Summer ozone in the Northern Front Range Metropolitan Area: Weekend-weekday effects, temperature dependences and the impact of drought

Andrew A. Abeleira¹, Delphine K. Farmer¹

1. Department of Chemistry, Colorado State University, Fort Collins, CO, 80523, USA

Correspondence to: Delphine K. Farmer (delphine.farmer@colostate.edu)

Abstract. Contrary to most regions in the U.S., ozone in the Northern Front Range Metropolitan Area (NFRMA) of Colorado was either stagnant or increasing between 2000 and 2015, despite substantial reductions in NOx emissions. We used available long-term ozone and NOx data in the NFRMA to investigate these trends. Ozone increased from weekdays to weekends for a number of sites in the NFRMA with weekend reductions in NOx at two sites in downtown Denver, indicating that the region was in a NOx-saturated ozone production regime. The stagnation and increases in ozone in the NFRMA are likely the result of (1) decreasing NOx emissions in a NOx-saturated environment, and (2) increased anthropogenic VOC emissions in the NFRMA. Further investigation of the weekday-weekend effect showed that the region outside of the most heavily trafficked Denver area was transitioning to peak ozone production towards NOx-limited chemistry. This transition implies that continued NOx decreases will result in ozone being less sensitive to changes in either anthropogenic or biogenic VOC reactivity in the NFRMA. Biogenic VOCs are unlikely to have increased in the NFRMA between 2000 and 2015, but are temperature dependent and likely vary by drought year. Ozone in the NFRMA has a temperature dependence, consistent with biogenic VOC contributions to ozone production in the region. We show that while ozone increased with temperature in the NFRMA, which is consistent with a NOx-saturated regime, this relationship is suppressed in drought years. We attribute this drought year suppression to decreased biogenic isoprene emissions due to long-term drought stress.

1. Introduction

Tropospheric ozone (O3) is detrimental to human health, impacting asthma attacks, cardiovascular disease, missed school days, and premature deaths. Based on these impacts, the Environmental Protection Agency (EPA) projects that reducing the O3 standard to the new 70 ppb, 8-hour average will result in health benefits of $6.4-13 billion/yr (EPA, 2014). O3 also damages plants, reducing agricultural yields (Tai et al., 2014). Using crop yields and ambient O3 concentrations for 2000, Avnery et al. (2011) estimate the loss of $11-18 billion/yr worldwide as a result of the reduction of staple worldwide crops (soybean, maize, and wheat) from O3 damage. During summer months, the Northern Front Range Metropolitan Area (NFRMA) of Colorado consistently violated the pre-2016 U.S. EPA National Ambient Air Quality Standard (NAAQS) of 75 ppb, fourth-highest daily maximum 8-hour average (MDA8) ambient O3 concentration, despite proposed reductions in anthropogenic emissions (CDPHE, 2014). The NFRMA has been an O3 non-attainment zone since 2008 (CDPHE, 2009), prompting the Colorado Air Pollution Control Division and the Regional Air Quality Council to develop the Colorado Ozone Action Plan in 2008 to target key O3 precursors: volatile organic compounds (VOCs) and NOx (NO+NO2)(CDPHE, 2008). Despite these control efforts, 2013 was the NFRMA’s fourth year in a row to exceed the federal O3 standard (CDPHE, 2016), and the eight NFRMA non-attainment counties, with their combined population >3.5 million, exceeded the MDA8 75 ppb, O3 standard 9-48 days between 2010 and 2012 (AMA, 2015). However, Colorado must comply with the new 70 ppb, MDA8 standard by 2018. In order to accurately design and implement O3 reduction schemes, a thorough understanding of local O3 trends and chemistry is required.

Ground-level or boundary layer O3 depends on local production, transport, and meteorological parameters:

\[
\frac{\partial [O_3]}{\partial t} = P(O_3) + \frac{w_o [O_3] - u_d [O_3]}{H} - \nabla \times \left[ \nu [O_3] \right] \quad (1)
\]

where \(\partial [O_3]/\partial t\) represents the time rate of change of O3 concentration, \(P(O_3)\) is the instantaneous net photochemical O3 production rate (production – loss), \(w_o [O_3] - u_d [O_3]/H\) represents the entrainment rate (\(w_o\)) of O3 in and deposition...
rate \( u_d \) of O\(_3\) out of the mixing layer height \( H \), and \( \nabla \times (\vec{v} \cdot \vec{O}_3) \) describes the advection of O\(_3\) mixing layer height.

