Investigation of the influence of transport from oil and natural gas regions on elevated ozone levels in the northern Colorado front range

Jason M. Evans & Detlev Helmig

To cite this article: Jason M. Evans & Detlev Helmig (2017) Investigation of the influence of transport from oil and natural gas regions on elevated ozone levels in the northern Colorado front range, Journal of the Air & Waste Management Association, 67:2, 196-211, DOI: 10.1080/10962247.2016.1226989

To link to this article: http://dx.doi.org/10.1080/10962247.2016.1226989
Investigation of the influence of transport from oil and natural gas regions on elevated ozone levels in the northern Colorado front range

Jason M. Evans and Detlev Helmig

Institute of Arctic and Alpine Research (INSTAAR), University of Colorado Boulder, Boulder, CO, USA

ABSTRACT

The Northern Colorado Front Range (NCFR) has been in exceedance of the ozone National Ambient Air Quality Standard (NAAQS) since 2004, which has led to much debate over the sources of ozone precursors to the region, as this area is home to both the Denver, CO, metropolitan area and the Denver–Julesburg Basin, which has experienced rapid growth of oil and natural gas (O&NG) operations and associated emissions. Several recent studies have reported elevated levels of atmospheric volatile organic compounds (VOCs) as a result of O&NG emissions and the potential for significant ozone production from these emissions, despite implementation of stricter O&NG VOC emissions regulations in 2008. Approximately 88% of 1-hr elevated ozone events (>75 ppbv) occur during June–August, indicating that elevated ozone levels are driven by regional photochemistry. Analyses of surface ozone and wind observations from two sites, namely, South Boulder and the Boulder Atmospheric Observatory, both near Boulder, CO, show a preponderance of elevated ozone events associated with east-to-west airflow from regions with O&NG operations in the N-ESE, and a relatively minor contribution of transport from the Denver Metropolitan area to the SE-S. Transport from upwind areas associated with abundant O&NG operations accounts for on the order of 65% (mean for both sites) of 1-hr averaged elevated ozone levels, while the Denver urban corridor accounts for 9%. These correlations contribute to mounting evidence that air transport from areas with O&NG operation has a significant impact on ozone and air quality in the NCFR.

Implications: This article builds on several previous pieces of research that implied significant contributions from oil and natural gas emissions on ozone production in the Northern Colorado Front Range. By correlating increased ozone events with transport analyses we show that there is a high abundance of transport events with elevated ozone originating from the Denver–Julesburg oil and natural gas basin. These findings will help air quality regulators to better assess contributing sources to ozone production and in directing policies to curb ozone pollution in this region.

PAPER HISTORY

Received April 11, 2016
Revised August 17, 2016
Accepted August 17, 2016

Introduction

The Northern Colorado Front Range (NCFR), including the Denver metropolitan area, was designated an ozone (O₃) non-attainment area (NAA) (Figure 1) by the U.S. Environmental Protection Agency (EPA) in 2004; actual NAA assignment was deferred until 2007, and as of 2016 the area remains in non-attainment. The U.S. National Ambient Air Quality Standard (NAAQS) for 8-hr average ground-level O₃ was lowered to 70 parts per billion by volume (ppbv) in October 2015 (EPA 2015), which now poses an even higher challenge for the NCFR to reach attainment. Non-attainment of the O₃ NAAQS is determined by 3-year averaging of the fourth highest daily 8-hr average maximum O₃ mole fractions.

Elevated O₃ levels are considered hazardous to human health due to detrimental effects on the human respiratory system; epidemiological studies found an ~0.86% increase in mortality rate per 10 ppbv increase of O₃ (Bates, 2005; Ito et al., 2005). High levels of O₃ are thought to be responsible for ~10,000 premature deaths per year in the United States (Caiazzo et al., 2013). Elevated O₃ levels can also have negative impacts on agriculture, as exposure to O₃ between 35 and 75 ppbv can result in yield losses of 5–48% for wheat and other crops due to repressed photosynthesis activity and reduced growth (Emberson et al., 2009).

Tropospheric O₃ is a secondary air pollutant primarily generated through multistep photochemical reactions involving volatile organic compounds (VOCs) and nitrogen oxides (NOₓ) (Chameides et al., 1992). Globally, total VOC emissions are dominated by biogenic compounds, such as isoprene; however, both VOCs and NOₓ can be emitted from various anthropogenic sources with
elevated mole fractions typically observed in large urban centers. Recent research has shown that shale regions with extensive oil and natural gas (O&NG) extraction operations, such as the Uintah Basin, Utah, and the Green River Basin, Wyoming, both located in the U.S. Midwestern Rocky Mountains, can produce significant VOC emissions, resulting in ambient levels exceeding those of major cities (Schnell et al., 2009; Helmig et al., 2014; Rappenglueck et al., 2014; Thompson et al., 2014). While the NCFR NAA covers several highly populated areas, including Denver, it also contains extensive O&NG operations centered in the Denver–Julesburg Basin (DJB), one of the largest O&NG production regions in the United States. Currently, the state of Colorado has over 52,000 active O&NG wells, ~21,000 of which are located in Weld County, centered in the Greater Wattenberg Gas Field (Colorado Oil and Gas Conservation Commission [COGCC], 2014). Studies have emerged showing that elevated atmospheric levels of VOC in O&NG development regions can contribute to production of surface O$_3$ (Kemball-Cook et al., 2010). In the Uintah Basin and the Upper Green River Valley, episodes with O$_3$ exceeding up to 150 ppbv have been reported (Schnell et al., 2009; Oltmans et al., 2014; Rappenglueck et al., 2014) during the winter months when snow covers the ground. These conditions promote strong surface inversions, which cause emissions to get trapped near the surface. The high albedo of snow cover increases available radiation, which further promotes photochemical reactions. Radicals from photolysis of carbonyls are a major oxidant source, and ozone production occurs at lower NO$_x$ and much larger VOC concentrations than what has previously been found during summertime ozone production in urban areas (Carter and Seinfeld, 2012; Edwards et al., 2013; Edwards et al., 2014; Ahmadov et al., 2015). The Uintah Basin and Green River Basin are similar in that they are high plains, rural areas in the Rocky Mountain Region with relatively low urban emissions, where O&NG operations dominate the industrial activity of the area. The NCFR, which encompasses the Wattenberg Field, shares similar topographic characteristics, but also contains a large, highly populated metropolitan area, and complex airflow conditions.

