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RESEARCH ARTICLE

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

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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 ≥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

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

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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 (≥75 ppb) are contrasted with days with minimal afternoon O_3 enhancements (O_3 ≤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 ~2000 m elevation gradient spanning central Boulder (1564 m above sea level (asl)) westward to the Tundra Lab

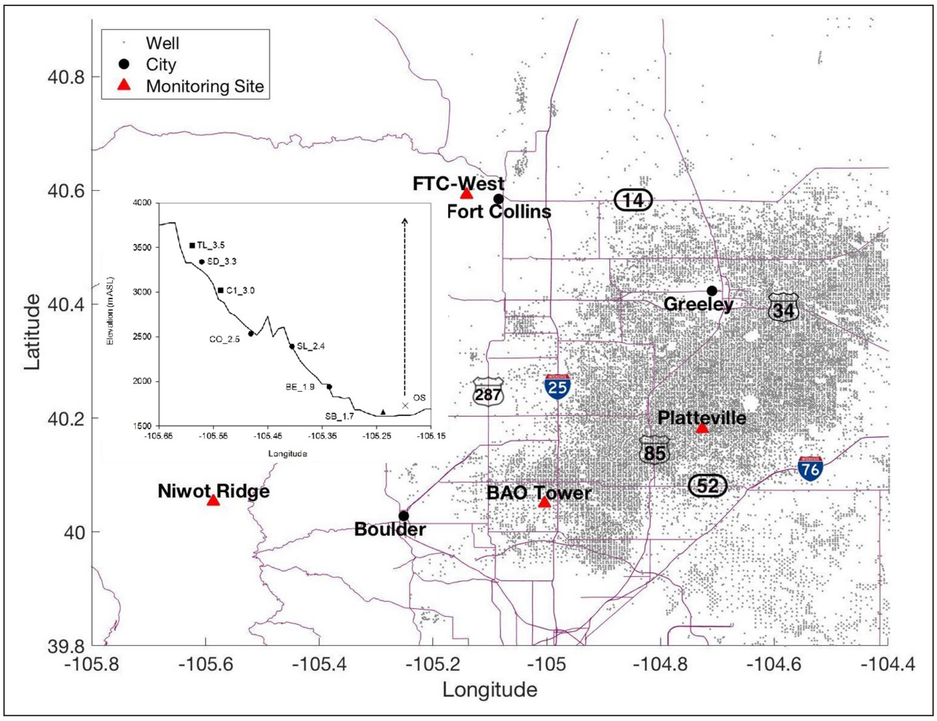

Figure 1: Map of the Northern Colorado Front Range. Map of the Northern Colorado Front Range showing monitoring sites (red triangles), population centers (black dots), and oil and natural gas wells (small gray dots). The inset shows sites along the Colorado Front Range in Boulder County that measured O_3 during this study. Numbers next to the site name indicate the site elevation in km. DOI: https://doi.org/10.1525/elementa.345.f1

at the Mountain Research Station (3528 m asl) (**Figure 1**). These surface observations were used to produce a continuous quasi O_3 vertical profile.

Measurement methodologies

All surface O_3 measurements relied on O_3 determination by UV absorption using commercial monitors. Hourly O_3 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 O_3 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%20 Instructions/). Similar instrumentation was deployed at Ft. Collins and Platteville.

Tethered ozonesondes (referred to here as tethersondes) are adaptations of the same O_3 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 reeled 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 O_3 profile with an uncertainty in the 1 second data of ±1.5 ppb (Sterling et al., 2018). A comparison between the surface O_3 measurement obtained with the tethersonde and the O_3 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 R^2 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 O_3 production including the initial transport of O_3 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 O_3 in the NCFR (Cheadle et al., 2017). However, there were a number of days with elevated surface O_3 >70 ppb indicative of significant afternoon O_3 enhancement (Cheadle et al., 2017). An overview of vertical O_3 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), O_3 in the lowest 2000 m agl was ≥80 ppb. On July 22 O_3 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 O_3 >80 ppb was also measured at the 300 m level at the BAO tower (discussed in the following section).

The vertical O_3 profile and concurrent meteorological observations at Platteville and Ft. Collins include days with minimal boundary layer O_3 enhancements as well as days with significant O_3 production. Typical examples of

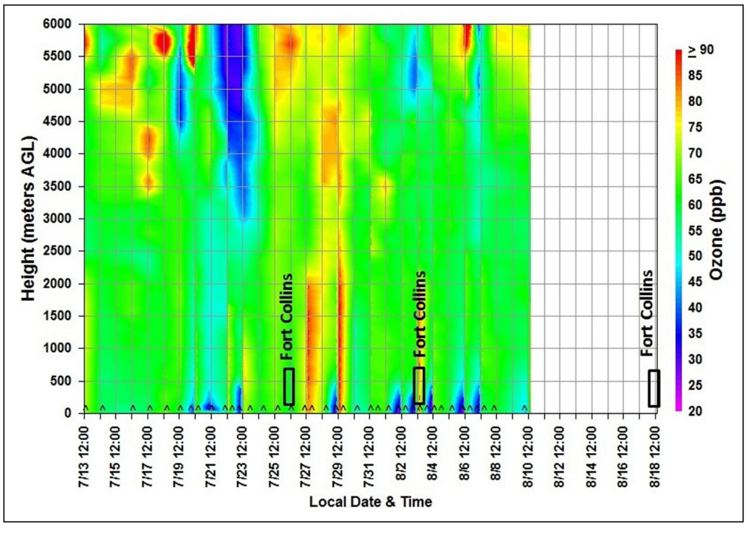

Figure 2: Height/Time cross-section of the O_3 mixing ratio from Platteville ozonesondes. Height/Time cross-section of the O_3 mixing ratio derived from Platteville ozonesondes during the period July 13–August 10, 2014. Days with available tethersonde measurements at the Ft. Collins West site are noted by black boxes. DOI: https://doi.org/10.1525/elementa.345.f2