Briefly, ground-level O\(_3\) is driven by a catalytic chain that is initiated by RO\(_2\) production from VOC oxidation (R1), and propagated by local NO\(_x\) emissions (R2,3).

\[
\text{RH} + \text{OH} + \text{O}_2 \rightarrow \text{RO}_2 + \text{H}_2\text{O}
\]

Chain propagation occurs through reactions between HO\(_2\) or RO\(_2\) radicals with NO to form NO\(_2\) (R2a,b, R3), which is photolyzed (R4) and leads to net O\(_3\) formation (R5). Reactions between NO and O\(_3\) also produces NO\(_2\) (R6), leading to a null cycle with no net O\(_3\) production. Alkox (RO) radicals form carbonyl-containing compounds and HO\(_2\) (R7).

\[
\begin{align*}
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RONO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O}(^1\text{P}) \\
\text{O}(^1\text{P}) + \text{O}_2 & \rightarrow \text{O}_3 \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{RO} + \text{O}_2 & \rightarrow \text{R}^*\text{CHO} + \text{HO}_2
\end{align*}
\]

For every VOC that enters the cycle, approximately two NO\(_2\) radicals are produced – but the resulting carbonyl-containing compounds and organic nitrates can be repeatedly oxidized or photolyzed, further propagating the P(O\(_3\)) chain. Chain termination occurs through RO\(_2\) and HO\(_2\) self-reactions to form peroxides (dominant termination reactions in the “NO\(_x\)-limited regime”), OH and NO\(_2\) reactions to form HNO\(_3\) (“NO\(_x\)-saturated” or “VOC-limited” regime), or RO\(_2\) and NO\(_x\) reactions to form organic nitrates (RONO\(_2\)) or peroxyacyl nitrates (RC(O)O\(_2\)NO\(_2\)). Formation of organic and peroxyacyl nitrates suppresses P(O\(_3\)), but does not shift the cross-over point between NO\(_x\)-limited and NO\(_x\)-saturated P(O\(_3\)) regimes (Farmer et al., 2011). This cross-over point of maximum, or peak, O\(_3\) production is controlled by the chain termination reactions, and is sensitive to the HO\(_2\), production rate and thus VOC reactivity. Decreasing NO\(_x\) is an effective O\(_3\) control strategy in a NO\(_x\)-limited system, but will increase O\(_3\) in a NO\(_x\)-saturated system. Controls for NO\(_x\)-saturated systems often focus on reducing anthropogenic VOC reactivity, and/or suppressing NO\(_x\) emissions sufficiently that the system becomes NO\(_x\)-limited.

Trends in O\(_3\) for 2000 – 2015 varied across the United States (EPA, 2016a). Using the annual 4th maximum of daily 8-hour averages (MDA-8), the EPA reported a 17% decrease in the aggregated national average O\(_3\). However, regional trends deviated substantially from the national average. For example, the EPA reported a 25% decrease in O\(_3\) throughout the southeast, while the northeast shows a 16% decrease. Smaller decreases in O\(_3\) occurred in the northern Rockies (1%), the southwest (10%) and the west coast (4-10%). These O\(_3\) reductions are concurrent with national reductions in O\(_3\) precursors of 54% for NO\(_x\), 21% for VOCs, and 50% for CO (EPA, 2016b). Due to the non-linear behavior of O\(_3\) chemistry described above, reductions in O\(_3\) precursors do not necessarily result in reductions of ambient O\(_3\). Cooper et al. (2012) reported that 83%, 66%, and 20% of rural eastern U.S. sites exhibited statistically significant decreases in summer O\(_3\) at the 95th, 50th, and 5th percentiles (1990-2010). No increases in O\(_3\) occurred at any sites, indicating that local emission reductions have been effective in those regions. In contrast, O\(_3\) in the western US followed a very different trend: only 8% of western U.S. sites exhibited decreased O\(_3\) at the 50th percentile; the 5th percentiles for O\(_3\) at 33% of the sites actually increased. These increases were larger for the lower percentiles, indicating that while local emissions reductions may have been effective at some sites, increased background O\(_3\) offset the improvement.

Lefohn et al. (2010) found that O\(_3\) decreased across many U.S. sites at a less rapid pace during 1994-2008 than during 1980-2008, indicating that O\(_3\) improvements had leveled off by the late 2000s. The leveling off could be a result of either slowed precursor emissions reductions, which is contrary to the EPA estimates, or, more likely, shifting O\(_3\) chemistry regimes as precursor emissions are changing. Lefohn et al. (2010) reported that the distributions of high
Cooper et al. (2012) showed that the intermountain West is an intriguing environment with potentially increasing background O₃. The NFRMA is of particular interest due to the challenge in effective O₃ regulation, its growing population and the dominantly anthropogenic sources of O₃ precursors. VOCs have been well-studied in the region, with a particular focus on the Boulder Atmospheric Observatory (BAO) in Erie, CO (e.g. Gilman et al., 2013; McDuffie et al., 2016; Pétron et al., 2012; Swarthout et al., 2013; Thompson et al., 2014). VOC composition in the NFRMA was heavily influenced by oil and natural gas (ONG) sources, as well as traffic. In winter 2011, ~50% of VOC reactivity was attributed to ONG-related VOCs and ~10% to traffic (Gilman et al., 2013; Swarthout et al., 2013). Recent studies have shown that ONG and traffic contributed up to 66% and 13% of the VOC reactivity respectively at BAO in mornings for both spring and summer 2015, but that biogenic isoprene was a large, temperature-dependent component of VOC reactivity in the summer, contributing up to 49% of calculated daytime VOC reactivity (Abeleira et al., 2017). We note that the anthropogenic VOCs were typically lower in 2015 than previous measurements, pointing to the complex roles of meteorology, transport and local emissions. In contrast, observed isoprene in summer 2012 was much lower than previous years, which may be due to shifting drought conditions. While temperatures across the two summers were similar, 2012 was a widespread drought year in the region, and 2015 was not; drought is typically associated with suppressed biogenic VOC emissions. Local anthropogenic and biogenic sources are not the only VOC sources in the region: longer-lived VOCs consistent with transport have also been observed (21-44% of afternoon reactivity in 2015), and smoke from both local and long-distance wildfires impacted air quality in the NFRMA in punctuated events. This smoke was sometimes, but not always, associated with elevated O₃ (Lindas et al., 2017).