Since 2004, the Colorado Air Quality Control Commission (AQCC) has enacted regulations aimed at reducing surface level O$_3$ mole fractions within the NAA, such as required reductions in condensate tank VOC emissions and stricter regulations for motor vehicles, including mandatory vehicle emissions testing (Colorado Department of Public Health & Environment [CDPHE], 2008a). Thompson et al. (2014), in their review of recent and available historic data, show that O&NG-associated VOC concentrations have increased in the NCFR, and that the VOC distribution has shifted from mobile and combustion sources more toward O&NG associated VOC. These comparisons suggest that the growth of O&NG operations has likely outpaced any potential reductions of condensate tank sources, and/or that possibly the transition from conventional to hydraulic fracturing drilling operations over the past 10 years may have been associated with an overall VOC emissions increase.

Despite the state efforts, Denver, CO, and the NCFR continue to experience frequent occurrences of O$_3$ levels above the NAAQS. The annual O$_3$ cycle in the NCFR exhibits a late fall/winter minimum, with O$_3$ increasing during spring and peaking in summer (Brodin et al., 2010) (Supplement Figure S1). An extensive O$_3$ monitoring network has been established by the Colorado Department of Public Health & Environment (CDPHE); the locations of monitors are shown in Figure 1. This figure also indicates how sites compare in the number and severity of NAAQS exceedances. Figure 2 shows the record of the fourth-highest 8-hr O$_3$ averages and NAAQS exceedances during 2000–2014 at five CDPHE sites and the Boulder Atmospheric Observatory (BAO). These sites were selected for their north–south distribution along the NCFR. Regression analysis (95% confidence) of these data shows no statistically significant trend.

There is a notable interannual variabilty in the annual O$_3$ data. A significant fraction of this variability is due to the prevalence of high-pressure weather systems during the summer, which affect the rate of O$_3$ production (Wise and Comrie, 2005; Reddy and Pfister, 2016). Reddy and Pfister (2016) demonstrate a relationship between high surface ozone episodes and persistence of high pressure weather systems, and a method in which monthly 500-mbar pressure heights offer a means of correcting for the yearly variability in fourth-highest 8-hr O$_3$ averages. Consideration of this correction did not yield statistically different trend results for residuals of weather-predicted and actual fourth-highest 8-hr O$_3$ maxima at these sites in our analysis, further confirming that there has been no statistically significant improvement in surface O$_3$ during 2000–2014. This is in contrast to O$_3$ changes seen in 8-hr O$_3$ maxima in many urban areas of the southwestern United States, where steady declines in surface O$_3$, which mostly are attributable to VOC and NO$_x$ emission reductions that have been implemented for stationary and mobile urban sources, have been seen since the early 1980s (Lefohn et al., 2010).

Emission inventories for top-down scenarios have estimated that 2.3–7.7% of the O&NG hydrocarbon production in the DJB is vented into the atmosphere (Pétron et al., 2012). This coincides with elevated VOC levels that are dominated by O&NG emissions in the DJB.
Based on VOC speciation and observed atmospheric mole fractions, two recent studies (Gilman et al., 2013; Swarthout et al., 2013) concluded that O&NG-related VOC emissions bear the potential to contribute to regional photochemical O$_3$ production in the NCFR. Gilman et al. (2013) found 55 ± 18% of the VOC-OH reactivity at BAO to be a result of O&NG emissions. Swarthout et al. (2013) reported similar findings from an independent study, that is, that O&NG-associated VOC constituted 57% of the VOC reactivity. While VOC–OH reactivity doesn’t directly translate into ozone production and more comprehensive atmospheric chemistry modeling is needed to calculate the amount of ozone produced from the VOC–OH
chemistry, these estimates nonetheless imply that O&NG VOC emission have a major role in ozone production and bear the potential to contribute to elevated O\textsubscript{3} levels in the NCFR.

Air transport plays a key role in determining O\textsubscript{3} in the NCFR. Wind direction along the Colorado Front Range is characterized by diurnally varying upslope and downslope air flow. Upslope flow is thermally driven by insolation on the eastern slopes of the Rocky Mountains, and is most prominent during the summer months (Johnson and Toth, 1982). Downslope flow arises from cooler air in the mountains descending to lower elevation and is the primary driving force at night.