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

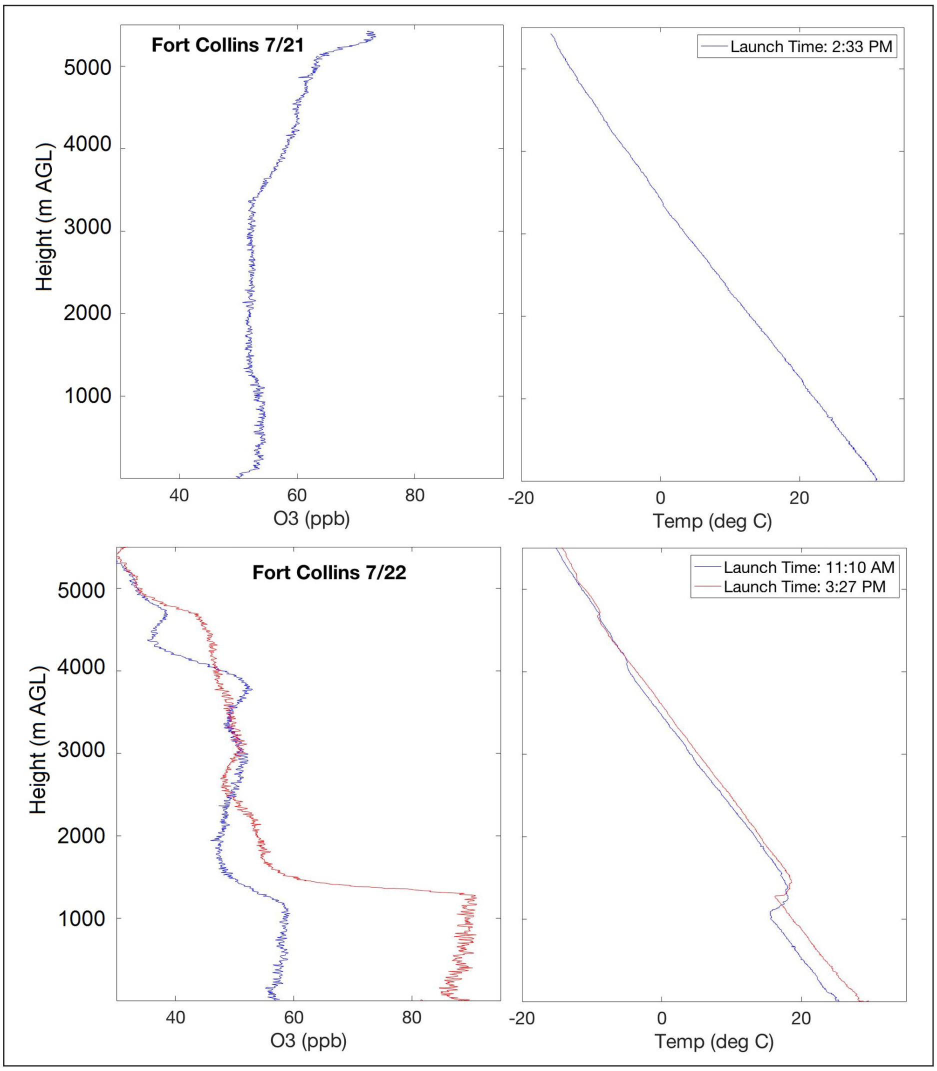

Figure 3: O_3 and temperature profiles on July 21 and 22, 2014 at Ft. Collins. DOI: https://doi.org/10.1525/elementa.345.f3