The impact of a changing climate on air quality is poorly understood due to the complex climate-chemistry interactions and numerous feedbacks. Jacob and Winner (2009); Palut and Canziani, (2007). However, increasing temperature is expected to increase O₃ (Bloomer et al., 2009; Jacob and Winner, 2009; Palut and Canziani, 2007). The O₃-temperature relationship is attributed to (1) temperature-dependent biogenic VOC emissions that provide a source of VOCs for OH oxidation leading to increased HO₂ cycling (Guenther, 2006; Guenther et al., 1996), (2) thermal decomposition of peroxyacetylnitrate (PAN) to HO₂ and NO₂ (Fischer et al., 2014; Singh and Hanst, 1981), and (3) increased likelihood of favorable meteorological conditions for ozone formation (i.e. high insulation, stagnation, circulating wind patterns) (Reddy and Pfister, 2016; Thompson et al., 2001). In addition, increased temperatures and changing soil moisture could alter soil emissions of NOₓ. Due to the non-linearity of P(O₃) chemistry as a function of NOₓ, the increased VOC and NOₓ emissions associated with warming can either increase or decrease P(O₃) depending on local NOₓ concentrations (i.e. NOₓ-limited vs. NOₓ-saturated). Interactions between climate change and regional-scale meteorology are complex, and may also impact O₃. High and low O₃ in the U.S is coupled to a variety of meteorological parameters including planetary boundary layer (PBL) heights (White et al., 2007; Reddy and Pfister, 2016), surface temperatures (Bloomer et al., 2009), soil-moisture and regional winds (Davis et al., 2011; Thompson et al., 2001). PBL height is coupled to increased temperatures, reduced cloud cover, stronger insolation, and lighter circulating wind patterns with higher 500 hPa heights correlating to higher average July O₃ in the NFRMA (Reddy and Pfister, 2016).

In this paper, we used temperature, O₃, and NO₂ data from 2000-2015 at multiple sites in the NFRMA to investigate why O₃ has not decreased in the region despite decreases in NOₓ. We used a weekday-weekend analysis to elucidate the NOₓ regime for P(O₃) in Denver, and explored the temperature dependence of O₃ and the role of drought in influencing that relationship in the NFRMA.

