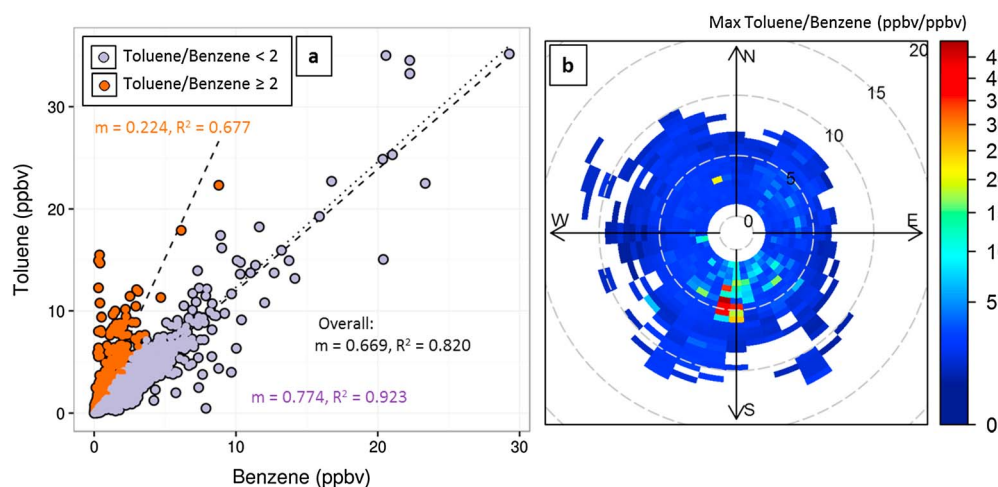


Figure 10. Regression plot of toluene and benzene as observed by PTR-QMS at PAO. (a) Regression plot of toluene and benzene for the entire DISCOVER-AQ 2014 campaign. The points are color coded by the toluene-to-benzene ratio (grey < 2, orange ≥ 2; the latter being associated with fresh vehicular emissions). (b) Polar frequency plot of the toluene-to-benzene ratio showing that the highest ratios were associated with southerly winds.

calculated by wind sector is presented in Table 4. The tabulated data and the maximum values viewed spatially in a polar frequency plot (Figure 10b) show that high toluene-to-benzene ratios are only observed in air masses originating south of PAO, an area that is not associated with elevated benzene (see Figure 5).

A previous study at BAO [Swarthout *et al.*, 2013] also found the highest mean toluene-to-benzene ratio (1.09 ± 0.04) in the southern sector and explained this by advection of the Denver plume. Lower toluene-to-benzene ratios in the NE (0.76 ± 0.25) were attributed to O&NG emissions. When the mean toluene-to-benzene ratio is calculated by wind sector for PAO (Table 4), we also see the highest ratios associated with southerly winds (1.41 ± 1.86). The PAO ratios show a diurnal variation from all wind directions, with higher ratios observed at night in all sectors. The lowest mean ratios are observed in the E and SE wind sectors, but these two sectors are also associated with the lowest mean values of both benzene (E = 0.28 ± 0.36 ppbv, SE = 0.20 ± 0.25 ppbv) and toluene (E = 0.35 ± 0.55 ppbv, SE = 0.25 ± 0.37 ppbv).

While the spatial TOGA data would indicate that this southerly contribution is an urban outflow, potentially from the Denver metro region, there is some nuance to these measurements that needs to be investigated. The polar frequency analysis in Figure 10b shows that the toluene-to-benzene ratio is higher in the south, but it is much higher than we would expect for fresh vehicle emissions or urban outflow. Based on studies of

Table 4. Mean Toluene-to-Benzene Ratios (\pm Standard Deviation) Observed at PAO, Separated by Wind Sector, All Data and Data Separated by Daytime and Nighttime Values