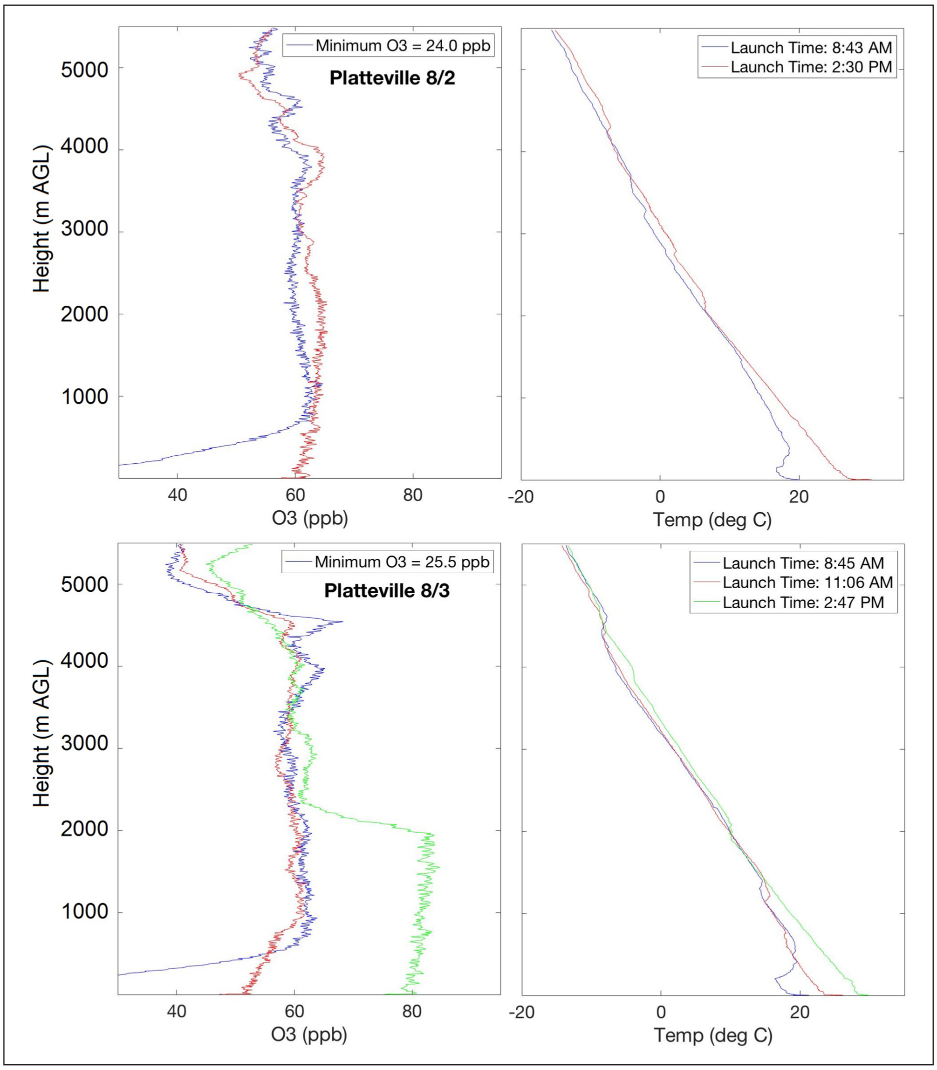

Figure 4: O_3 and temperature profiles at Platteville on August 2 and 3, 2014. DOI: https://doi.org/10.1525/elementa.345.f4

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 peak. 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