In this work, we investigate the hypothesis derived from the VOC monitoring studies (Gilman et al., 2013, Swarthout et al., 2013) that O&NG-associated emissions contribute to elevated O\textsubscript{3} by analyzing the climatology of occurrences of elevated O\textsubscript{3} levels in the NCFR. We utilize 4 years of continuous O\textsubscript{3} data from two monitoring sites within the NCFR NAA to investigate the distribution of and source contributions to elevated levels of O\textsubscript{3}. For these analyses we used colocated, respectively nearby wind data for investigating O\textsubscript{3}-air transport relationships. Wind direction data have been shown in other previous studies to be useful for examining atmospheric transport of pollutants on local to regional scales (0–50 km). Three other recent experiments at the BAO investigated relationships between wind direction and concentration changes of a series of O\textsubscript{3} precursor compounds (Pétron et al., 2012; Brown et al., 2013; Swarthout et al., 2013). These studies agreed in identifying elevated levels of light alkanes being transported to the site primarily from the N-SE sectors, which are the upwind sectors where most of the O&NG activities are located. A similar approach was applied by Schade and Roest (2015) in their investigation of VOC and their effect on O\textsubscript{3} formation from shale O&NG fields in Texas. Differentiating observed ethane mixing ratios by local wind direction revealed that ethane levels were highest when winds were blowing from upwind shale regions.

By correlating wind and O\textsubscript{3} data we aim to better characterize the distribution of elevated O\textsubscript{3} levels and to identify O\textsubscript{3} production source areas. O\textsubscript{3} polar histograms were utilized to investigate the relative contribution of source regions to elevated O\textsubscript{3} mole fractions. The South Boulder (SB) and Boulder Atmospheric Observatory (BAO) monitoring sites were chosen because of the availability of high-resolution and high-quality O\textsubscript{3} and wind data, unimpeded fetch, and their east–west alignment, which allowed investigation of the east–west upslope/downslope wind patterns. Both sites show similar seasonality of the annual O\textsubscript{3} cycle (Supplement Figure S1) and trends of the fourth highest annual 8-hr O\textsubscript{3} maximum as other NCFR O\textsubscript{3} monitoring sites (Figure 2) during the time of overlapping records; however, observed yearly O\textsubscript{3} maxima at SB and BAO during recent years have been slightly lower than at the four other sites included in this comparison.

In the following we first evaluate the applicability and regional consistency of surface winds. Wind data were available at higher temporal resolution than trajectory data, allowing a higher time resolution of the analysis. Furthermore, the proximity of the wind measurement and O\textsubscript{3} monitoring was deemed to allow a more direct correlation than use of transport model outputs, particularly as there was uncertainty in the accuracy and spatial resolution of model outputs of near-surface air mass transport in this plains–mountain transition zone and proximity to the eastern slopes of the Rocky Mountains. After the evaluation of the wind observations we investigate the seasonality of O\textsubscript{3} transport in the NCFR, and subsequently focus specifically on the summer season, when photochemical O\textsubscript{3} production is highest.

**Experimental**

**Site locations**

Data considered in this analysis are from two NCFR sites from which colocated, respectively nearby high-quality ozone and wind data were available. The BAO site is operated by the National Oceanic and Atmospheric Administration (NOAA), and the SB O\textsubscript{3} monitoring site is operated by the CDPHE. BAO (40.05° N, 105.00° W) is located north of Denver and within the southwest portion of Wattenberg Field, the largest O&NG field in Colorado (Figure 1). The SB site (39.96° N, 105.24° W) lies to the south of Boulder, northwest of Denver, and
approximately 30 km SW of the Wattenberg Field. Meteorological data are not collected at the SB site; therefore, wind speed and direction data were obtained from the nearby National Center for Atmospheric Research (NCAR) Marshall Field site (39.95° N, 105.20° W), ~3.5 km away. SB is WSW of BAO, placing it downwind of BAO during hours of upslope flow. Neither site is located within a densely populated urban area. For SB, most of the O&NG development is to the N-E, with the nearest wells being some 20 km away. The classification of O&NG influenced upwind sectors is less straightforward for BAO. The site is surrounded by dense O&NG operations in all directions, with the nearest well at ~200 m. However, there are higher abundance and further reaching upwind O&NG activity to the N to SE. For the analyses presented in this paper, we define primary upwind O&NG operation areas to range from 23° to 113° (respectively NNE–ESE) at SB, and 315°–135° (respectively NWN–ESE) at BAO (see sector lines included in Figure 1). Note that these sectors are not exclusively O&NG influenced, but also have variable other various potential emission sources. The Denver metro area ranges from 113° to 158° at SB, and from 158° to 203° at BAO. Population distribution roses in Figure 1 illustrate that while O&NG operations encompass a large region, they also represent lower population density areas.

**Instrumentation**

Commercial ultraviolet (UV) absorption O₃ monitors housed within instrument shelters are used at both sites. Monitors are connected to PFA Teflon sampling lines that are less than 10 m in length. The BAO O₃ monitor takes samples from 6 m and the SB O₃ monitor takes samples from 8 m above ground level, respectively. The SB O₃ monitor is operated via the standard operating procedures found in the CASTNET Quality Assurance Project Plan for the EPA (EPA, 2011). CDPHE O₃ monitors are calibrated against the EPA Region 8 Standard Reference Photometer (SRP) (Golden, CO) in accordance with EPA-600/4-79-056 (Air Quality Assessment Division [AQAD], 1979). O₃ monitors at BAO are calibrated against the National Institute of Standards and Technology (NIST) SRP (Boulder, CO). O₃ precision is reported to be within 1 ppbv, and overall bias against the SRPs is equal/less 1 ppbv.