2. Methods

2.1 Measurement sites

We used publicly available O₃, NO₂ and temperature data (https://aqs.epa.gov/aqswqdocs/data_mart_welcome.html) from eight sites in the NFRMA (Fig. 1, Table 1). The CAMP site is 1 mile east of the I-25 interstate highway in downtown Denver. O₃ data was available for 2005–2007 and 2012–2015, while NO₂ data was...
available for 2001 – 2007 and 2010 – 2015. Welby is roughly 8 miles northeast from the CAMP site, and is adjacent
to a large lake and less than 1-mile west of the Rocky Mountain Arsenal open space. O3 data was available for 2000 –
The Carriage site is <1 mile west of the I-25 interstate at the same latitude as the CAMP site. O3 data was available
for 2000 – 2012 for the Carriage site. The Fort Collins site is adjacent to Colorado State University near downtown
Fort Collins. O3 data was available for 2000 – 2015. The Greeley site was located on the southeast side of Greeley and
<1 mile south of CO state highway 34. O3 data was available for 2002 – 2015. The Rocky Flats site is in a rural area
adjacent to the Rocky Flats Wildlife Refuge <15 miles south of Boulder. The I-25 site is adjacent to the I-25 interstate
2-miles south of the Carriage and CAMP sites, and intercepts fresh NO3 emissions directly from the I-25 interstate.
NO2 data was available for 2015, but not O3. The La Casa site is <1 mile west of the I-70 and I-25 interstate junction.
O3 and NO2 data were available for 2015. Temperature data was available for all sites for all years.
2.2 Ozone and NO2 data treatment
Ambient NO2 concentrations were measured by chemiluminescence monitors equipped with molybdenum oxide
converters. These monitors are used as the EPA Federal Reference Method for monitoring ambient NO2
concentrations, and have a known interference from nitric acid and organic nitrates (Dunlea et al., 2007). The true
ambient NO2 mixing ratio is a component of the reported values. NO2* will be used in this manuscript to refer to the
EPA NO2 measurements, which includes the interference, and can be considered to be a proxy for total reactive
nitrogen oxides (NOx). While the absolute NO2* concentration will be greater than NO2 but less than NOx, trends in
NO2* provided insight on trends in local NO3 emissions. The O3 and NO2* mixing ratios are filtered to summer months
(June 1 – August 31), and averaged to a daytime value (10:00 am – 4:00 pm local). A site was excluded for a given
year when <50% of data is available for that summer.
2.3 Trend analysis
Following the analyses of Cooper et al. (2012), the statistical significance of the linear trends were tested with a
standard F-test with the null hypothesis that there is no linear trend (R2 = 0). The null hypothesis was rejected with a
confidence level ≥ 95% if the probability (p) associated with the F-statistics was low (p ≤ 0.05).
3 Results and Discussion
3.1 Long term trends in O3 and NO2* in the Northern Front Range Metropolitan Area
Contrary to most other places in the U.S., O3 in the NFRMA was either stagnant or increasing between 2000 and 2015,
despite substantial decreases in NOx emissions. At most sites in the eastern U.S. and some on the west coast, O3 was
decreasing at all percentiles. In the NFRMA, however, five out of six monitoring sites exhibited no change or
increasing O3 at the 50th and 95th percentiles in the 2000 – 2015 period (Fig. 2). The 5th percentile is often taken as
background O3. With the exception of the Greeley site, the 5th percentile of O3 increased across the NFRMA between
2000 and 2015. However, only the downtown Denver CAMP site had statistically significant increases in O3 of 2.6 ±
0.9, 2.3 ± 0.3, and 1.8 ± 0.7 ppb/yr for the 5th, 50th, and 95th percentiles, respectively. The Welby site had increases of
1.5 ± 0.5, 1.3 ± 0.4, and 1.4 ± 0.4 ppb/yr from 2000 – 2015 (Fig. 2b), but with a statistical significance at only the
95th percentile. Cooper et al. (2012) reported that the Welby site exhibited no statistically significant increase in O3
from 1990 – 2010, contrary to what we found for 2000 – 2015 at the 95th percentile.
The increasing O3 trends in the NFRMA occurred despite reductions in NOx. NO2* at the CAMP site decreased
significantly from 2000 at a rate of 1.2 ± 0.2 and 1.5 ± 0.2 ppb/yr for the 50th and 95th percentiles for CAMP (Fig. 3).
Welby exhibited a non-significant decreasing NO2* trend at the 95th percentile of 0.5 ± 0.3 ppb/yr (Fig. 3). The
increased O3 may be due to increased summer temperatures in Colorado, increased regional baseline O3, or increased
local P(O3) from unknown emission sources (Cooper et al., 2012). VOC emissions steadily increased in Colorado
from 2000 to 2012 according to the EPA NEI-2014. To the best of our knowledge, the NFRMA does not have any
long-term VOC datasets, but the EPA NEI-2014 for Colorado provided an estimate for yearly anthropogenic VOC
(AVOC) emissions (EPA, 2016b). All categories of AVOC emissions decreased slightly from 2000 – 2015, except
for petroleum related VOCs which increased from 7.4 x 103 tons in 2000 to 2.6 x 103 tons in 2011 with a decrease to
1.5 x 103 tons in 2015 (Fig. 4). However, we note the NEI is only an estimate and does not include biogenic sources
of VOCs, which can contribute substantially to VOC reactivity in the region, but vary substantially from year to year (Abeleira et al., 2017). The increased $O_3$ is thus unsurprising for the 2000 – 2015 timeframe. The long-term reduction in NO$_2$ with increasing VOC emissions concurrent with an increase in $O_3$ at both sites suggests that the downtown Denver sites were in a NO$_2$-saturated P($O_3$) regime, and as NO$_2^*$ decreases and VOC reactivity increases, P($O_3$) was increasing towards peak production.

3.2 Weekday-Weekend effect in Denver, CO

The ‘weekday-weekend effect’ describes how emissions can be statistically different on weekdays versus weekends, resulting in different secondary chemistry. This effect can be used to elucidate information about local chemical regimes (i.e. CARB, 2003;Murphy et al., 2007;Fujita et al., 2003;Warneke et al., 2013;Pollack et al., 2012;Cleveland et al., 1974;Heuss et al., 2003). Traffic patterns in urban regions are different between weekdays and weekends, with heavier traffic and thus higher NO$_x$ on weekdays due to rush-hour and commercial trucking patterns. VOCs are expected to be stable across the week, as major VOC sources do not vary by day-of-week. Despite this drop in traffic, NO$_3$ can be higher on weekends than on weekdays if the system is in a NO$_x$-saturated regime because decreased NO$_3$ increases P($O_3$), while decreased NO also reduces $O_3$ titration to NO$_2$ (Fujita et al., 2003;Heuss et al., 2003;Marr and Harley, 2002;Murphy et al., 2007;Pollack et al., 2012;Pusede and Cohen, 2012). Thus urban regions, which are often NO$_x$-saturated, tend to follow a day-of-week pattern in both NO$_x$ and $O_3$ (Fujita et al., 2003;Heuss et al., 2003;Pusede and Cohen, 2012), while rural and semi-urban areas often experience no change in NO$_x$ or $O_3$ from weekdays to weekends. Rural regions have a lower population density, less defined daily traffic patterns, and minimal or no commercial trucking (Heuss et al., 2003). The weekday-weekend effect typically relies on the assumption that the VOC reactivity and thus HO$_x$ production is unchanged between the weekend and weekday. However, this is not always the case, as decreased weekend NO$_x$ reduces NO$_x$+OH reactions, and thereby increases weekend OH and increased $O_3$ (Warneke et al., 2013). Few studies of VOCs in the NFRMA exist, but our previous work found no significant difference in measured VOC reactivity at the BAO site between weekends and weekdays in summer 2015 (Abeleira et al., 2017).