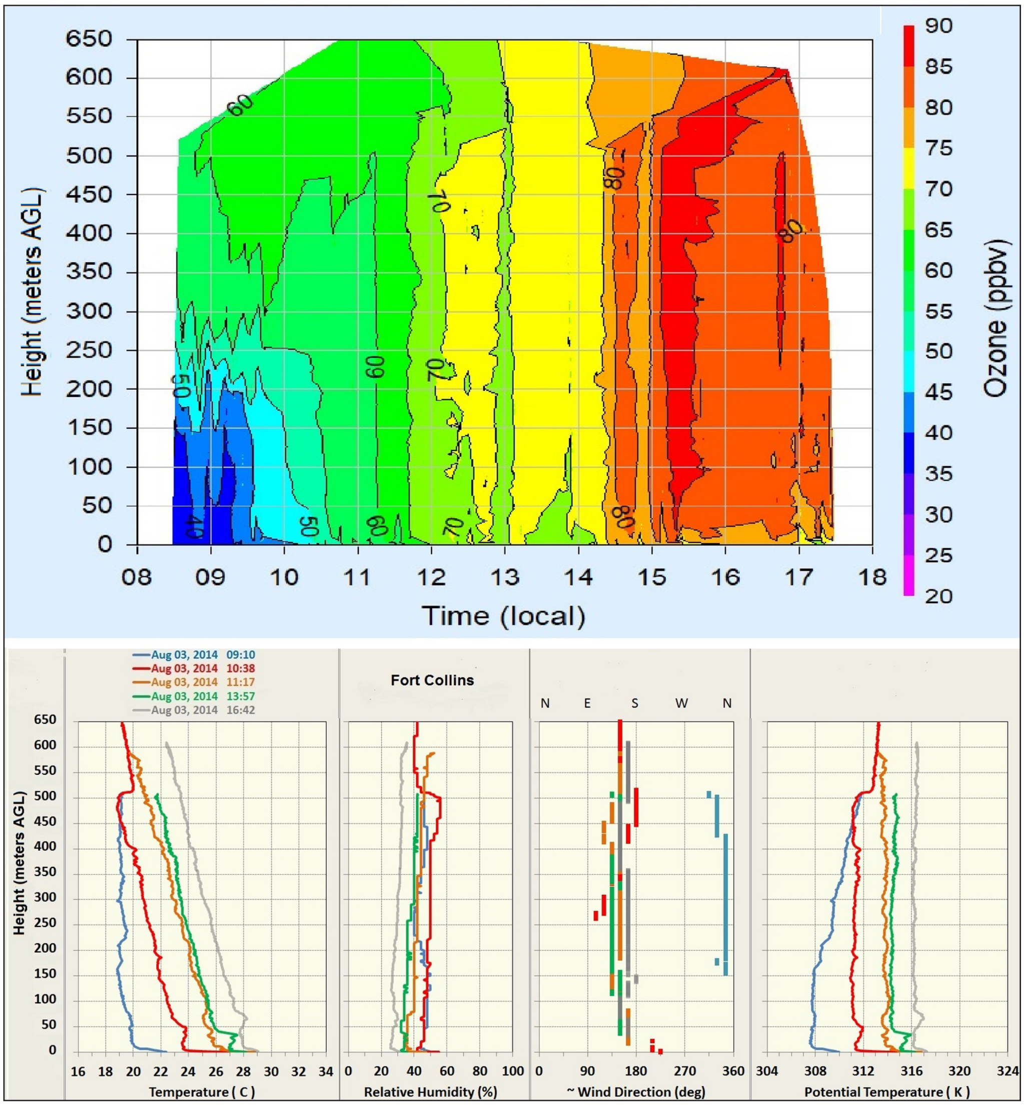

Figure 5: Height/Time cross-section of O_3 at Ft. Collins West on August 3, 2014. Height/Time cross-section of O_3 mixing ratio from tethersonde profiles at Ft. Collins West on August 3, 2014 (upper panel). Selected meteorological profiles (lower panel). DOI: https://doi.org/10.1525/elementa.345.f5

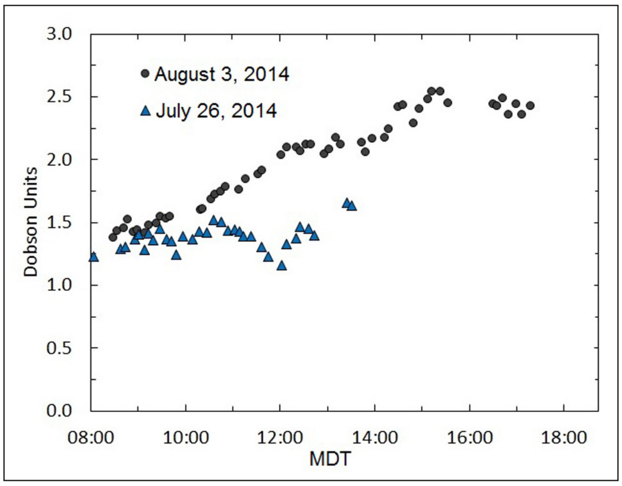

Figure 6: Integrated O_3 from each profile at Ft. Collins West from tethersonde measurements. Integrated O_3 from each profile at Ft. Collins West from tethersonde measurements on July 26 and August 3, 2014 between the Surface – 400 m (See tabulated data in Table S1). DOI: https://doi.org/10.1525/elementa.345.f6

profiles. 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 ~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 ~2 km, and a constant O_3 mixing ratio above 400 m) the full 2 km O_3 growth at Ft Collins was ~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 (~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