**Meteorological data**

Meteorological data are recorded at 3 m and 10 m height for the Marshall Field and BAO sites, respectively. Wind speed and direction are recorded at the Marshall Field site using an Abbeon WS600 Ultrasonic Weather Sensor with an accuracy of ±3° for wind direction. At BAO, wind speed and direction are recorded using a Campbell Scientific pop-vane with accuracy of ±4° wind direction.

For a comparison of surface flow patterns of the two O₃ sites with the surrounding area, wind data from eight other NCFR locations were considered. These records were obtained from MesoWest (http://mesowest.utah.edu/). Chosen records were regional airport observations (Figure 1, top), as these were expected to be well-maintained measurements and of good representativeness because of the relatively open and flat surface terrain at these airports. These sites cover approximately an 80 × 100 km area of the NCFR. Median daytime hourly wind speeds during the summer for SB and BAO were 1.8 and 2.5 m s⁻¹, which would correspond to a transport distance in the surface layer of 6–9 km h⁻¹. Even considering that wind speeds will likely be somewhat higher within the mixed boundary layer aloft, the area covered by the MesoWest sites considered for the wind direction analysis for both sites extends well beyond the easterly upwind transport distance during the daytime O₃ production period.

**Data management**

All reported data are available through publically accessible archives from NOAA (ftp://ftp1.esrl.noaa.gov/psd3/bao/Tower/Processed) and the Colorado State Government (http://apcd.state.co.us/report.aspx), except for the Marshall Field meteorological data, which were provided by NCAR. All data sets were converted to and are reported in Mountain Standard Time (MST). Data analyses reported here were conducted while the 75-hr NAAQS was in place, and reported standard exceedances are based on this former threshold. Data considered cover the period from January 1, 2009, through December 31, 2012, for surface O₃, wind speed, and wind direction. Data were reported as 1-hr average for both O₃ data sets and for the wind data from BAO. Wind data provided by NCAR for Marshall Field were reported at 1-min frequency and averaged to the hour; wind direction data were averaged on a 360° circular scale such that the average of 350° to 10° is 0°. Wind speed, wind direction, and O₃ mole fractions were paired for each site. Data points recorded at wind speeds <0.5 m s⁻¹ were excluded from the analysis because of the higher uncertainty in wind direction at low wind speeds. This filter removed 4.4% of the BAO data, including one hourly data point with O₃ above 75 ppbv. For the SB data set, the filter removed 8.9% of data, including 19 hourly O₃ data points above 75 ppbv.
**Results and discussion**

**Evaluation of wind direction data**

The utility of using surface wind data for deciphering air transport was evaluated in two ways:

1. We studied surface wind direction patterns in the NCFR, comparing diurnal flow patterns from the two O₃ sites with eight MesoWest locations. Mean hourly wind direction was calculated for SB, BAO, and the eight comparison sites, using a minimum of 3 years of data for June 1–August 31. Results in Figures 3a and 3b show that SB and BAO have similar diurnal wind direction patterns, with westerly (220–250°, downslope) winds being predominant during night, and NE/E winds (60–90°, upslope) dominating from mid-morning to late afternoon. At SB, located closer to the mountains, that is, ~4 km compared to ~26 km for BAO, the shift between the two flow conditions appears to occur ~2 hr earlier than at BAO. The other NCFR wind direction data (Figures 3c to 3h) show similar features in diurnal wind regimes, with westerly downsloping winds dominating at night, and easterly upslope winds dominating during daytime hours. The consistency in these data is rather remarkable. Between all sites, including SB and BAO, wind direction during night and during midnight to late afternoon generally agrees to within ~30–40°.

2. SB and BAO surface wind data were compared with modeled surface flow trajectories that were computed with the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) using meteorological data at 12 km resolution from the North American Mesoscale model for days when O₃ exceeded 75 ppbv for ≥2 hr (Supplemental Tables S3 and S4 for BAO and SB, respectively). The mean wind direction was calculated (including for the low wind speed cases for <0.5 m s⁻¹) from the site measurements for 15:00–16:00 hr and compared with the mean direction (inferred from a graphical display of the trajectory) of the air transport trajectory for the 15:00 hr back-trajectory for the 1-hr prior to the arrival at the site. The majority of these trajectories corresponded with surface observations and illustrated the upslope wind behavior (Supplement Figures S2 and S3). Of 19 considered high-O₃ days for BAO and SB, 58% and 53%, respectively, of the comparisons yielded agreement between the site-recorded wind direction and the transport direction derived from back-trajectories started at the site to within ±45°. 84% (BAO) and 68% (SB) agreed to within ±90°. Overall, BAO comparisons gave better agreement than SB. There were a number of cases with higher deviation (lower agreement) between the recorded wind direction at the site and the back trajectory path. This finding suggests that while for the majority of the comparisons there was reasonable agreement within these error margins, under certain conditions the back-trajectory model had deficiencies in representing wind conditions that were recorded at the surface. Disagreement could also indicate a change in wind direction in the upwind flow path of the trajectory.