In the NFRMA, long-term (i.e. 10+ years) NO$_2^*$ datasets only existed at the CAMP and Welby sites. Two sites in Denver added NO$_2^*$ measurements in 2015, the I-25 and La Casa sites. The CAMP, I-25, and La Casa sites are all located within a 4-mile radius that straddles the I-25 motorway; are surrounded by a dense network of roads, businesses, and industrial operations; and experience high traffic density. Welby was located roughly 8-miles northeast from the three other sites, and borders a large lake and the Rocky Mountain Arsenal open space. Welby was thus more ‘suburban’ than the other sites. Median NO$_2^*$ at CAMP has decreased from 37 ppb, in 2003 to 13 ppb, in 2015. The median weekday I-25 and La Casa NO$_2^*$ mixing ratios in 2015 were similar to CAMP in 2007 (Fig. 5) indicating that although NO$_2^*$ emission reductions have been effective in the region, mixing ratios in Denver are very site specific.

An observable weekday-weekend effect in NO$_2^*$ existed for all sites with NO$_2^*$ data in all years except for Welby in 2007 (Fig. 5). NO$_2^*$ decreased by 20-50% from weekdays to weekends. Assuming that meteorology doesn’t systematically change between weekends and weekdays, we consider the weekend-weekday effect in NO$_2^*$ to be indicative of changes in P($O_3$) due to lower NO$_2$. Figure 6 follows the analysis of Pusede and Cohen (2012), presenting summer average weekday and weekend NO$_3$ values for Welby and CAMP with the values tethered for each year. The values followed a curve similar to a modeled P($O_3$) curve, and indicates that reductions in NO$_x$ emissions from 2000 to 2015 have placed NO$_3$ production in the Denver region in a transitional phase from NO$_2$-saturated to peak P($O_3$). Regions that have higher NO$_3$ should observe greater impacts from changing VOCs than those that are closer to the peak P($O_3$). This analysis also suggested that continued reduction of NO$_x$ would shift the system to a NO$_x$-limited regime, in which changes in VOC reactivity due to shifting anthropogenic or biogenic emissions would have little effect on NO$_3$.

The average change in O$_3$ ($\Delta O_3$) and NO$_2^*$ ($\Delta$NO$_2^*$) from weekend to weekday is plotted as a function of year for the two available NFRMA sites (Fig. 7a, Fig. 7b). A positive $\Delta O_3$ reflects a higher $O_3$ concentration on the weekend than weekday, consistent with a NO$_x$-saturated system. The weekday-weekend effect decreased from 2000 to 2015 for five of the six sites, all with similar $\Delta O_3$. This is consistent with the decreased regional NO$_x$ emissions, which would move the system from NO$_2$-saturated to peak P($O_3$). The CAMP site was the exception, and consistently had a larger $\Delta O_3$ than the other sites. This was consistent with the CAMP site’s higher NO$_2^*$ relative to Welby and the 30-50% decrease
in NO2* from weekdays to weekend. Measured NO2* decreased at both CAMP and Welby (Fig. 3), although the
ΔNO2* at CAMP and Welby was unchanged, with average NO2* of -11 ± 3 ppb, and -1.7 ± 0.9 ppb, respectively.
Thus while absolute NOx emissions have changed, weekly traffic patterns have not. Applying a one-sided linear
regression to the five-site ΔO3 median for 2001-2015 yielded a statistically significant decreasing trend of -0.5 ± 0.1
ppb/yr with an r2 = 0.55. The ΔO3 decreased across the NFRMA outside of the highest traffic regions in Denver, again
consistent with the hypothesis that the NFRMA P(O3) regime has transitioned from NOx-saturated chemistry towards
peak P(O3). Two specific sites, Greeley and Rocky Flats, show negative ΔO3 values in recent years, suggesting that
those sites have, at least in those specific years, transitioned to NOx-limited chemistry.

Collectively, this weekend-weekday analysis suggested that the region is NOx-saturated, but transitioning to a NOx-
limited region. Increases in O3 are likely due to a combination of decreasing NOx and increasing VOC emissions.
While the lack of long-term VOC measurements prevents identification and quantification of those VOC sources, the
NEI suggested that petroleum-related VOCs have increased.