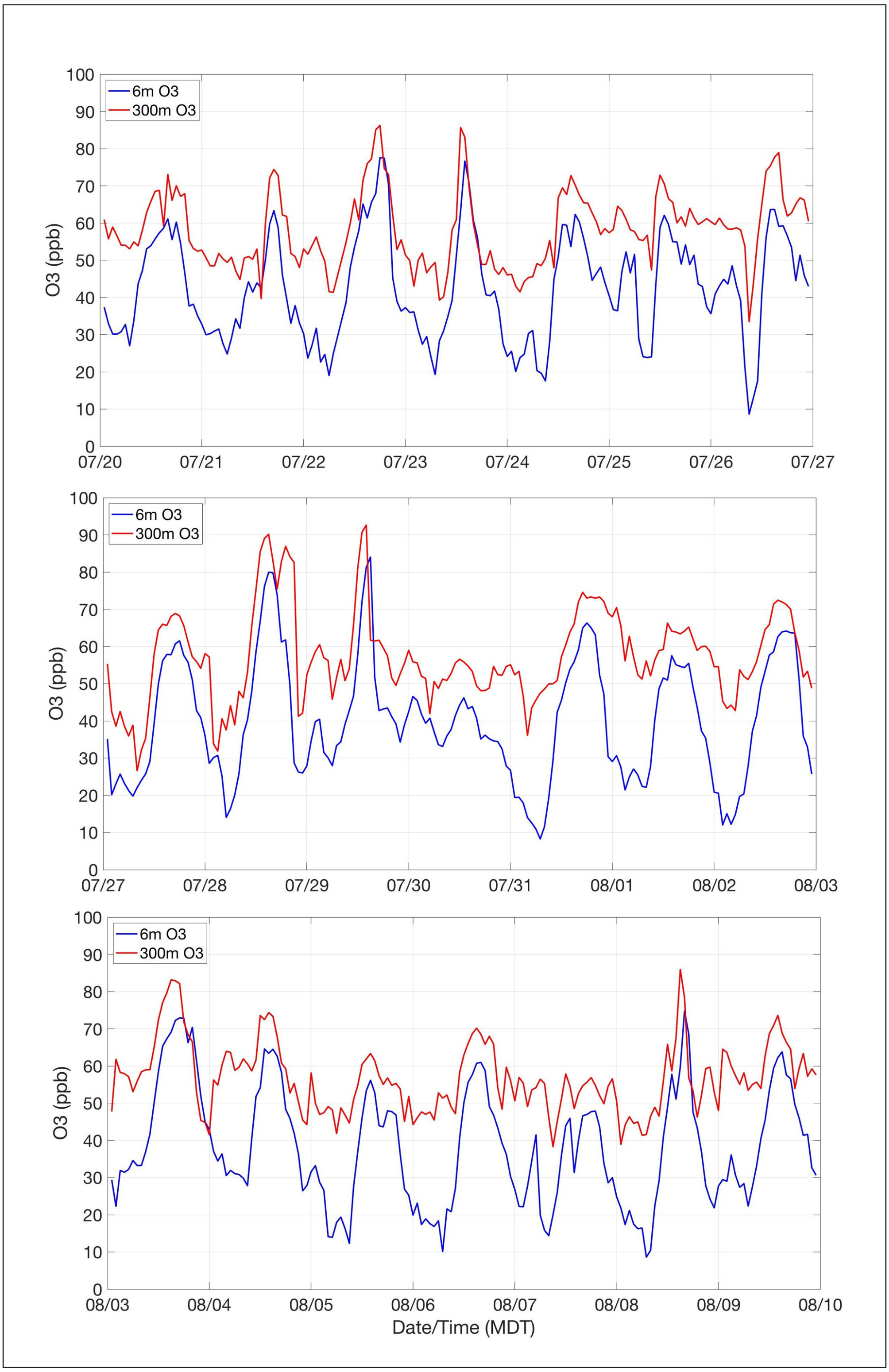

Figure 7: O_3 hourly average mixing ratios at two levels at the BAO. O_3 hourly average mixing ratios at two levels (6 m and 300 m) at the BAO for the period July 20–August 9, 2014. DOI: https://doi.org/10.1525/elementa.345.f7

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., 2017; Bien and Helmig, 2018). A surface site located to the east of the NCFR (Pawnee Buttes – Figure S10), where NO_x amounts are lower (Pfister et al., 2017a), showed on average 10–25 ppb higher morning minimum O_3 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 O_3 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 O_3 ~60 ppb), and a day with significant O_3 production (6 m peak hourly O_3 ~78 ppb). As noted above, these were also days with contrasting O_3 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 O_3 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 O_3 days

At the 300 m tower level, average early morning O_3 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 O_3 days, reflecting the expected greater O_3 loss near the surface at night than aloft. From early to mid-morning, O_3 mixing ratios barely changed on both high and low peak O_3 days (~2 ppb) at the 300 m level. At the 6 m level, during this period O_3 increased 17 ppb and 22 ppb on low and high O_3 days, respectively, (Table S2) reflecting the mixing of O_3 into the lower boundary layer with the breakdown of the nocturnal stable layer. There was a notable difference between high and low peak O_3 days in terms of the late morning to mid-afternoon growth. On low peak O_3 days, O_3 mixing ratios increased 11–13 ppb (6 m and 300 m), while on high O_3 days the increase was 24–29 ppb, more than twice that seen on low/moderate days (Table S2).