In summary, given the reasonable consistency in the wind direction regimes seen at the considered NCFR sites, we concluded that the local wind data were a suitable indicator, to within a 20–30° error margin (approximate margin of observed afternoon differences in wind direction between the sites; see Figure 3), for the primary direction of air transport. It is noteworthy that winds were most consistent (from NE–E), indicating that the robustness of this analysis is particularly strong, during midday to afternoon, which is the period coinciding with the diurnal O₃ maxima. Furthermore, with fully developed boundary layer heights during the midday to afternoon hours, surface winds during that time are likely to be the most representative of boundary layer transport (in contrast to nighttime, when wind shear above a shallow nocturnal boundary layer can develop). Therefore, below, we particularly focus on the afternoon O₃ versus wind direction relationship.

**Characterization of diurnal flow patterns**

In the summer, wind direction data show a strong diurnal cycle of airflow patterns (Figures 3, 4, and 5). Nighttime winds (20:00–6:00 hr) originate from the SW quadrant at both sites, and shift slightly from the south toward the west as the night progresses. This nighttime downsloping flow indicates that cold air from the mountains drains into the NCFR toward the lower elevations of the Platte River Valley (Figure 1, top). After sunrise there is a shift to upsloping flow from the NNE to SE at BAO, and from the ENE to SE at SB. During the afternoon, the wind direction at SB shifts further to the south, favoring the SE quadrant more than the NE quadrant.
Winds at BAO do not show this pattern and consistently remain from the NNE–SE throughout the hours of sunlight. Interestingly, upsloping winds do not exclusively originate from the lower elevation areas of the Platte River Valley. Rather, upslope flow brings air from all eastern areas of the Front Range.

BAO shows a more distinct predominance of easterly winds than SB. On average, during the summer,
upslope flow conditions occur from 7:00 to 16:00 hr at SB, and 9:00 to 19:00 hr at BAO, while downslope flow occurs from 18:00 to 7:00 hr at SB, and 21:00 to 7:00 hr at BAO (Figure 3). This difference is likely due to the difference in distance to the mountain range between the two sites. The comparison of the Mesonet data shows differences in the timing of the transition between these two predominant flow directions, with further easterly sites lagging by up to 2 hr the further westerly sites. This finding is similar to what was already noted in the SB–BAO comparison. This behavior suggests that in the early morning upslope flow begins close to the mountains along the Front Range and then slowly propagates east. These findings are consistent with the extensive study on surface flows in northeast Colorado by Johnson and Toth (1982). These

Figure 4. Polar histograms representing O$_3$ mole fractions based on wind direction at BAO (top) and SB (bottom). Wind direction frequency is represented by bar length from the circle center, and O$_3$ mole fractions are indicated by the color scale to the right. Concentric circles are spaced at 2% frequency intervals. Boundaries of the oil and natural gas production region sectors are indicated by the dashed blue lines. Data from 2009–2012 are separated into four seasons for each site: fall, winter, summer, and spring (season definition provided in the text) and include observations for all times of the day.
Figure 5. Polar histograms representing \( \text{O}_3 \) mole fractions as dependent on wind direction at BAO (top) and SB (bottom) during summer broken up into four different time windows (MST). Wind direction frequency is represented by bar length from the circle center and \( \text{O}_3 \) mole fractions are indicated by the color scale to the right. Concentric circles are spaced at 2% frequency intervals. Boundaries of the oil and natural gas production region sectors are indicated by the dashed blue lines. Data are divided into four periods of day based around the photochemically active hours of the day and the changes in upslope and downslope flow.
authors, using surface wind data from 20 Mesonet stations for the month of July 1981, determined characteristics of surface flow patterns, and noted consistent surface flow directions within their network, with drainage easterly flow at night, and upslope, westerly flow in the daytime. Similar to our findings, they report that the “donslope-to-upslope and upslope-to-downslope transitions begin at the foothills of the Rocky Mountains and propagate eastward toward the plains.” Notably, and important for interpretations developed in our work, surface flow patterns were the most consistent, in terms of wind direction, during noon to late afternoon.

**Seasonal ozone behavior**

Ambient O3 mole fractions and air mass transport have significant variability throughout the year; therefore, in Figure 4, we report yearly, all-day data separated into four different seasons for the two sites: fall (September 1–November 30), winter (December 1–February 28), spring (March 1–May 30), and summer (June 1–August 31). Each season combines data from all four years, 2009–2012. Data from both sites show a seasonal pattern in surface flows. Wind directions recorded at BAO are dominated by westerly winds during the fall and winter, arriving from SW–WNW. During spring and summer there is a more even distribution of winds from all directions due to the increasing prevalence of upslope flow. Winds arriving at SB are dominated by westerly, downsloping winds throughout the year. During the fall and winter, westerly winds originate from a narrow range between the WSW and WNW. Winds exhibit a wider distribution of directions during the spring and summer. Easterly winds, representing upslope flow, are almost absent at SB during the winter. They account for ~25% of the wind distribution during the summer. Easterly winds occur at BAO ~25% during the winter, increasing to ~50% during the summer. While northerly and southerly winds are not prevalent at either site, they do play a role in air mass transport along the NCFR. Southerly winds arrive from the SSE–SSW at relatively equal frequencies during each season. Northerly winds show some seasonal variation and are more frequently recorded at both sites during the spring.

