**RESEARCH ARTICLE**

**Boundary layer ozone in the Northern Colorado Front Range in July–August 2014 during FRAPPE and DISCOVER-AQ from vertical profile measurements**


Data from ground-based ozone (O$_3$) vertical profiling platforms operated during the FRAPPE/DISCOVER-AQ campaigns in summer 2014 were used to characterize key processes responsible for establishing O$_3$ profile development in the boundary layer in the Northern Colorado Front Range. Morning mixing from the upper boundary layer and lower free troposphere into the lower boundary layer was the key process establishing the mid-morning boundary layer O$_3$ mixing ratio. Photochemical O$_3$ production throughout the boundary layer builds on the mid-morning profile. From late morning to mid-afternoon the continuing O$_3$ increase was nearly uniform through the depth of the profile measured by the tethersonde (~400 m). Ozonesondes flown on a near daily schedule over a four week period with multiple profiles on a number of days captured the full 1500 to 2000 m vertical extent of O$_3$ enhancements in the mixed boundary layer confirming O$_3$ production throughout the entire boundary layer. Continuous O$_3$ measurements from the Boulder Atmospheric Observatory (BAO) tall tower at 6 m and 300 m showed hourly O$_3$ at the 6 m level $\geq$75 ppb on 15% of the days. The diurnal variation on these days followed a pattern similar to that seen in the tethersonde profiles. The association of high O$_3$ days at the BAO tower with transport from sectors with intense oil and natural gas production toward the northeast suggests emissions from this industry were an important source of O$_3$ precursors and are crucial in producing peak O$_3$ events in the NCFR. Higher elevation locations to the west of the NCFR plains regularly experience higher O$_3$ values than those in the lower elevation NCFR locations. Exposure of populations in these areas is not captured by the current regulatory network, and likely underestimated in population O$_3$ exposure assessments.

**Keywords:** Ozone; Ozone profiles; Northern Colorado Front Range; Oil and natural gas emissions; FRAPPE/DISCOVER-AQ

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**Introduction**

The Northern Colorado Front Range (NCFR) east of the foothills of the Rocky Mountains and north of Denver and its nearby suburbs includes the moderate sized (~100,000) population centers of Boulder, Longmont, Ft. Collins, and Greeley. To the east is the Denver-Julesburg Basin (DJB), a major oil and natural gas production region that also includes significant agricultural and livestock operations. To the west, the Rocky Mountains with a number of 3000 m peaks rise abruptly and contribute to a complex geographical and meteorological regime (Losleben et al., 2000). During summer months, the Front Range and nearby foothills and mountains regularly experience high ozone (O$_3$) episodes that exceed the National Ambient Air Quality Standard (NAAQS). The U.S. EPA classifies the region as an O$_3$ non-attainment area.

During July–August 2014 a multi-institution campaign was carried out to investigate contributors to the high O$_3$ episodes and possible solutions for controlling air pollution in the region. Two major components of the campaign were the Front Range Air Pollution and Photochemistry Experiment (FRAPPE), led by the Colorado Department of Public Health and Environment (CDPHE) and the National Center for Atmospheric Research (NCAR), and a Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) deployment led by NASA. An array of measurement platforms was deployed during the study period that included multiple aircraft, instrumented...
surface sites, mobile instrumented vans, and profiling capabilities using lidar, tethered balloons, release balloons, and a tall tower. Along with an extensive suite of chemical measurements many of the platforms and sites included meteorological parameters as well.

In this paper several vertical profile observing platforms including tethered and free release ozonesondes, a tall tower, and surface sites along a vertical elevation gradient (Figure 1) are used to relate surface $O_3$ observations that are the basis for $O_3$ regulatory actions to $O_3$ dynamics and synoptic transport within the boundary layer. The focus of this study is primarily the NCFR, stretching approximately from Boulder to Ft. Collins and the area to the east. This region (Figure 1) is subject to several $O_3$ precursor sources including urban emissions, agricultural and landfill emissions, and notably oil and natural gas related emissions (Pétron et al., 2012; Thompson et al., 2014; McDuffie et al., 2016; Halliday et al., 2016; Abeleira et al., 2017; Cheadle et al., 2017). Elevated $O_3$ occurrences in the NCFR have been found to be influenced by both local and synoptic meteorology patterns (Toth and Johnson, 1985; Pfister et al., 2017b; Evans and Helmig, 2016).