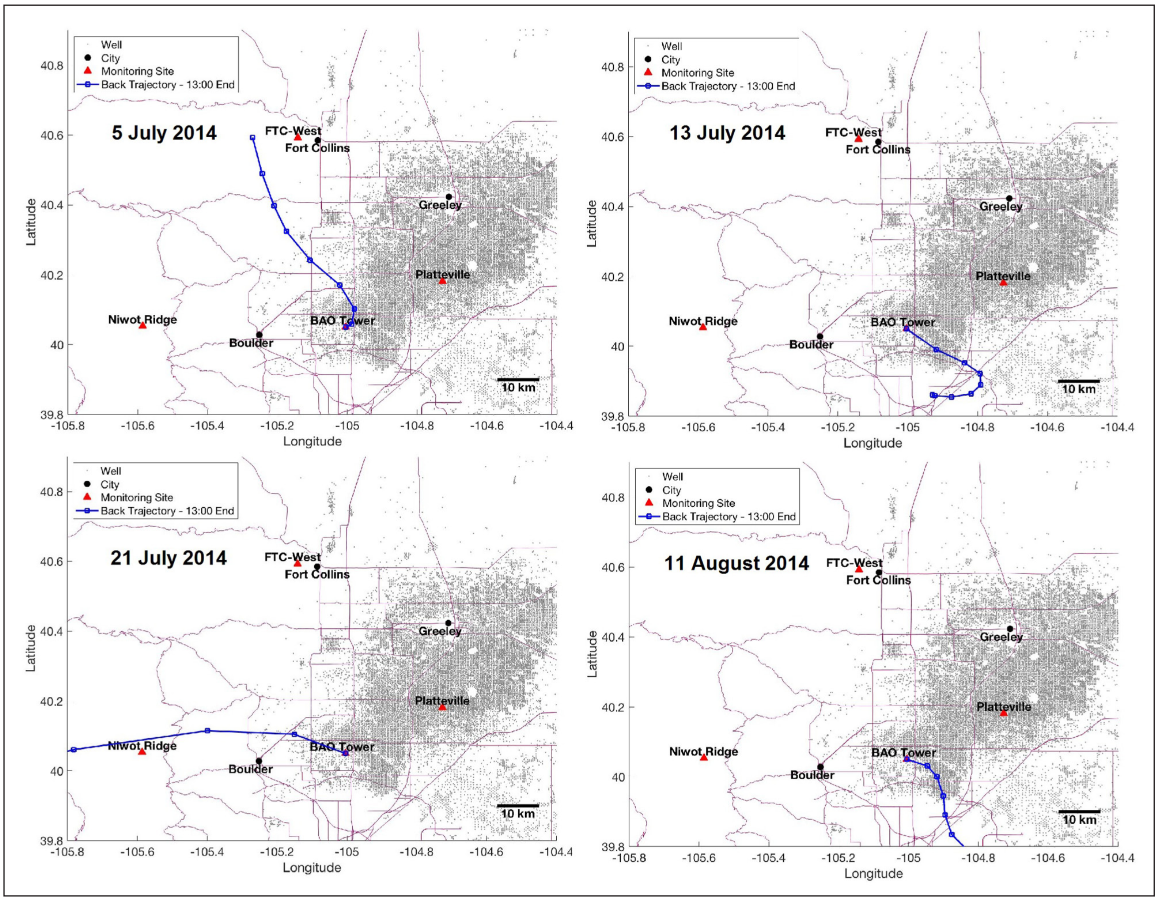

Figure 8: Back trajectories on days with low/moderate O_3 at the BAO. Back trajectories on days with low/moderate O_3 (BAO 6 m peak hourly O_3 ≤65 ppb) arriving at the 300 m tower level at 1:00 PM MDT. DOI: https://doi.org/10.1525/elementa.345.f8

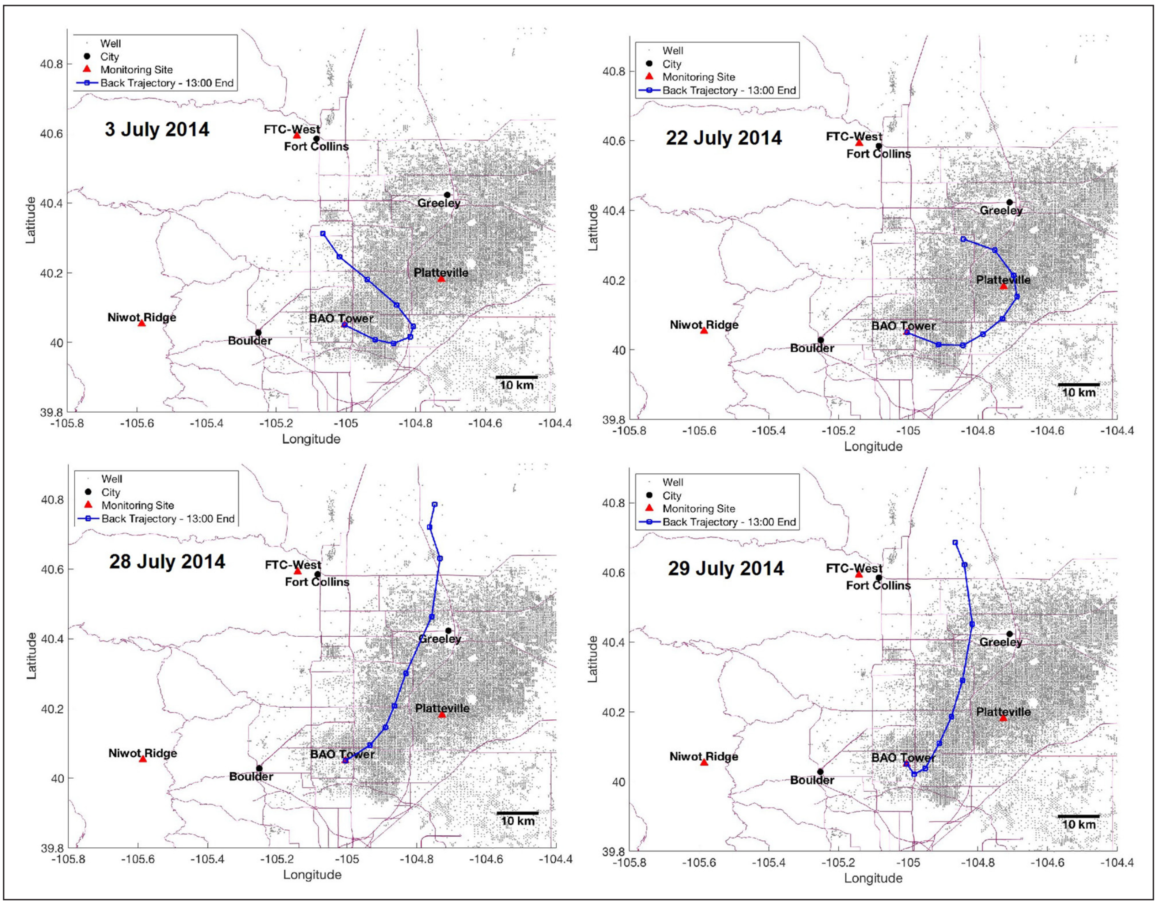

Figure 9: Back trajectories on days with high O_3 at the BAO. Back trajectories on days with high O_3 (BAO 6 m peak hourly O_3 ≥75 ppb) arriving at the 300 m tower level at 1:00 PM MDT. DOI: https://doi.org/10.1525/elementa.345.f9