O3 levels at both sites follow a distinct seasonal cycle with the largest mole fractions recorded in the summer and the smallest in the winter (2011 time series shown in Supplement Figure S1). Westerly winds show an annual pattern with O3 mole fractions that are smallest during the winter, peaking during variable times of the spring and remaining elevated throughout the summer. Transport events bringing elevated O3 levels originating from the upper troposphere/lower stratosphere over the Rocky Mountains are most common in the spring and early summer, and may account for a significant fraction of elevated O3 arriving primarily in downslope air from the west–north seen during these seasons (Langford, 1999; Brodin et al., 2010). O3 mole fractions above 50 ppbv are present in easterly winds at BAO and SB in every season except winter. During the spring and summer, easterly winds, especially from the NNE–SE, contain higher O3 mole fractions compared to other wind directions. O3 above 75 ppbv is most common during summer transport from the NNW–SE and NNE–SE at BAO and SB, respectively. Northerly and southerly winds generally bring lower O3 values than either easterly or westerly winds throughout the year.

**Summer transport and distribution of ozone**

As already discussed, O3 above 50 ppbv is observed throughout the year; however, the summer season, when photochemical activity is at its peak, is responsible for 88% of the O3 values above 75 ppbv. Eight-hour O3 NAAQS exceedances are also most frequent during the summer. In the plains of the NCFR summer O3 shows a dynamical diurnal cycle, with daytime maxima exceeding nighttime minima by 20–60 ppbv (Supplement Figure S1; Brodin et al., 2010). Previous measurements along an elevation gradient have shown that diurnal amplitudes become weaker with elevation, dropping to an average of ~5 ppbv at the ~2000 m higher elevation of the continental divide. This behavior implies that most of the high ozone observed in the NCFR is the result of local production on the same day, and that there is only a minor contribution from transport of high O3 from outside of the region. In the remainder of this section, we focus on O3 behavior during the summer season (June–August). Due to the photochemical nature of O3 production and the diurnal wind characteristics of the area it is useful to assess behavior occurring at different times of day. We first broke up data into day and night, primarily using solar irradiance as the criterion. These periods were based on the motivation to investigate the ozone dependency on the photochemically active hours of the day between sunrise and sunset. Since days are longer than nights at this latitude during summer, this gave us a 14-hr daytime window, and a 10-hr nighttime window. We then split each of these into two equal length periods, giving us four periods total: two 7-hr periods from 06:00 to 13:00 hr and 13:00 to 20:00 hr.
and two 5-hr periods from 20:00 to 01:00, and 01:00 to 06:00 hr. When analyzed on these time periods, BAO and SB exhibit markedly similar characteristics. Figure 5 shows O₃ polar histograms for BAO and SB summer data separated into these times of day. Winds from the NE–SE at SB, and the NNE–SE and BAO, respectively, contain the highest O₃ mole fractions during the day (Figure 5). Besides O₃ mole fractions following a diurnal cycle (Figure 6), they are correlated with certain wind directions. Morning, 06:00–13:00 hr, upsloping winds carry elevated distributions of O₃, frequently exceeding 70 ppbv. Upsloping winds continue to carry increasing O₃ levels west throughout the afternoon, until downsloping winds become dominant. SB shows a rate of 5.2 ppbv hr⁻¹ increase in O₃ during the morning to early afternoon hours. At 5.9 ppbv hr⁻¹ this rate is ~15% higher at BAO (Figure 6). Both of these diurnal cycles are indicative of a steady morning to mid-day ozone increase. This ozone increase is likely driven by two processes: 1) Entrainment of higher O₃-containing air from aloft caused by the growth of the boundary layer depth; and 2) Chemical O₃ production in the region as air is transported from east to west during the morning-afternoon. After the shift from upslope to downslope flow, air containing elevated O₃ flows back east and can be seen in westerly winds during the early evening. At the start of the night, O₃ mole fractions can exceed 50 ppbv at BAO and 60 ppbv at SB. During the night, O₃ levels slowly decrease and by early morning, fall well below these values at both sites.

Figures 7a and 7b present the statistical distribution of O₃ values in box-whisker plot format for afternoon (13:00–20:00 hr) data, categorized by wind sector. At BAO air arriving from the N–E has ~10 ppbv higher O₃ levels (interquartile range) than air arriving from S–W directions. At SB, the directional O₃ gradient is larger than at BAO, with air arriving from the NE–SE containing notably higher O₃ mole fractions than air arriving from other wind sectors. The SB median O₃ in air from ENE is 14 ppb higher than in air arriving from the SSW, which is the sector with the lowest O₃ levels.

**Elevated ozone behavior and local production**

In the following, we narrow our focus to examine only periods of elevated O₃ levels with hourly averages greater than the 75 ppbv NAAQS. Figures 7c and 7d show histograms of hourly-averaged measurements of elevated O₃ with respect to wind direction. Here, we include all data from 2009–2012, including data for winds below 0.5 m s⁻¹. High levels of O₃ are most prominent in the summer season, and specifically during the afternoons. O₃ was above 75 ppbv for 279 hr at SB, and 167 hr at the BAO. Both sites are most frequently impacted by elevated O₃ levels in winds arriving from the NNE–ESE. The majority of elevated O₃ events at SB was measured in wind from the N–SE, and the ENE sector has the largest number of individual elevated O₃ events, with 98 events recorded from this sector alone. Winds from the E–SE (i.e., North Denver) sector account for a total of 58 hr of elevated O₃ events, with far fewer occurrences of elevated O₃ events being transported from central Denver by SSE winds (8 hr total). At BAO, transport from the N-SE sectors accounts for 94 hr of elevated O₃ (56% of total), with the NNW sector being ranked fourth (28 hr, 17% of total). Southerly winds to BAO, which pass over the Denver metropolitan area, rarely contain elevated O₃ levels at any time of the year (Figure 4). O₃ >45 ppbv is