3.3 The O3-temperature penalty in the NFRMA

Increasing temperature can increase P(O3) by enhancing biogenic and evaporative VOC emissions, but has variable
impacts on the weekday-weekend effect as a result of changing NOx emissions (Pusede et al., 2014). We showed that
while O3 increased with temperature in the NFRMA, consistent with a NOx-saturated regime, this relationship was
variable year to year. Ambient O3 was correlated with increasing temperature across the U.S. (Bloomer et al.,
2009; Jacob and Winner, 2009; Pusede et al., 2014). While one study in the NFRMA from summer 2012 found that
biogenic VOCs (i.e. isoprene) had a minor impact on VOC reactivity (McDuffie et al., 2016), Abeleira et al. (2017)
found that isoprene contributed up to 47% of VOC reactivity on average in the late afternoon in summer 2015.

Studying the temperature dependence of O3 allowed us to investigate the extent to which biogenic VOCs influenced
P(O3) in the NFRMA and the interannual variability in those temperature-dependent VOC sources, as well as the shift
from a NOx-saturated to NOx-limited P(O3) regime. NOx-saturated regimes should be sensitive to changes in VOC
reactivity, while NOx-limited systems should not. We note that while anthropogenic VOCs, such as solvents, may be
temperature dependent and contribute to this trend, we only observed temperature trends in isoprene at the BAO site
in 2015 — though we acknowledge that the observed VOC suite in that study was limited (Abeleira et al., 2017).

O3 in the NFRMA demonstrated a clear temperature dependence at all percentiles for all sites, but with slopes that
vary by site and year (Fig. 8, Fig. 9). The NFRMA appears to be NOx-saturated or near peak P(O3) for all years,
consistent with temperature dependent biogenic emissions having large impacts on ambient local O3. The variance in
the O3-temperature dependence was likely external to meteorological effects. High temperature and linked
meteorological parameters such as high 500 hPa heights, and stagnant winds, or circulating wind patterns do indeed
 correlate with high O3 events in Colorado (Reddy and Pfister, 2016), but those parameters should not affect the O3
temperature relationship.

Figure 8a shows daytime, summer O3 averaged in 3°C temperature bins for CAMP, Fort Collins, and Rocky Flats for
years in which data was available at all sites. For every temperature bin, O3 was higher at Rocky Flats than at Fort
Collins, and both were higher than at CAMP. The Rocky Flats site was the most rural of the chosen sites adjacent to
the 4,000 acre Rocky Flats Wildlife Refuge, but was <15 miles from downtown Boulder. Rocky Flats likely had higher
O3 because it was downwind of both NOx (Boulder, Denver) and VOC sources (forested regions in the neighboring
foothills), had fewer nearby fresh NOx sources and thus less NOx+O3 titration, and experienced enhanced P(O3) due to
the region being near at the cross-over point between NOx-saturated and NOx-limited (Fig. 6).

Bloomer et al. (2009) reported average O3-temperature relationships of 2.2 – 2.4 ppb/°C for the Northeast, Southeast,
and Great Lakes regions of the U.S. across all O3 percentiles. In contrast, the Southwest region, including Colorado,
had an average relationship of 1.4 ppb/°C (Bloomer et al., 2009). We find that O3 was indeed correlated with
temperature at all NFRMA sites, with relationships that ranged from 0.07 to 1.95 ppb/°C with an average of 1.0 ± 0.4
ppb/°C (Fig. 8) for all sites and years. Quantitatively, this temperature dependence was low relative to other U.S.
sites, consistent with previous findings that biogenic VOCs contribute to, but did not dominate the VOC reactivity in
the NFRMA (McDuffie et al., 2016; Abeleira et al., 2017). However, the six NFRMA sites exhibited significant
variability in the 5th, 50th, and 95th percentiles among the sites both within a given year and across years (Fig. 9). The
5th and 95th O₃ percentiles showed greater variability and larger uncertainties in the slopes than the 50th percentile. This indicated that baseline O₃ and high O₃ events in the region were less dependent on temperature. Baseline O₃ was likely tied to the transport of O₃ and O₃ precursors from the west coast (Cooper et al., 2012), while the high O₃ events were likely tied to a combination of meteorological parameters, including 500 hPa heights and stagnation events (Reddy and Pfister, 2016), and local, temperature independent VOC emissions. In contrast, the 50th percentile showed a clear temperature dependence at all sites in most years (Fig. 8, Fig. 9), indicating that mean O₃ was typically influenced by local temperature dependent, and likely biogenic, VOC emissions.

Unlike ambient O₃ and the weekend to weekday ΔO₃, we noted no clear long-term trend in the O₃-temperature relationship. The O₃-temperature relationships showed similar interannual patterns for the six sites at the 50th percentile, except for years 2000-2003 (Fig. 9). Specifically, years 2001-2002, 2008, and 2011-2012 have suppressed O₃-temperature slopes for the 50th percentile. Reddy and Pfister (2016) reported high 500 hPa heights and O₃ for 2002-2003, 2006, and 2012 while 2004 and 2009 had low 500 hPa heights and low O₃, so those exceptional years cannot be explained solely by meteorology. However, those exceptional years (2002-2003, 2008, and 2011-2012) did correspond to years in which Colorado was in moderate-severe drought with little soil moisture (NOAA, 2017).