Meteorological conditions during July and August 2014 were generally typical of those seen during the summer in the NCFR (Toth and Johnson, 1985) with prevailing daytime upslope and nighttime downslope flow (Losleben et al, 2000). On selected occasions closed cyclonic circulations NE of Denver developed under conditions when synoptic frontal system passed through the region (Pfister et al., 2017b). Especially in July several periods of high pressure dominated the region leading to the thermally driven circulation systems noted above. Transport pathways computed from back trajectories reflected both these more local circulations patterns and periods when synoptic scale disturbances dominated.

In this paper profiles of $O_3$ and accompanying meteorological variables are used to investigate the contribution of $O_3$ mixed down into the boundary layer, boundary layer $O_3$ dependence on transport, and the production of $O_3$ within the boundary layer including near the surface. Cases with enhanced afternoon $O_3$ levels ($\geq 75$ ppb) are contrasted with days with minimal afternoon $O_3$ enhancements ($O_3 \leq 65$ ppb).

**Measurement sites**

The continuous measurements of $O_3$ at two heights on the BAO tower tracked $O_3$ vertical profile development over the course of a day. In addition to $O_3$ measurements at 6 m and 300 m, observations of temperature, wind direction, and wind speed were made at 10, 100, and 300 m. As part of FRAPPE, NOAA/GMD operated a tethered ozonesonde system and a NASA GSFC group launched release ozonesondes at a site designated as Ft. Collins West. In conjunction with the DISCOVER-AQ portion of the July–August 2014 campaign, daily, and on some days twice daily, release ozonesondes were launched from a site near Platteville, Colorado. These balloon instruments also measure meteorological parameters including temperature, humidity, wind speed, and wind direction that provide valuable information for interpreting the $O_3$ profiles. $O_3$ was monitored continuously at 10-min time resolution during the 2014 summer at seven surface sites along a $\sim 2000$ m elevation gradient spanning central Boulder (1564 m above sea level (asl)) westward to the Tundra Lab.

![Figure 1: Map of the Northern Colorado Front Range](https://doi.org/10.1525/elementa.345.f1)
Measurement methodologies

All surface O₃ measurements relied on O₃ determination by UV absorption using commercial monitors. Hourly O₃ measurements from the BAO tower followed NOAA/GMD calibration procedures (ftp://aftp.cmdl.noaa.gov/data/ozwv/SurfaceOzone/readmeSO.pdf). Measurements at the sites along the altitude gradient followed a similar protocol (Brodin et al., 2010). The altitude gradient measurements have been shown to well-represent the O₃ vertical profile based on comparisons with ozonesonde measurements from a site near Boulder (Brodin et al., 2011).

The preparation of free release electrochemical concentration cell (ECC) ozonesondes at Platteville and Ft. Collins West followed protocols similar to those used in the NOAA/GMD global ozonesonde network (ftp://aftp.cmdl.noaa.gov/data/ozwv/Ozonesonde/Ozonesonde%20Instructions/). Similar instrumentation was deployed at Ft. Collins and Platteville.

Tethered ozonesondes (referred to here as tethersondes) are adaptations of the same O₃ and meteorological capabilities of free release ozonesondes. The ascent and descent of the measurement package were accomplished with a computer controlled motorized deep sea fishing reel that allowed the balloon to lift the package to a height of ~500 m and then reel the package back in (Figure S1). A set of up and down profiles could be accomplished in ~20 minutes, producing 30–40 profiles in a day.

The ozonesonde package provided a high quality O₃ profile with an uncertainty in the 1 second data of ±1.5 ppb (Sterling et al., 2018). A comparison between the surface O₃ measurement obtained with the tethersonde and the O₃ value from the surface monitor operated by the CDPHE at the Ft. Collins West site shows agreement between the observations (Figure S2) over the full range of mixing ratios sampled with a linear regression slope of 1.03 and R² of 0.99.

Air mass back trajectories

Air mass backward trajectory analyses were done using NOAA’s HYSPLIT atmospheric transport and dispersion modeling system (Stein et al., 2015; Rolph et al., 2017). Eight-hour back trajectories were calculated for Ft. Collins, Platteville, and BAO for selected days at a height of 300 m above ground level (agl) using the North American Model (NAM) 12 km meteorological reanalysis. Ending time was 1:00 PM MDT (all times MDT), and the eight-hour length was chosen to encompass the period of potential photochemical O₃ production including the initial transport of O₃ precursors to the affected sites.