![Figure 6](image.png)  
**Figure 6.** Averaged hourly O₃ values during the summer months, June 1–August 31, at BAO (a) and SB (b). Regression line equations for the average ozone increase (indicated by the solid line), that is, 5.9 and 5.2 ppbv hr⁻¹, reflecting the rate of midmorning to early afternoon O₃ increase, are provided in the top right of each graph. Hours during which upslope flow is primarily present (see Figure 3) are highlighted in peach.
present in these southerly winds, especially during summer afternoons, but $O_3$ tends to generally remain below 65 ppbv. As can be seen from Figure 1, for both sites, the sectors with the highest number of elevated $O_3$ transport hours overlap with the sectors with extensive O&NG operations upwind. Transport from these sectors is the dominant source for elevated $O_3$ events throughout the spring, summer, and fall seasons, accounting for 72% of total hours of elevated $O_3$ levels at SB, and 57% at BAO. In contrast, direct transport from the central Denver sector has a relatively minor contribution to elevated $O_3$ events. There are several possible explanations for the differences seen between the two sites: (1) SB could be further downwind from the $O_3$ producing source region, allowing more time for $O_3$ production in a given air mass, and (2) NOx/VOC ratios may be less favorable for ozone production and/or higher NOx levels at BAO might cause a relatively higher rate of $O_3$ loss from titration with NO during dark hours. Nighttime drainage flows from Denver have been shown in a campaign study to bring increased NOx levels to BAO (Brown et al., 2013).

Unfortunately, there are no available concurrent NOx observations for the data considered in our study to further investigate this speculation.

In 2008 CDPHE conducted an $O_3$ source region analysis using monitoring data from four sites along the NCFR (Fort Collins, Rocky Mountain National Park, Rocky Flats, Highlands Ranch) (CDPHE, 2008b). For elevated $O_3$ events during mid-May to mid-August 2006 observed at these sites, HYSPLIT-back trajectories were calculated for all exceedance hours to investigate the source of the air mass transport. The CDPHE study showed that air transport from the DJB was associated with the highest $O_3$ values, whereas transport from surrounding areas, including the Denver metro area, brought in air with lower $O_3$ levels to the site. These results, relying on observations ~3–6 years prior to the data used in our study, from four different NCFR monitoring sites, and using a different analysis approach, are qualitatively in good agreement with our findings. Both studies identify the DJB as a primary source region for transport of elevated $O_3$ to the NCFR.
While the correlation between high ozone events and easterly transport from the DJB, as well as the high O&NG VOC loading in easterly transport (see below), clearly point towards a major role of DJB O&NG emissions in the occurrence of high ozone episodes, it is possible that emissions from the metro Denver area cause high ozone levels at other sites or further downwind, and that there is additional O$_3$ production in the NCFR from recirculation of emissions during multiday stagnant air flow conditions. Such conditions could not be assessed with the analyses approach used in this study. Ozone and O$_3$ precursor monitoring within the DJB and its periphery, in particular at daytime upwind locations (i.e., on the eastern border of the basin), would be helpful for further investigating these questions.

The DJB contains dense O&NG operations, but also includes a portion of the Platte River Valley. Evening/nighttime downsloping drainage into the Platte River Valley and pooling of emissions from the NCFR and Denver, followed by redistribution of these emissions into the NCFR in upsloping flow the next day, could potentially be a source of O$_3$ production. Recent studies, however, have shown that the dominant atmospheric VOCs in the Wattenberg Field have a strong O&NG, rather than an urban signature: VOC transported from the Wattenberg Field are composed primarily of C$_2$–C$_7$ alkanes, with 72% of ambient ethane to 96% of ambient n-pentane levels in the region attributed to O&NG operations (Gilman et al., 2013). Furthermore, morning (6:00–9:00) VOC data from Platteville, in the center of the Wattenburg Field, show large enhancements of short-chain alkanes associated with O&NG operations and strong correlations of the aromatics benzene and toluene with the O&NG tracer propane (Thompson et al., 2014). If the O$_3$ precursors in this region were the result of advection from, for example, the Denver metropolitan area, one would expect these compounds to show stronger correlations with urban tracers, such as acetylene or ethene. Additionally, average yearly total measured VOC carbon is approximately seven times greater in Platteville than in downtown Denver (Thompson et al., 2014). The findings from these VOC tracer studies demonstrate that air transported in upslope flow from the DJB is dominated by O&NG and not by recycled Denver urban emissions.