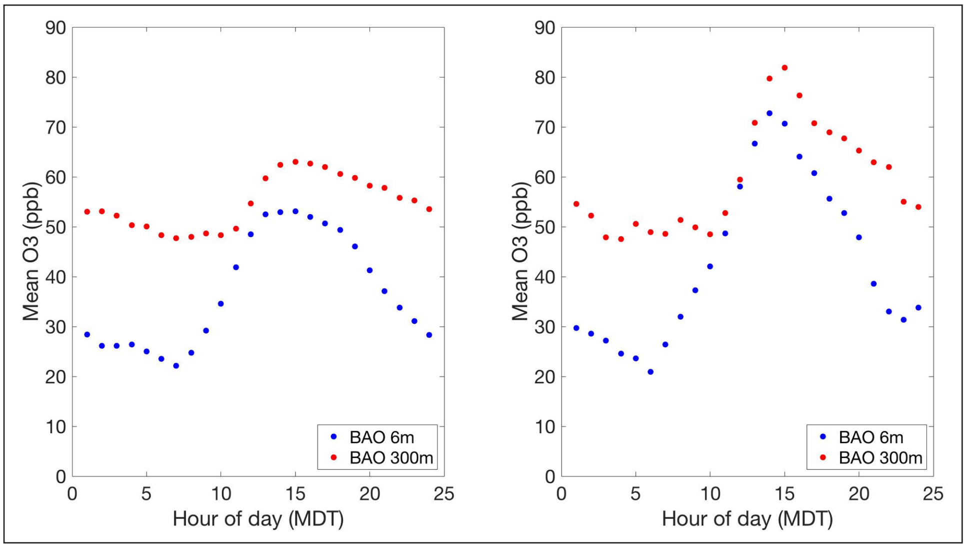

Figure 10: O_3 hourly average mixing ratios at BAO at two levels. O_3 hourly average mixing ratios at BAO at two levels (6 m and 300 m) for each hour for days when peak O_3 at the 6 m level was ≤65 ppb (45 days) (left panel) and for days when the peak at 6 m was ≥75 ppb (9 days) (right panel) for July and August 2014. Numerical values are given in Table S2. DOI: https://doi.org/10.1525/elementa.345.f10

The occurrence of high and low O_3 days shown in **Figure 10** was closely linked to wind direction (**Figure 11**). On high O_3 days, both at 300 m and 10 m winds (O_3 measured at 6 m) from the NE to ENE dominate. On lower 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 O_3 days were selected based on O_3 at the 6 m level, 300 m O_3 >70 ppb is observed on a few days categorized as low O_3 days.

Trajectories for low/moderate O_3 days (**Figures 8** and S13) and trajectories for high O_3 days (**Figures 9** and S14) (all high O_3 days were in July), as with the local wind