Wind Sector	Total	Day	Night
N	1.26 ± 0.62	1.16 ± 0.81	1.37 ± 0.28
NE	1.32 ± 0.52	1.03 ± 0.40	1.55 ± 0.49
E	1.03 ± 0.42	0.88 ± 0.36	1.25 ± 0.40
SE	1.09 ± 0.71	0.97 ± 0.70	1.36 ± 0.65
S	1.41 ± 1.86^a	1.13 ± 1.22^a	1.61 ± 2.19^a
SW	1.34 ± 0.48	1.06 ± 0.71	1.41 ± 0.38
W	1.29 ± 0.43	0.95 ± 0.64	1.39 ± 0.26
NW	1.33 ± 0.46	1.21 ± 0.41	1.42 ± 0.27
Calm	1.32 ± 0.41	1.02 ± 0.56	1.39 ± 0.32

^aThe highest toluene-to-benzene ratios are observed during southerly wind flow over the site. The high standard deviations for these southerly observations are due to the low number of observations with a high toluene to benzene ratio, with 5% of the total benzene observations occurring with a toluene-to-benzene ratio above 2.

O&NG regions, we tentatively identify these high toluene-to-benzene ratio observations as being associated with condensate tanks [Hendler *et al.*, 2009; Field *et al.*, 2015]. Condensate emissions have been measured as having a toluene-to-benzene ratio $\gg 2$, and is the most likely explanation of the extremely high toluene mixing ratios we see to the S of PAO. This is in contrast to the high benzene that we see associated with the SW flow over the site, which has a ratio toluene-to-benzene of about 1, as seen in other O&NG studies [Field *et al.*, 2015; Rutter *et al.*, 2015].

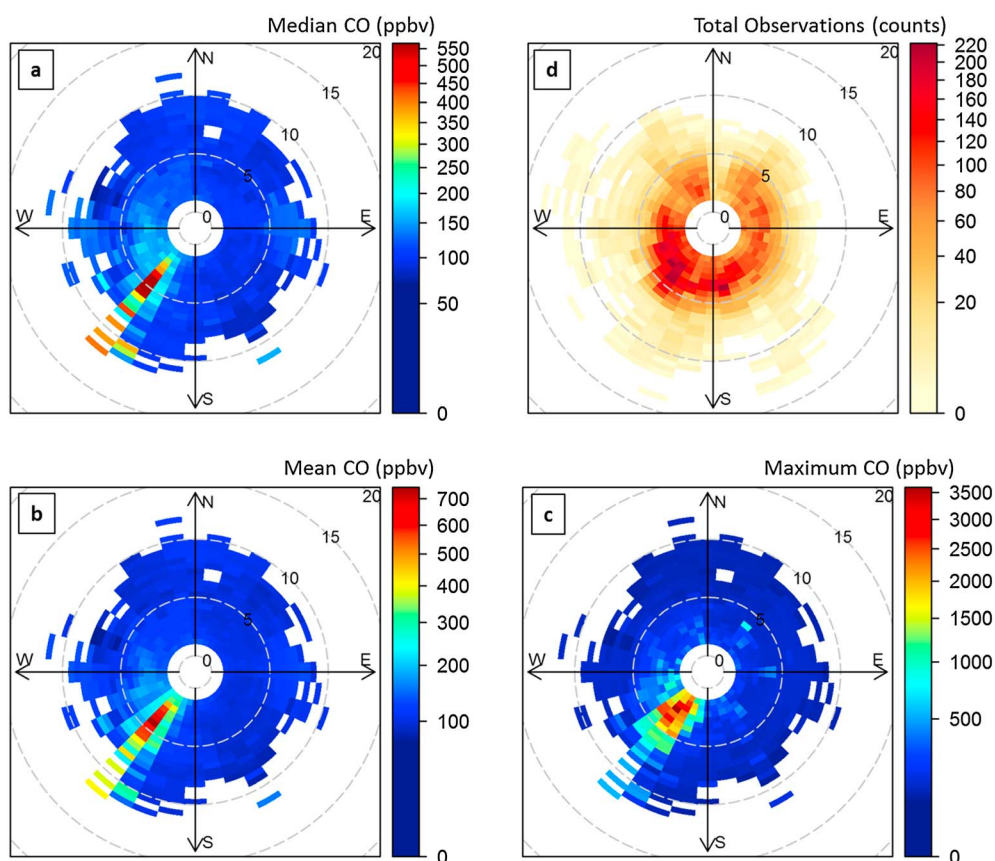


Figure 11. Polar frequency plots of CO measured at PAO during the DISCOVER-AQ 2014 campaign. The wind observations are binned by 10° wind direction and 0.5 m s⁻¹ wind speed. Enhanced CO has a directional dependence associated with SW flow over the site, similar to the results for benzene (Figure 6).