The efficiency of O$_3$ production in outflow from O$_3$ precursor source regions is determined by absolute VOC and NO$_x$ concentrations, the VOC/NO$_x$ ratio, and available radicals for facilitating NO to NO$_2$ conversion (Chameides et al., 1992). Due to the lack of concurrent VOC and NO$_x$ observations with the O$_3$ data used here, there is no direct way for assessing ozone production efficiency and relative contribution of VOC versus NO$_x$ in air transported from different sectors. There are numerous studies that have pointed out highly elevated VOC levels from within the DJB and the peripheral area, with several of them relying on data from the BAO (Pétron et al., 2012; Gilman et al., 2013; Swarthout et al., 2013; Thompson et al., 2014). Measurements of NO$_x$ made at BAO during late winter/spring 2011 showed daytime median values of ~1–12 ppbv. NO$_x$ displayed a strong wind direction dependency, with higher median values (>10 ppbv) being transported from the Denver urban corridor, low values from the west (<3 ppbv), and intermediate values (4–8 ppbv) from the N–E sector (Brown et al., 2013). This analysis is supported by satellite studies that show metro Denver to be a higher NO$_x$ source than surrounding areas (Witman et al., 2014). This is much in contrast to the directional analyses of VOC, which showed overall highest VOC levels arriving in transport form the NE sector (Pétron et al., 2012; Swarthout et al., 2013). Speciated VOC analyses showed that combustion tracers were highest in air transported from the south, whereas C$_2$–C$_5$ alkanes, branched alkanes, dimethyl sulfide, and alkyl nitrates were highest in air transported from the NE (Swarthout et al., 2013). These dependencies point out towards higher VOC/NO$_x$ ratios in air transported from the O&NG regions in the NE sectors versus lower VOC/NO$_x$ ratios in air from the Denver urban corridor. The clear tendency toward higher O$_3$ originating from the NE sector suggests that overall O$_3$ is produced at a higher rate, resulting in overall higher ambient O$_3$ mixing ratios, in the higher VOC and higher VOC/NO$_x$ containing air that is transported from the NE O&NG sector than in air transported from the urban corridor.

**Conclusion**

Two recent studies (Gilman et al., 2013; Swarthout et al., 2013) have postulated that the elevated VOC levels in the DJB exhibit significant O$_3$ production potential based upon calculated OH reactivity of observed VOC. The analyses presented here demonstrate that elevated O$_3$ events mostly occur during the photochemically active summer period. Our analyses show that elevated O$_3$ levels in the NCFR are predominantly correlated with air transport from N–ESE, which are the upwind sectors where the O&NG operations in the Wattenberg Field area of the DJB are located. Over the 4 years of 2009–2012, the majority, that is, 65% (mean for both sites) of O$_3$ values above 75 ppbv were recorded in transport originating from upwind DJB sectors. Only 9% of elevated ozone events originated from the Denver metropolitan area. These correlations contribute to mounting evidence that air transport from areas with O&NG fields has a significant impact on elevated ozone and air quality in the NCFR.
Ambient monitoring of VOCs has shown highly elevated ambient mole fractions in the NCFR, and comparisons with historical data suggest a continuing increase in VOC mole fractions and increasing contributions from O&NG emissions (Thompson et al., 2014), while vehicular hydrocarbon emissions have shown steady declines in Denver in recent decades (Bishop and Stedman, 2008). This accumulation of observations suggests that emissions from O&NG operations in the DJB have potentially become an increasing contributor to elevated O₃ in the NCFR NAA over recent years.

Previous approaches for O₃ mitigation in the NCFR have centered on NOₓ controls, relying on the assumption of the Denver metro area being a primarily NOₓ sensitive region (Witman et al., 2014). The abundance of high O₃ transport from the DJB into the NCFR suggests that NOₓ VOC emissions from the DJB play an important role in O₃ NAAQS exceedances in the NCFR. These findings add to other recent research that has demonstrated that O&NG emissions contribute to regional O₃ production and pollution events during the summer (Kemball-Cook et al., 2010; Ahmadi and John, 2015; Mahdi and Kuruvilla, 2015). Recent modeling furthermore suggests that transport and continuing ozone production in outflow from O&NG basins is enhancing surface ozone after multiple days of transport downwind (Helmig et al., 2016; Kort et al., 2016).

Two coordinated multiagency ground and aircraft campaigns, that is, the Front Range Air Pollution and Photochemistry Experiment (FRAPPE), and the DISCOVER-AQ mission conducted during the summer of 2014, have generated new and rich data on O₃ emissions from selected sources in the NCFR. Ongoing analyses of these observations are expected to yield a more accurate description of the spatial distribution, transport, of the diverse sources of VOC and NOₓ, resulting VOC/NOₓ ratios, and ozone production in the NCFR. Atmospheric air quality modeling building on these data is ongoing; outcomes from this modeling will allow further evaluating the conclusions from this study, to improve our understanding of the sources and efficiency of O₃ production, and in directing policy toward the most efficient measures for curbing precursor emissions from selected sources in the NCFR.

Acknowledgments

The authors appreciate the Colorado Department of Public Health and Environment (CDPHE), the National Oceanic and Atmospheric Administration (NOAA), and the University of Utah for providing the publically accessible data at http://apcd.state.co.us/report.aspx, ftp://ftp1.esrl.noaa.gov/psd3/bao/Tower/Processed, and http://mesowest.utah.edu, respectively, that were used in our analyses. We also thank Scott Landolt of the National Center for Atmospheric Research (NCAR) for providing meteorological data from the Marshall Field Site.

Funding

JE thanks the University of Colorado Undergraduate Research Opportunity Project (UROP) for providing a research fellowship grant. DH was in part supported through Front Range Air Pollution and Photochemistry Experiment (FRAPPE) funding provided by CDPHE. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of CDPHE.

About the authors

Jason M. Evans conducted this study in the context of an undergraduate research project. He graduated from the University of Colorado, Boulder, in spring 2016.

Detlev Helmig holds an Associate Research Professor position with the Institute of Arctic and Alpine Research at the University of Colorado, Boulder.

References