Results

Ozonesonde and tethersonde data

Summer 2014 was not a year with a large number of exceedances of the NAAQS for O₃ in the NCFR (Cheadle et al., 2017). However, there were a number of days with elevated surface O₃ >70 ppb indicative of significant afternoon O₃ enhancement (Cheadle et al., 2017). An overview of vertical O₃ behavior from the surface to 6000 m agl was provided by the daily profiles (on several days multiple profiles) at Platteville (Figure 2). On three days (July 27 and 29, August 3), O₃ in the lowest 2000 m agl was ≥80 ppb. On July 22 O₃ was ~70 ppb in the layer below 2000 m agl at Platteville, but exceeded 85 ppb in the lowest 2000 m layer (Figure 5) at the Ft. Collins site (Sullivan et al., 2015). On the days noted above, as well as several additional days, hourly average O₃ >80 ppb was also measured at the 300 m level at the BAO tower (discussed in the following section).

The vertical O₃ profile and concurrent meteorological observations at Platteville and Ft. Collins include days with minimal boundary layer O₃ enhancements as well as days with significant O₃ production. Typical examples of
days with minimal afternoon $O_3$ enhancement followed by a day with significant $O_3$ afternoon growth were July 21 and July 22 at Ft. Collins (Figure 3) and Platteville (Figure S3). The afternoon $O_3$ mixing ratio at Ft. Collins on July 21 was 50–55 ppb through the lowest 2000 m. On July 22 the late morning profile showed a few ppb less in a 1000–1500 m layer than the afternoon value of the previous day. By later in the afternoon the lower boundary layer $O_3$ mixing ratio had grown to >85 ppb. At Platteville, the pattern was similar (Figure S3), but the afternoon $O_3$ lower boundary layer mixing ratio on July 22 was a more modest 70 ppb, which still represented significant growth over the late morning value of ~55 ppb. At both Ft. Collins and Platteville, back trajectories (Figure S3) ending at 1:00 PM MDT at the 300 m level indicated different air parcel origins on July 21 and 22. On July 21 air parcels originated to the west of each site. On July 22, at Ft Collins air parcels originated to the SE, while at Platteville, the origin was from the N. Profiles on July 27 and 29 at Platteville have similar high afternoon boundary layer $O_3$ (>80 ppb) (Figures 2, S5, and S6).

A similar sequence to that seen on July 21 and 22 occurred in the August 2 and August 3 profiles at Platteville (Figure 4). In the morning profiles there was a shallow layer defined by an inversion at ~500 m agl (right upper panel), constituting a nocturnal stable layer (Stull, 1988), where $O_3$ was <25 ppb. By mid-afternoon on August 2, the near surface layer had $O_3$ of ~60 ppb, similar to the upper boundary layer, the top of which was weakly defined. There was minimal afternoon $O_3$ enhancement in this layer.

On August 3, a day with significant $O_3$ buildup, there were three profiles at Platteville (Figure 4) spread throughout the day. The early morning profile (top panel) had a highly depleted $O_3$ layer near the surface associated with a strong temperature inversion, very similar to what was seen on the previous day. By mid-morning, the low level inversion had disappeared and $O_3$ below 2000 m agl approached the level defined by the layer between the temperature inversions at 2500 and 4000 m agl. By mid-afternoon, a mixed layer (Stull, 1988) with $O_3$ >80 ppb extended from the surface to 2500 km agl. The depth of the enhanced $O_3$ layer on August 3 was similar to that seen on other high $O_3$ days captured in the ozonesonde measurements at Platteville and Ft. Collins (e.g. July 22, 27, and 29). On July 21, at both Ft. Collins and Platteville flow was strongly from the west while on July 22 both sites were
influenced by air parcels to the east of the site (Figure S4). At Platteville, the trajectories on August 2 showed air parcels arriving from the south on the western edge of the oil and gas development area (Figure S7). On August 3 flow from the north and east toward Platteville was primarily over a region of oil and gas related activity (Figure S7).