Drought in the NFRMA is connected to changes in mountain-plains circulation and lower surface moisture, which reduces the surface latent heat flux and causes increased surface temperature. These increased surface temperatures lead to strong mountain-plains circulation, stagnant wind conditions, higher PBLs, and 500 hPa heights, all of which are known to correlate with high O₃ episodes (Reddy and Pfister, 2016; Ek and Holtslag, 2004; Zhou and Geerts, 2013). Drought is also connected to reduced isoprene emissions (Brilli et al., 2007; Fortunati et al., 2008; Guenther, 2006).

Consistent with this concept, Abeleira et al. (2017) noted that isoprene was 4 times higher at the Boulder Atmospheric Observatory site in summer 2015 (a non-drought year) than in summer 2012 (a drought year). Such a decrease in biogenic isoprene emissions should also suppress the O₃-temperature dependence in NOₓ-saturated regimes, a trend that was observed in the NFRMA (Fig. 9).

The suppressed O₃-temperature relationship during drought years in the NFRMA demonstrated the importance of temperature dependent VOCs in driving P(O₃) in the region, particularly at the mid-range 50th percentile – but not at the baseline 5th percentile. A standard t-test showed that the 50th and 95th percentile slopes (i.e. temperature dependence of average and high O₃ concentrations) are indeed different between the drought and non-drought years at the 95% confidence limit. If NOₓ emissions continue to decrease, and the NFRMA continues its trend towards a NOₓ-limited regime (Fig. 7), the O₃-temperature dependence should also decrease and temperature-dependent VOCs will play a smaller role in driving O₃ production. However, this would require substantial decreases in NOₓ for the heavily trafficked Denver to become fully NOₓ-limited, so temperature-dependent VOCs will likely remain important in at least some regions of the NFRMA.

4. Conclusions

O₃ was decreasing across most of the country as NOₓ and VOC emissions continue to be reduced, with the exception of background O₃ in the west (Cooper et al., 2012). In contrast, five out of six sites in the NFRMA showed no change or increasing O₃ at the 50th and 95th percentiles between 2000 and 2015. While NOₓ levels have been reduced at the CAMP and Welby sites in Denver, anthropogenic VOC emission estimates have increased as a result of increased petroleum related activities (Fig. 4). A weekend-weekday analysis demonstrated that most sites in the NFRMA were NOₓ-saturated, but are transitioning to, and in one case may already have reached, the peak P(O₃) cross-over point between NOₓ-saturated and NOₓ-limited regimes. Some of the more rural NFRMA sites may already be in or near a NOₓ-limited system. This transition suggests that increasing anthropogenic VOC emissions will have less of an effect on P(O₃) in the region if NOₓ reductions continue, though VOCs still remain the limiting reagent for ozone production in most of the NFRMA sites in 2015. Thus, the combined factors of increasing anthropogenic VOC emissions and decreasing NOₓ in a NOₓ-saturated system are likely culprits for the increasing O₃ trends within the NFRMA over the past 15 years. Although the median NOₓ⁎ has decreased at the CAMP site from 37 ppb, in 2003 to 13 ppb, in 2015, the site remains on the steep transitional part of the P(O₃) curve between NOₓ-saturated and peak P(O₃) chemistry (Fig. 6). Continued reductions in NOₓ emissions alone could lead to increased O₃ in the downtown Denver area until the P(O₃) chemistry passed the peak production region, although concurrent reductions in VOCs could mitigate the increase in P(O₃). As sources of VOCs and NOₓ change in the NFRMA with increased population, growth in the oil...
and gas sector, and changing emissions regulations, continued analysis of O$_3$ and NO$_x$ will be essential for understanding the shifting P(O$_3$) regime. However, such analyses would benefit greatly from long-term NO$_x$ measurements at additional sites in the NFRMA.

O$_3$ in the NFRMA exhibits temperature dependence at all sites, but with varying intensities for different years. The 5$^{th}$ and 95$^{th}$ O$_3$ percentiles demonstrated significant variability in temperature dependence for different sites in the same year and across the study period, indicating that high O$_3$ events and background O$_3$ have other important controlling factors such as transport of long-lived O$_3$ precursors from the west or meteorological parameters. Three time periods exhibit a suppressed O$_3$-temperature dependence (2002-2003, 2008, and 2011-2012), coinciding with moderate to extreme drought conditions in the NFRMA. These observations are consistent with the hypothesis that long-term drought stress reduces biogenic VOC emissions and suppresses the O$_3$-temperature dependency. Climate change is predicted to increase temperatures and thus increase O$_3$ by 1 – 10 ppb, on a national scale (Jacob and Winner, 2009). However, climate change models predict more extreme precipitation events in many areas, and estimates for Colorado and the intermountain west suggest that drought may become more common in the region (Change, 2014). Our work suggests that drought can temporarily suppress the O$_3$-temperature penalty in the NFRMA and potentially other NO$_x$-saturated regions by reducing temperature dependent biogenic VOC emissions.