3.7. Polar Frequency Analysis of CO and Benzene-to-CO Correlation

An analysis of the CO data obtained at PAO was carried out to gain additional insights into benzene sources. Benzene of urban origin is usually well correlated with CO due to a common traffic source. Two previous WGF studies at BAO used correlations with CO to differentiate between benzene sources [Pétron *et al.*, 2012; Swarthout *et al.*, 2013]. At BAO, benzene originating from the S was found to correlate well with CO

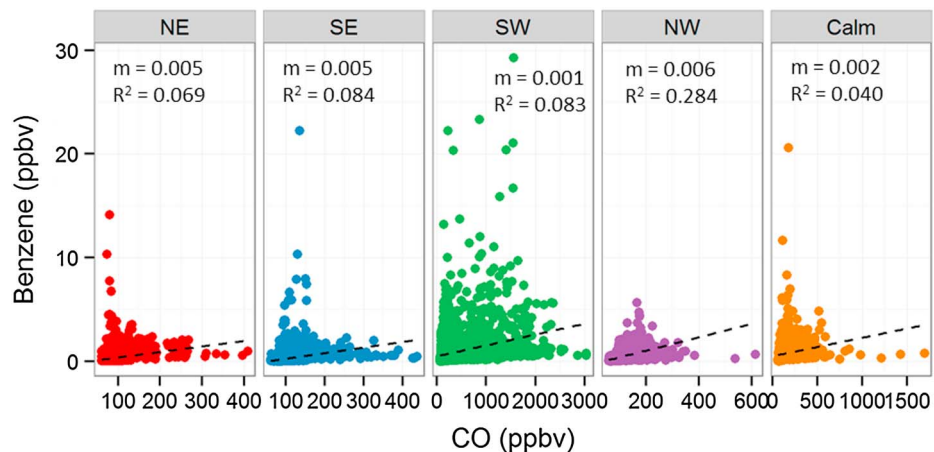


Figure 12. Regression plots of benzene versus CO, grouped by wind direction. Calm winds had a measured wind speed less than 1 m s⁻¹ for the minute average. The CO axis scaling changes based on wind direction.

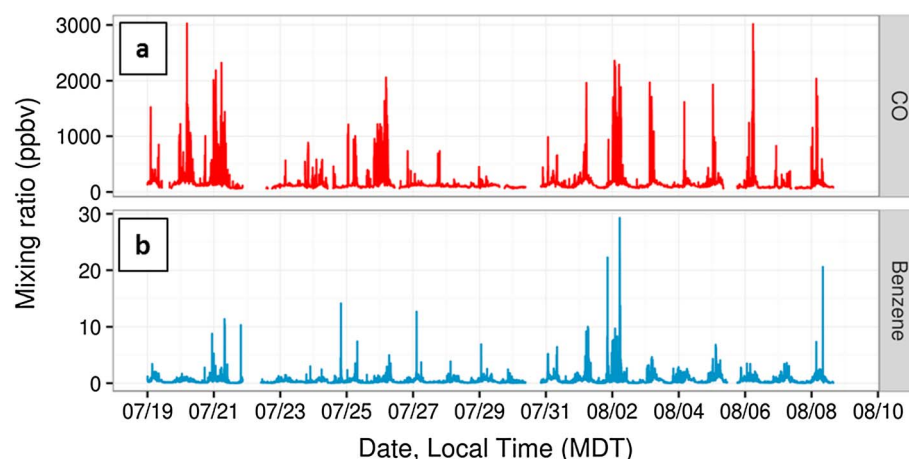


Figure 13. The time series comparison of (a) CO (red) and (b) benzene (blue).