A detailed picture of lower boundary layer $O_3$ profile development was captured by 30 tethersonde profiles obtained at Ft. Collins on August 3, shown as a height/time cross section in Figure 5 (upper panel). The early morning tethersonde profile at Ft. Collins showed a depleted layer of $O_3$ up to a temperature inversion at ~400 m where $O_3$ is ~60 ppb. The gradual disappearance of the depleted $O_3$ layer likely reflects entrainment from above (Stull, 1988) of higher $O_3$ mixing ratio air until the lower boundary layer (nocturnal layer) achieved the value of the overlaying portion of the boundary layer by ~11:30 AM MDT. During the day $O_3$ increased throughout the layer measured with the tethersonde to >80 ppb. This represents a 20–25 ppb enhancement above the late-morning value of 55–60 ppb.

Selected profiles of the accompanying meteorological observations (Figure 5 – lower panel) show that the erosion of the $O_3$ depleted nocturnal boundary layer was closely tied to warming and destabilizing of the layer as indicated by the potential temperature profiles. Tethersonde observations were made on two other days at Ft. Collins; July 26 (Figure S7) was typical of low peak $O_3$ days with an early morning depleted $O_3$ layer and a mid-afternoon value of ~55 ppb. On August 18 (Figure S8), the pattern was similar to the August 3 case, but with more modest enhancement peak values of 65–70 ppb.

The integrated profile from the surface to 400 m (the level most consistently reached by the tethersonde) showed the buildup through the measured column on July 26 and August 3 (Figure 6). Prior to ~11:00 a.m. the increase each day of 0.10 to 0.15 DU (Dobson units) represented the breakdown of the low level nocturnal inversion and mixing of air from above the inversion into the lower boundary layer (Figures 5, 6 and S8). On July 26 the column $O_3$ increased only about another 0.05 DU before the end of the profiling at 1:30 p.m. after a late morning dip. On August 3 column $O_3$ increased ~0.35 DU by 1:30 p.m. adding an additional 0.35 DU when the 400 m column reached its peak at 3:30 p.m. This enhancement takes place through the entire layer captured by the tethersonde.
During the 4.5 hour period from 11:00 a.m. to 3:30 p.m. the O$_3$ column on August 3 increased from $\sim$1.75 DU to 2.45 DU, representing a 40% increase in this partial column. O$_3$ growth was nearly constant throughout the column during this time period (Figure S10). Based on the boundary layer thickness (2 km) from the ozonesonde data from Platteville (and assuming a similar column thickness of the boundary layer at Ft. Collins of $\sim$2 km, and a constant O$_3$ mixing ratio above 400 m) the full 2 km O$_3$ growth at Ft Collins was $\sim$2.7 DU. Based on the late morning and mid-afternoon profiles at Platteville (Figure 4), the O$_3$ column change at Platteville was similar ($\sim$2.5 DU).

Three weekly time series of hourly average O$_3$ mixing ratios during the FRAPPE/DISCOVER-AQ campaign period were chosen to illustrate O$_3$ behavior at the BAO tower (Figure 7). These three periods (July 20–26, July 27–August 2, and August 3–9) include times discussed earlier in relation to the ozonesonde and tethersonde measurements at Ft. Collins and Platteville.

Notable features of these measurements are the strong O$_3$ loss at the 6 m level during the night into the early morning.

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**Figure 5: Height/Time cross-section of O$_3$ at Ft. Collins West on August 3, 2014.** Height/Time cross-section of O$_3$ mixing ratio from tethersonde profiles at Ft. Collins West on August 3, 2014 (upper panel). Selected meteorological profiles (lower panel). DOI: https://doi.org/10.1525/elementa.345.f5

**Figure 6: Integrated O$_3$ from each profile at Ft. Collins West from tethersonde measurements.** Integrated O$_3$ from each profile at Ft. Collins West from tethersonde measurements on July 26 and August 3, 2014 between the Surface – 400 m (See tabulated data in Table S1). DOI: https://doi.org/10.1525/elementa.345.f6
morning, and two days during each week with high daytime peaks of ~75 ppb at 6 m and >85 ppb at 300 m. On all other days the peak daily hourly average O$_3$ at 6 m was ≤65 ppb.