Acknowledgements

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Figure 1. Site map for O$_3$ and NO$_2$ measurements in the NFRMA identified by shapes and colors. Producing oil and gas wells as of 2012 are identified on the map with gold dots. Urban areas are outlined with thick light-blue lines. Major interstates and state highways are identified by thick pink lines.
Figure 2. a) Trends in summer (June 1 – August 31) daytime (10:00 am – 4:00 pm) \(O_3\) for six sites in the NFRMA between 2000 and 2015. Whiskers correspond to 5th and 95th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the marker corresponds to the 50th percentile. Percentiles were determined from hourly daytime \(O_3\) measurements at each site. The number of days used for each year’s statistics depended on available data (n = 64 – 92). b) \(O_3\) temporal trends were determined as the slope from annual trends (ppb, \(O_3/\text{year}\)) from simple one-sided linear regression for the six NFRMA sites for the 95th (blue triangles), 50th (black squares), and 5th (red circles) percentiles. Error bars were calculated from the regression slope at one standard deviation.
Figure 3. Box and whisker plots of NO$_2^*$ for the CAMP and Welby sites in Denver for all available data from 2000 – 2015. Whiskers correspond to 5th and 95th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the black marker corresponds to the 50th percentile.
Figure 4: VOC emission estimates from EPA National Emissions Inventory 2014 (NEI-2014) for Colorado. Emission sources are separated by color, and are added to give the total VOC emission estimates for anthropogenic VOCs. Biogenic VOCs and VOCs from biomass burning (controlled fires and wildfires) are not included.
Figure 5. O$_3$ and NO$_2^*$ as a function of day of week for the CAMP, Welby, La Casa, and I-25 sites in Denver. All sites have plots for 2015, but only CAMP and Welby are plotted for 2007 and 2012 due to data availability. Solid lines are the 50th percentile for daytime hourly NO$_2^*$ (blue) and O$_3$ (black) measurements. The shaded regions are bounded by the 67th and 33rd percentiles. Note that the NO$_2^*$ y-axis scale is different on the upper and lower panels.
Figure 6. Weekday and weekend O$_3$ versus NO$_2$* for Welby (red) and CAMP (black) sites. Tethered symbols correspond to averages of Wednesday values for weekdays, and average Sunday values for weekends for each year depending on data availability. Standard errors of means for each year are <4 ppb for O$_3$ and <2 ppb for NO$_2$*. The dashed blue line is a visual aid to guide the reader's eye to the non-linear O$_3$ curve, and was generated from the simple analytic model described by Farmer et al. (2011).
Figure 7: (a) The change in O$_3$ calculated as median weekend (Saturday to Sunday) minus summer weekday (Tuesday to Thursday) for the six NFRMA sites identified by color and marker for each year of available data. The solid grey line is the average median of the sites with the exception of CAMP. The inclusion of a site in the averaging for a given year was dependent on available data for that year. The light grey shading represents ± 1 standard deviation of the five site average. (b) The change in NO$_2^*$ calculated as median summer weekend (Saturday to Sunday) minus summer weekday (Tuesday to Thursday) for the CAMP and Welby sites.
Figure 8. a) $O_3$ versus temperature for CAMP, Fort Collins, and Rocky Flats. $O_3$ is binned into 3°C temperature bins. Markers and colors represent yearly averages for each site. Error bars represent ± 1 standard error of the mean. Years were selected based on availability of overlapping data for multiple sites. b) One-sided linear regressions of 5°C temperature bins for 5th (red open diamond), 33rd (grey hash), 50th (blue open triangle), 67th (green open square), and 95th (black open circle) percentiles for the CAMP site for 2007 (left), 2012 (middle), and 2015 (right).
Figure 9. Slopes from one-sided linear regression of O$_3$ versus temperature (i.e. the temperature dependence of O$_3$) are binned into 5°C Celsius bins for daytime (10:00 am – 4:00 pm) data at the 5th, 50th, and 95th percentiles for O$_3$. Data are shown for CAMP (black squares), Welby (grey solid circles), Carriage (blue open triangles), Fort Collins (green solid squares), Greeley (teal X’s), and Rocky Flats (magenta open diamonds). Shaded years correspond to Colorado summers with moderate to severe drought conditions. Error bars are ±1 standard deviation of the slopes.
References


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Pusede, S. E., and Cohen, R. C.: On the observed response of ozone to NO\textsubscript{x} and VOC reactivity reductions in San Joaquin Valley California 1995–present, Atmospheric Chemistry and Physics, 12, 8323-8339, 10.5194/acp-12-8323-2012, 2012.


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Table 1. Summary of Measurements sites used in this analysis. Note that NO₂* refers to the NO₂ detected by the EPA reference method, and thus includes a fraction of NOy species.