($R^2 > 0.8$). Both of these studies also identified enhanced aromatics in the NE, while the NE benzene-to-CO correlations were somewhat weaker ($R^2 = 0.58\text{--}0.86$). The enhanced NE aromatic signature was attributed to gas field benzene emissions.

In the PAO analysis, CO enhancements were found to have a strong directional component and it was the southwestern sector where highest CO levels (several ppmv) were observed (Figure 11). While this finding may suggest common sources of CO and benzene, the correlation between these two species was very weak for all wind sectors (full campaign R^2 value of 0.099), and particularly weak for the SW (Figure 12). A time series comparison of these two species is shown in Figure 13. Benzene and CO track occasionally, as expected for a common traffic source, but generally benzene and CO enhancements occurred independently. There are three major benzene/CO regimes observed during the campaign: benzene and CO tracking from a common traffic or urban source, benzene increases without associated CO increases, and CO increases without associated benzene.

The tightly constrained wind regimes associated with very high CO levels of several ppmv and the lack of correlation with benzene indicate that high CO is unlikely to have originated from either the Denver urban area or from major freeways to the W and SW of PAO. Instead, our observations suggest a stationary CO source and a separate, temporally variable benzene source, both located in the same general region to the SW of PAO. In Colorado CO emissions have been attributed to gasoline vehicles (66%) and nonroad gasoline-powered equipment (26%) [LaFranchi *et al.*, 2013]. The remaining emissions are attributed to a variety of processes, including industrial activity and natural gas processing. The extremely high observed mixing ratios of CO coupled with the lack of a correlation with benzene or other tracers indicates that a close range CO production is not associated with vehicle emissions.

4. Discussion

Our observations lead us to conclude that the benzene enhancements observed at PAO during the 2014 DISCOVER-AQ study were primarily related to O&NG production and distribution activities in the WGF. If the high benzene observed at PAO was primarily from the Denver Metropolitan Area, we would expect a correlation to the combustion tracers, acetylene and CO [Borbon *et al.*, 2013; Apel *et al.*, 2010]. However, we see weak to nonexistent correlations over the entire campaign for these species. In addition, the highest benzene levels occurred when CO mixing ratios were low. High benzene that is not correlated with vehicle combustion tracers has been observed in areas with heavy petrochemical industry, such as Houston, TX [Gilman *et al.*, 2009].

Benzene emitted by O&NG activities is expected to tightly correlate with propane, an O&NG tracer, and we did observe a strong correlation between those two species at PAO. Studies in areas of heavy O&NG production have shown a similar behavior, especially for sites associated with NG production [Swarthout *et al.*, 2013; Helmig *et al.*, 2014; Pétron *et al.*, 2014; Warneke *et al.*, 2014].

Previous studies at BAO have found anomalously large benzene mixing ratios in the NE, which were attributed to O&NG production in Weld county without further specification, except to assume a WGF mix of natural gas and automotive sources [Pétron *et al.*, 2012; LaFranchi *et al.*, 2013; Swarthout *et al.*, 2013]. Our measurements at PAO took place NE of BAO, much deeper into the WGF. In contrast, the PAO measurements of the benzene found the greatest enhancement of benzene to the SW, with a strong spatial dependence. This puts some spatial constraint on the WGF benzene source, to the SW corner of the field between PAO and BAO, although the strong wind dependence at PAO indicates that the benzene sources are closer to PAO than to BAO. In addition to narrowing the source area, our online benzene data also show that mixing ratios are highly variable, especially at night. While we expect elevated mixing ratios at night, the lack of correlation with CO suggests a nonvehicle source, and the vertical diurnal cycle of benzene indicates a buildup of benzene at the surface overnight. We believe we are observing emissions from a transient benzene source related to O&NG production that is operating close to PAO. Benzene emissions have been identified for various parts in the NG extraction and distribution process. Specifically, these processes are (1) diesel vehicle emissions; (2) emissions from gas flaring and deliberate venting; (3) evaporation from drilling flowback of waste mud and water; (4) fugitive emissions from infrastructure and maintenance; and (5) emissions from condensate tanks [Adgate *et al.*, 2014; Verma *et al.*, 2000; Buzcu-Guven *et al.*, 2013].