The average minimum hourly O$_3$ at the surface was 30 ppb lower than at the 300 m level. This O$_3$-depleted layer was observed on nearly all days in July and August 2014. This ubiquitous feature was a likely consequence of O$_3$ reaction with NO, which is expected to dominate over surface deposition (Galbally and Roy, 1980; Bien and Helmig, 2018) as the nighttime sink in the NCFR based on the relatively high NO$_x$ levels in the NCFR (McDuffie et al., 2016; Pfister et al., 2016, Abeleira et al., 2017; https://www.colorado.gov/airquality/report.aspx; http://instaar.colorado.edu/arl/boulder_reservoir.html). Surface O$_3$ sites throughout the NCFR exhibit behavior similar to that seen at BAO (Figure S9) with a morning minimum in O$_3$ (Cheadle et al.,

Figure 7: O$_3$ hourly average mixing ratios at two levels at the BAO. O$_3$ hourly average mixing ratios at two levels (6 m and 300 m) at the BAO for the period July 20–August 9, 2014. DOI: https://doi.org/10.1525/elementa.345.f7
2017; Bien and Helmig, 2018). A surface site located to the east of the NCFR (Pawnee Buttes – Figure S10), where NOx amounts are lower (Pfister et al., 2017a), showed on average 10–25 ppb higher morning minimum O3 than sites to the west (Cheadle et al., 2017), another indication that reaction with NO rather than surface deposition was the primary cause of low morning O3 at BAO.

July 21 and July 22 are examples of the vertical profile structure development from the tower measurements (Figure S12) on a day with a limited afternoon enhancement (6 m peak hourly O3 ~60 ppb), and a day with significant O3 production (6 m peak hourly O3 ~78 ppb). As noted above, these were also days with contrasting O3 daytime enhancements at both Ft. Collins and Platteville (Figures 4 and S3). At BAO, on both days early in the morning there was ~20–25 ppb more O3 at the 300 m level than near the surface. Through the morning the nocturnal temperature inversion weakened. A noticeable difference between these days was the direction of the wind in the late morning and afternoon (Figure S12). On July 21, morning wind direction was westerly becoming more southerly in the afternoon. On July 22, winds shifted by mid-morning from the north to the northeast, and gradually became more easterly through the day. Eight-hour back trajectories at 300 m ending at 1:00 PM MDT for each day (Figure 8 – July 21 and Figure 9 – July 22) support the very different origin of air reaching BAO. On July 21, the air parcels came from the west descending 1000 m in five hours. On July 22, the trajectory began northeast of the BAO and reached the tower from the east.

Comparison of high and low/moderate O3 days
At the 300 m tower level, average early morning O3 mixing ratios for all days in July and August 2014 were ~50 ppb both on days with modest afternoon peaks (~65 ppb at the 6 m level), as well as on days with significant production (peak hourly values ≥75 ppb at 6 m) (Figure 10). In the morning the difference between the upper and lower tower measurements was ~25 ppb, while peak values were ~10 ppb less at the lower level on both high and more modest peak O3 days, reflecting the expected greater O3 loss near the surface at night than aloft. From early to mid-morning, O3 mixing ratios barely changed on both high and low peak O3 days (~2 ppb) at the 300 m level. At the 6 m level, during this period O3 increased 17 ppb and 22 ppb on low and high O3 days, respectively, (Table S2) reflecting the mixing of O3 into the lower boundary layer with the breakdown of the nocturnal stable layer. There was a notable difference between high and low peak O3 days in terms of the late morning to mid-afternoon growth. On low peak O3 days, O3 mixing ratios increased 11–13 ppb (6 m and 300 m), while on high O3 days the increase was 24–29 ppb, more than twice that seen on low/moderate days (Table S2).

Figure 8: Back trajectories on days with low/moderate O3 at the BAO. Back trajectories on days with low/moderate O3 (BAO 6 m peak hourly O3 ≤65 ppb) arriving at the 300 m tower level at 1:00 PM MDT. DOI: https://doi.org/10.1525/elementa.345.f8
The occurrence of high and low \( \text{O}_3 \) days shown in Figure 10 was closely linked to wind direction (Figure 11). On high \( \text{O}_3 \) days, both at 300 m and 10 m winds (\( \text{O}_3 \) measured at 6 m) from the NE to ENE dominate. On lower \( \text{O}_3 \) days, at 300 m preferred directions were from the NNE and ESE, while at 10 m SE and N winds were most frequent. Since high and low \( \text{O}_3 \) days were selected based on \( \text{O}_3 \) at the 6 m level, 300 m \( \text{O}_3 >70 \text{ ppb} \) is observed on a few days categorized as low \( \text{O}_3 \) days.