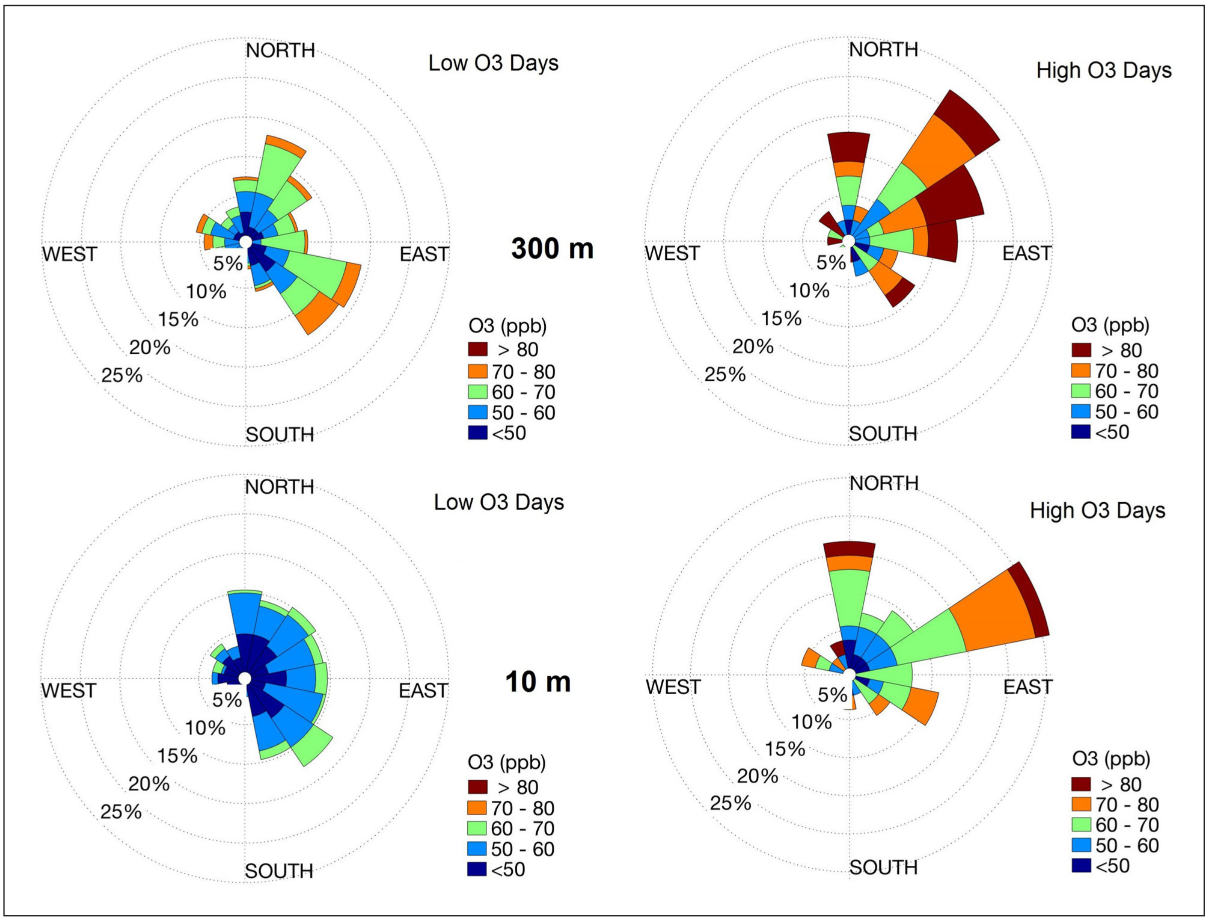

Figure 11: Polar histograms of hourly O_3 mole fractions based on wind direction. Polar histograms of hourly O_3 mole fractions based on wind direction between 11:00 AM and 3:00 PM at 300 m and 10 m at BAO on days when peak O_3 at the 6 m level was ≤65 ppb (45 days) (left panels) and for days when the peak at 6 m was ≥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

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 ≤65 ppb), and days when afternoon peak hourly O_3 was ≥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

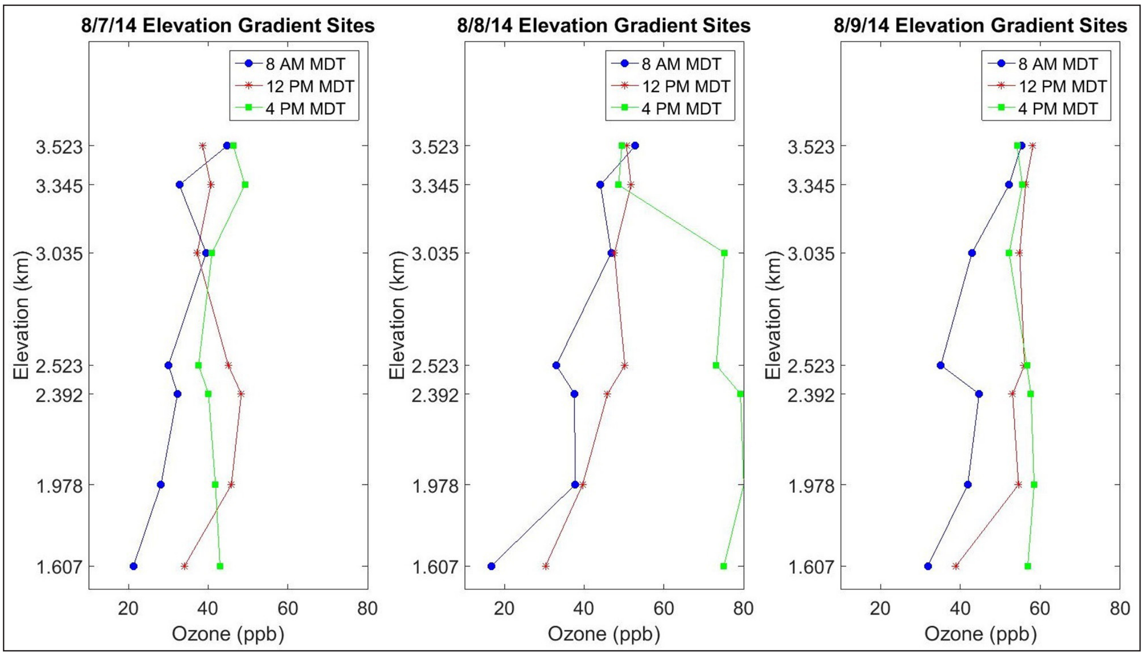

Figure 12: O_3 profiles at three times during the day at surface sites along an elevation gradient. O_3 profiles at three times during the day (8:00 AM, 12:00 AM, and 4:00 PM on August 7, 8, and 9, 2014 based on measurements at surface sites along an elevation gradient. DOI: https://doi.org/10.1525/elementa.345.f12

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 the 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 asses 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/ArcView/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 (≤65 ppb) and high O_3 (≥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.** Ozonesondes 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.** Ozonesondes at Platteville on July 27, 2014 with O_3 and temperature. DOI: https://doi.org/10.1525/elementa.345.s1
- **Figure S6.** Ozonesondes 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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