The poor correlation of benzene with CO eliminates diesel vehicle emissions from the list of potential sources. Benzene emissions from gas flaring [Buzcu-Guven *et al.*, 2013] would imply a correlation with formaldehyde as observed by Knighton *et al.* [2012]. No such correlation was observed at PAO ($R^2 = 0.003$, data not shown). Drilling flowback and waste water is stored in temporary waste pits at the drilling sites [Colborn *et al.*, 2011], the locations of which are monitored and reported by Colorado Oil and Gas Conservation Commission (COGCC). Regulatory advances have phased out this type of storage in favor of closed systems [Air Pollution Control Division, 2012], but active locations are still recorded in the WGF by the COGCC. There is a dense group of these pits located between PAO and BAO as shown in Figure S6. Water and drilling wastes have, however, not been associated with high atmospheric benzene concentrations in previous studies [Bloomdahl *et al.*, 2014; Bunch *et al.*, 2014], although published atmospheric measurements of these waste pits are difficult to locate. Environmental impacts from these waste pits are more likely to be associated with poor water quality [Eiceman *et al.*, 1986; Gross *et al.*, 2013]. Also, the transient nature of the benzene source is hard to explain by slow evaporative emissions from drilling flowback of waste mud and water. This leaves the following potential O&NG sources of benzene: fugitive emissions or gas venting during O&NG production or distribution and emissions from condensate tanks.

Increased levels of benzene have been observed in the proximity of O&NG processing facilities [Burstyn *et al.*, 2007]. PAO is located 4.5 km to the NE of the Platte Valley Gas Plant (Figure S6), which was operational through our study period. Fugitive emissions of VOCs, including benzene and toluene, are expected in O&NG processing facilities, mostly from storage tanks but also from conversion and treatment processes and venting [Rao *et al.*, 2005; Bar-Ilan *et al.*, 2008; Chambers *et al.*, 2008].

Condensate tanks have been implicated as VOC sources in previous studies [Moore *et al.*, 2014]. A study using a mobile platform in the Uintah Basin found a clear aromatic source from the condensate and water tanks on the gas well pads [Warneke *et al.*, 2014]. Gas dehydrator units have been implicated as the largest single factor of benzene exposure for workers [Capleton and Levy, 2005]. Pétron *et al.* [2012] estimated that flashing from such units produce about 65% of the total NG extraction-related VOCs in Colorado [Pétron *et al.*, 2012]. Condensate tank flashing and vented emissions were implicated as benzene sources, but it was noted that the benzene-to-propane ratio modeled from these processes was a factor of 2 lower than the benzene-to-propane ratio measured at BAO. The benzene-to-propane ratio measured at BAO (10.1 pptv benzene per ppbv propane) is very similar to the value found in our study (11 pptv benzene per ppbv propane) (Figure 7). Pétron *et al.* [2012] used the correlation between benzene and propane to assert that O&NG operations were a nonnegligible source of benzene within the WGF. The summer lifetimes of these two species are similar, so the measured ratio should be indicative of the emission ratio.

In statewide emissions budgets, benzene is primarily attributed to combustion emissions. The CDPHE keeps a bottom-up emission inventory based on permit data and empirical calculations, and the 2011 inventory assessments assigned nearly 90% of the total front range benzene emissions to vehicles, both highway and nonroad [Pétron *et al.*, 2014]. Benzene in the WGF has been quantified in three previous works: two

studies at BAO [Pétron *et al.*, 2012; Gilman *et al.*, 2013] and the Thompson *et al.* [2014] study in the City of Platteville. Gilman *et al.* [2013] attributed 32% of the observed benzene in their study to O&NG sources, while Thompson *et al.* [2014] found that benzene in Platteville has contributions from both traffic and noncombustion evaporative sources but did not further quantify the O&NG contributions. A top-down estimate of benzene over Weld County was 7 times higher than the CDPHE inventory estimates of benzene emissions for the same region [Pétron *et al.*, 2014]. They conclude that the benzene emissions from O&NG sources over the WGF are on the same order of magnitude as the vehicle emissions, and that mismatch between the top-down measurements and the state inventory assessment is consistent with missing benzene emissions in the Colorado Front Range Region. The assertion that the benzene evaporative emissions could be equal or greater than the vehicle emissions in the WGF is substantiated by the correlation results that we see in our work, with the propane tracer having a stronger correlation to benzene than acetylene.