Trajectories for low/moderate \( \text{O}_3 \) days (Figures 8 and S13) and trajectories for high \( \text{O}_3 \) days (Figures 9 and S14) (all high \( \text{O}_3 \) days were in July), as with the local wind
pattern, showed separation in the transport on low/moderate and high \(O_3\) days. The low/moderate \(O_3\) days were dominated by trajectories with air parcel paths from the W, NW, and S, and in most cases the trajectories spent minimal time over the primary oil and gas region to the NE of BAO. High \(O_3\) days were more often marked by air parcels that originated, or spent several hours immediately before reaching BAO, NE and E to ESE of BAO. On all high \(O_3\) days sky conditions at BAO were clear or only had scattered clouds (NASA, 2014) indicative of potential for photochemical \(O_3\) formation. Low/moderate \(O_3\) days were a mix of sunny and cloudy days. Both meteorological conditions and transport pathways that did not support \(O_3\) formation appear to have contributed to lower peak daily \(O_3\) on low/moderate \(O_3\) days. For example, on July 27, a low peak \(O_3\) day at BAO, the trajectory was very similar to trajectories on July 28 and 29 noted as high peak \(O_3\) days. However, July 27 was a day with cloudy conditions through much of the day.

**Altitude gradient measurements**

Surface measurements along an altitude gradient encompassed an altitude change of ~1950 m from BAO to the Tundra Lab site near the summit of Niwot Ridge (Figure 1). Several days were selected to illustrate conditions with smaller afternoon \(O_3\) enhancements (peak profile hourly average \(\leq 65\) ppb), and days when afternoon peak hourly \(O_3\) was \(\geq 75\) ppb. While the altitude gradient measurements do not represent a vertical profile in the same manner as a profile obtained at a fixed location, it has been shown that they do capture the essential behavior of a profile (Brodin et al., 2011). With the removal of the BAO tower and the relatively infrequent ozonesonde measurements (weekly soundings south of Boulder), the altitude gradient measurements such as those obtained during the summer of 2014 provide a potential source for routine \(O_3\) profile monitoring.

A series of three days when peak \(O_3\) mixing ratios were relatively low (August 7), relatively high (August 8) and moderate (August 9), during July–August 2014 were captured in the profiles along the elevation gradient (Figure 12). At the highest elevation sites, there was a minimal nighttime loss, indicated by the small difference between the early morning and late morning profiles. The highest mid-afternoon \(O_3\) seen in these profiles on high \(O_3\) days was at the mid elevation sites. On August 8, high afternoon \(O_3\) was not seen at the highest elevation locations. The altitude gradient profiles followed the pattern seen at the BAO (Figure 8) and were associated with distinct meteorological conditions. On August 7, westerly flow

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**Figure 11: Polar histograms of hourly \(O_3\) mole fractions based on wind direction.** Polar histograms of hourly \(O_3\) mole fractions based on wind direction between 11:00 AM and 3:00 PM at 300 m and 10 m at BAO on days when peak \(O_3\) at the 6 m level was \(\leq 65\) ppb (45 days) (left panels) and for days when the peak at 6 m was \(\geq 75\) ppb (9 days) (right panels) for July and August 2014. \(O_3\) mole fractions (in ppb) are indicated by color and the percentages represent the frequency of wind coming from a particular direction. DOI: https://doi.org/10.1525/elementa.345.f11
resulted in low \(O_3\) and no daytime growth. August 8 had transport from the S based on the trajectory at BAO, and relatively high \(O_3\). At BAO, August 8 was an intermediate \(O_3\) day, with an \(O_3\) peak hourly mixing ratio of 73 ppb at 6 m, but 86 ppb at 300 m, consistent with the elevation gradient profile. On August 9, generally cloudy conditions provided limited potential for afternoon production. Profiles on several other days (Figure S15) also captured the \(O_3\) buildup at the mid-level sites consistent with the depth of the afternoon boundary layer height measured by the other platforms. On multiple occasions \(O_3\) at these mid-level elevation sites is higher than in the plains. This represents elevated \(O_3\) exposure to populations in the Rocky Mountains foothills, where \(O_3\) is not routinely monitored and considered for regulatory decisions within the State of Colorado surface ozone network.

**Discussion and Conclusions**

\(O_3\) measurements from multiple observing platforms established the characteristics and processes primarily responsible for \(O_3\) profile behavior in the planetary boundary layer (PBL) during the summer of 2014 in the NCFR. The prominent diurnal variation seen in NCFR \(O_3\) profiles in the PBL separated into two distinct temporal and altitude regimes. All measurement platforms observed a large early morning near-surface \(O_3\) deficit relative to the overlaying upper boundary layer and free troposphere. A daily nocturnal stable layer seen between the surface and 200–400 m height gave rise to a prominent diurnal variation with depleted \(O_3\) levels during the night and early morning. The average minimum hourly \(O_3\) at the surface at BAO was 30 ppb lower than at the 300 m level. This \(O_3\)-depleted layer was observed on nearly all days in July and August 2014. This ubiquitous feature was likely a consequence of \(O_3\) reaction with NO.

The replenishment of \(O_3\) in the nocturnal (surface) layer took place during the mid-morning with heating of the surface driving the breakdown of the surface inversion and entrainment of air from above, consistent with other analyses (Kaser et al., 2017). In the PBL above the nocturnal inversion, there was little or no change during the 7:00–10:00 AM time window, an indication that photochemical production of \(O_3\) was not yet a source of \(O_3\) growth. By late morning, \(O_3\) through the PBL was often similar to the free tropospheric \(O_3\) just above the PBL, which based on the ozonesondes at Ft. Collins and Platteville was typically 55–65 ppb.

A second component in the diurnal variation was late morning to afternoon growth of \(O_3\) throughout the PBL. Since the early morning replenishment of the lower boundary layer takes place over several hours, it can be the result of local vertical mixing of air from above as well as transport of air that has been mixed into the boundary layer upwind. The growth through the remainder of the day was dependent primarily on conditions that were favorable for photochemical \(O_3\) formation including transport pathways that tapped into \(O_3\) precursor emissions, and availability of photochemistry promoting solar radiation (lack of cloudiness). By categorizing days at BAO as high \(O_3\) days (peak surface \(O_3\) ≥ 75 ppb) and low/moderate \(O_3\) days (peak surface \(O_3\) ≤ 65 ppb), a strong relationship between daily peak \(O_3\) and air transport to the site was demonstrated. At BAO, on low/moderate \(O_3\) days winds were distributed more widely with some preference for the NNE and SE that suggest more dispersed NCFR precursor sources that could include Denver area urban emissions. Trajectories on low/moderate days demonstrate the variety of conditions leading to lower afternoon peak afternoon \(O_3\). Trajectories representing synoptic conditions dominated by transport from the west to BAO produced
lowest afternoon O$_3$. In a number of cases southerly and southeasterly transport pathways tapped into potential precursor sources, however, it appears that these sources were less likely to lead to high O$_3$ at the NCFR sites investigated here. On the few days of low/moderate peak hourly O$_3$ when the transport path suggested intersection with a potential O$_3$ precursor source to the NE of BAO (e.g. July 27 – Figure S12), generally cloudy conditions likely limited afternoon O$_3$ production. Results from several studies during summer 2014 also found a strong relationship between meteorological conditions and transport characteristics and O$_3$ levels in observed profiles at the Ft. Collins site (Sullivan et al., 2016) and in numerous aircraft profiles (Kaser et al., 2017).

The strong preference for wind directions from the NE coupled with transport paths based on back trajectories during high O$_3$ days suggests that emissions from oil and gas related activities in these upwind sectors could play a prominent role as a source of O$_3$ precursors. On high O$_3$ days, varying paths from the NE and E showed that air parcels immediately before arriving at BAO usually spent several hours in the region of oil and gas development. An analysis of mobile laboratory and fixed site surface observations (Cheadle et al., 2017) found significant enhancements of O$_3$ in the NCFR that on a number of occasions could be linked to emissions from oil and natural gas exploration and processing activities. A recent report (Pfister et al., 2017a) attributed high O$_3$ in the NCFR to both urban and oil and gas activity with urban and oil gas sources contributing in the corridor west of interstate highway 25 and oil and gas emissions dominating northeast of Boulder. Our analyses presented here provide further evidence for the crucial role of oil and gas industry emissions on peak O$_3$ occurrences in the NCFR.

The detailed tethersonde profiles emphasize the O$_3$ production through the PBL with O$_3$ increasing at all altitudes nearly simultaneously, indicating the availability of precursors mixed through the boundary layer. Based on the elevation gradient observations, O$_3$ at higher elevation locations to the west of the NCFR is often higher than at lower elevation NCFR locations. These higher altitude areas currently are not included in the regulatory O$_3$ monitoring network. Therefore, the exposure of populations to O$_3$ in these areas is not well-measured, and likely underestimated, in current population O$_3$ exposure assessments.