5. Conclusions

A PTR-QMS instrument collected continuous benzene data at PAO in the WGF as part of the DISCOVER-AQ field campaign in July and early August 2014. The interpretation of the obtained data is supported by meteorology and general air quality monitoring, as well as compressed air canister samples and regional airborne surveys. Unexpectedly high mixing ratios of benzene were observed at PAO during this study. The lowest benzene mixing ratios were observed during daytime; strong nighttime increases in benzene were explained by local gas field sources emitting into a low nocturnal boundary layer. Airborne vertical profiling of benzene confirmed the essential role of boundary layer height in driving surface level benzene concentrations. High nighttime mixing ratios of benzene significantly increased long-term statistical averages, proving the need to include nighttime measurements in correct benzene exposure assessments. In addition, further measurements during wintertime (i.e., when the boundary layer is lower) are warranted to correctly assess the yearly average benzene exposure.

Canister data show an overall strong O&NG signature in hydrocarbons detected at PAO and several tracer-tracer correlations confirm the dominant role of O&NG emissions over traffic sources. Short-range O&NG benzene sources are more important at PAO than the more remote Denver signal. A polar frequency analysis of the benzene reveals that there is a directional component, locating the benzene source to the SW of PAO. The high benzene measured from the SW of PAO corresponds to high benzene levels located in previous studies to the NE of BAO. Our observations allow us to constrain the source of elevated benzene between the two atmospheric observatories. We were able to exclude diesel vehicle emissions and emissions from gas flaring as potential sources of benzene. The most likely sources of benzene at PAO are emissions from condensate tanks and fugitive emissions of benzene from O&NG operations in the Platteville area. To better resolve the benzene source question, we need more directed measurements around the O&NG infrastructure in the region and long-term stationary measurements in the WGF.

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Acknowledgments

We wish to acknowledge NASA grants NNX10AR39G (DISCOVER-AQ), NNX11AQ44G, and NNG05G062G (extended) to the Pennsylvania State University. PTR-MS measurements during DISCOVER-AQ were supported by the Austrian Federal Ministry for Transport, Innovation and Technology (BMVIT) through the Austrian Space Applications Programme (ASAP) of the Austrian Research Promotion Agency (FFG). A.W. and T.M. received support from the Visiting Scientist Program at the National Institute of Aerospace (NIA). P.E. received support from the European Commission's 7th Framework Programme under grant agreement 287382 (PIMMS ITN). The canister measurements collected at the Platteville Atmospheric Observatory were supported by funding from DISCOVER-AQ. The National Center for Atmospheric Research ran the FRAPPE campaign to correspond to the DISCOVER-AQ campaign and is sponsored by the National Science Foundation. We thank the DISCOVER-AQ leadership, Jim Crawford and Mary Kleb, and the FRAPPE leadership, Gabrielle Pfister and Frank Flocke, for arranging the use of the Platteville Atmospheric Observatory. Generous field support came from NOAA/ESRL's Physical Sciences and Chemical Sciences Division through Gerhard Huebler, Tom Ayers, Eric Williams, and David Fahey. Discussions with Patrick Reddy and Daniel Bon (CDPHE) were very helpful, as well as input from Lisa McKenzie (Colorado School of Public Health). Thanks and acknowledgments for perseverance during the data collection stage are extended to Ryan Stauffer, Bianca Baier, and Nikolay Balashov, and many thanks to William Brune at Penn State for his continued support of this work. All data used in this publication are accessible through NASA Langley's data repository (<https://www-air.larc.nasa.gov/data.htm>).

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