The pattern of daily boundary layer O$_3$ development described here was seen from all of the observation platforms and sites in the NCFR studied on both high and low O$_3$ days suggesting that this was an ubiquitous feature of summer time O$_3$ throughout the NCFR. Aircraft measurements of the O$_3$ profile in the NCFR in the summer of 2014 also found many of the characteristics of boundary layer O$_3$ development seen in the ground-based observations (Kaser et al., 2017).

Future work is planned to analyze the BAO longer term record that includes continuous O$_3$, CO$_2$, and CO observations from 2008–2016 from multiple tower levels. In addition, afternoon flask samples were obtained once daily from the 300 m tower level and were analyzed for a number of compounds including CH$_4$ and VOCs. These data will help to further refine the relationship between O$_3$ and possible O$_3$ precursor source regions.

**Data Accessibility Statement**

Ozonesonde data from Ft. Collins and Platteville, tethersonde data, BAO tower ozone data and solar radiation data (used to assess cloudiness), and surface O$_3$ from the sites used for the altitude gradient profiles are available from the FRAPPE/DISCOVER-AQ data archive at https://www-air.larc.nasa.gov/cgi-bin/ArchView/discover-aq-co-2014.

Surface O$_3$ observations at Ft. Collins West and sites shown in Figure S10 are available through the Colorado Department of Public Health and Environment (CDPHE).

**Supplemental files**

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

- **Table S1.** Integrated O$_3$ in DU (Dobson units) for each tethersonde profile at Ft. Collins on August 3 and July 26, 2014 from the surface to 400 m agl. Also shown is the integrated column to 2000 m agl on August 3 based on extrapolating the top of the measured profile using a constant mixing ratio. DOI: https://doi.org/10.1525/elementa.345.s1
- **Table S2.** Tabulation of hourly mean O$_3$ and standard deviation for each hour of the day at the 6 m and 300 m levels at the BAO tower for July–August 2014 on days with low/moderate O$_3$ ($\leq$65 ppb) and high O$_3$ ($\geq$75 ppb) as shown in Figure 12. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S1.** Schematic of the components of the tethersonde profiling system. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S2.** Comparison of measurements from the surface O$_3$ monitor and tethersonde O$_3$ measurements. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S3.** Ozone sondes at Platteville on July 21 and 22, 2014 with O$_3$ and temperature. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S4.** Back trajectories to Ft. Collins West and Platteville on July 21 and 22, 2014. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S5.** Ozone sondes at Platteville on July 27, 2014 with O$_3$ and temperature. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S6.** Ozone sondes at Platteville on July 29, 2014 with O$_3$ and temperature. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S7.** Back trajectories to Platteville on August 3, 2014 arriving at 1:00 PM MDT. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S8.** Tethersonde profiles at Ft. Collins on July 26, 2014. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S9.** Tethersonde profiles at Ft. Collins on August 18, 2014. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S10.** O$_3$ mixing ratios at Ft. Collins West from tethersonde measurements on August 3, 2014. DOI: https://doi.org/10.1525/elementa.345.s1


- **Figure S11.** $O_3$ hourly mixing ratios at selected surface $O_3$ monitoring sites in the NCFR. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S12.** $O_3$ hourly average mixing ratios at two levels at the BAO. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S13.** Back trajectories on days with low/moderate $O_3$ arriving at the BAO. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S14.** Back trajectories on days with high $O_3$ arriving at the BAO. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S15.** $O_3$ profiles at three times during the day based on measurements along an elevation gradient. DOI: https://doi.org/10.1525/elementa.345.s1

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**Competing interests**

The authors have no competing interests to declare.

**Author contributions**

- Contributed to conception and design: SJO, LCC, RCS, DH
- Contributed to acquisition of data: BJJ, PC, EH, AJ, CS, RCS, DH, AMT, AM-B, JTS, TPM, DW
- Contributed to analysis and interpretation of data: SJO, LCC, DH, RCS, AMT, JTS
- Drafted and/or revised the article: SJO, LCC, DH, BJJ, RCS, AMT, JTS, EH
- Approved the submitted version for publication: SJO, LCC, BJJ, RCS, DH, AMT, PC, EH, AJ, CS, AM-B, JTS, TPM, DW

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