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

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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 NO_x emissions. We used available long-term ozone and NO_x 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 NO_2 at two sites in downtown Denver, indicating that the region was in a NO_x-saturated ozone production regime. The stagnation and increases in ozone in the NFRMA are likely the result of (1) decreasing NO_x emissions in a NO_x-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 NO_x-limited chemistry. This transition implies that continued NO_x 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 NO_x-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 (O_3) 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 O_3 standard to the new 70 ppb_v 8-hour average will result in health benefits of $6.4-13 billion/yr (EPA, 2014). O_3 also damages plants, reducing agricultural yields (Tai et al., 2014). Using crop yields and ambient O_3 concentrations for 2000, Avnery et al. (2011) estimate the loss of $11-18 billion/yr worldwide as a result of the reduction of staple worldwide crops (soybean, maize, and wheat) from O_3 damage. During summer months, the Northern Front Range Metropolitan Area (NFRMA) of Colorado consistently violated the pre-2016 U.S. EPA National Ambient Air Quality Standard (NAAQS) of 75 ppb_v fourth-highest daily maximum 8-hour average (MDA8) ambient O_3 concentration, despite proposed reductions in anthropogenic emissions (CDPHE, 2014). The NFRMA has been an O_3 non-attainment zone since 2008 (CDPHE, 2009), prompting the Colorado Air Pollution Control Division and the Regional Air Quality Council to develop the Colorado Ozone Action Plan in 2008 to target key O_3 precursors: volatile organic compounds (VOCs) and NO_x ($NO+NO_2$)(CDPHE, 2008). Despite these control efforts, 2013 was the NFRMA's fourth year in a row to exceed the federal O_3 standard (CDPHE, 2016), and the eight NFRMA non-attainment counties, with their combined population >3.5 million, exceeded the MDA8 75 ppb_v O_3 standard 9-48 days between 2010 and 2012 (AMA, 2015). However, Colorado must comply with the new 70 ppb_v MDA8 standard by 2018. In order to accurately design and implement O_3 reduction schemes, a thorough understanding of local O_3 trends and chemistry is required.

Ground-level or boundary layer O_3 depends on local production, transport, and meteorological parameters:

$$\frac{\partial[O_3]}{\partial t} = P(O_3) + \frac{w_e O_3 - u_d[O_3]}{H} - \nabla \times (v[O_3]) \quad (1)$$

where $\partial[O_3]/\partial t$ represents the time rate of change of O_3 concentration, $P(O_3)$ is the instantaneous net photochemical O_3 production rate (production – loss), $w_e O_3 - u_d[O_3]/H$ represents the entrainment rate (w_e) of O_3 in and deposition

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rate (u_d) of O_3 out of the mixing layer height (H), and $\nabla \times (v[O_3])$ 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).

$$RH + OH + O_2 \rightarrow RO_2 + H_2O \quad (R1)$$

Chain propagation occurs through 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. Alkoxy (RO) radicals form carbonyl-containing compounds and HO_2 (R7).

$$RO_2 + NO \rightarrow RO + NO_2 \quad (R2a)$$

$$RO_2 + NO \rightarrow RONO_2 \quad (R2b)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (R3)$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (R4)$$

$$O(^3P) + O_2 \rightarrow O_3 \quad (R5)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R6)$$

$$RO + O_2 \rightarrow R'CHO + HO_2 \quad (R7)$$

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 ($RC(O)O_2NO_2$). 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_x 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

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and low hourly O_3 values narrowed toward mid-level values in the 12 cities studied, consistent with a reduction in domestic O_3 precursors and possibly increased transport of O_3 precursors from east Asia. A number of modeling and measurement studies have also reported increased baseline O_3 in the western U.S. due to the transport of O_3 precursors from east Asia (Cooper et al., 2010;Parrish et al., 2004;Pfister et al., 2011;Weiss-Penzias et al., 2006). These studies questioned the effectiveness of local precursor emission reductions in controlling local O_3 in impacted regions.

Cooper et al. (2012) showed that the intermountain West is an intriguing environment with potentially increasing background O_3. The NFRMA is of particular interest due to the challenge in effective O_3 regulation, its growing population and the dominantly anthropogenic sources of O_3 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 summer 2015, likely 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 O_3 (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 O_3 (Bloomer et al., 2009;Jacob and Winner, 2009;Palut and Canziani, 2007). The O_3-temperature relationship is attributed to (1) temperature-dependent biogenic VOC emissions that provide a source of VOCs for OH oxidation leading to increased HO_x cycling (Guenther, 2006;Guenther et al., 1996), (2) thermal decomposition of peroxyacetylnitrate (PAN) to HO_x and NO_x (Fischer et al., 2014;Singh and Hanst, 1981), and (3) increased likelihood of favorable meteorological conditions for ozone formation (*i.e.* high insolation, 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 NO_x. Due to the non-linearity of $P(O_3)$ chemistry as a function of NO_x, the increased VOC and NO_x emissions associated with warming can either increase or decrease $P(O_3)$ depending on local NO_x concentrations (i.e. NO_x-limited vs. NO_x-saturated). Interactions between climate change and regional-scale meteorology are complex, and may also impact O_3. High and low O_3 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 O_3 in the NFRMA (Reddy and Pfister, 2016).

In this paper, we used temperature, O_3, and NO_2 data from 2000-2015 at multiple sites in the NFRMA to investigate why O_3 has not decreased in the region despite decreases in NO_x. We used a weekday-weekend analysis to elucidate the NO_x regime for $P(O_3)$ in Denver, and explored the temperature dependence of O_3 and the role of drought in influencing that relationship in the NFRMA.

2. Methods

2.1 Measurement sites

We used publicly available O_3, NO_2 and temperature data (https://aqs.epa.gov/aqsweb/documents/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. O_3 data was available for 2005 – 2007 and 2012 – 2015, while NO_2 data was

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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. O_3 data was available for 2000 – 2009 and 2011 – 2015, while NO_2 data was available for 2001 – 2002, 2004 – 2005, 2007 – 2008, and 2010 – 2015. The Carriage site is <1 mile west of the I-25 interstate at the same latitude as the CAMP site. O_3 data was available for 2000 – 2012 for the Carriage site. The Fort Collins site is adjacent to Colorado State University near downtown Fort Collins. O_3 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. O_3 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 NO_x emissions directly from the I-25 interstate. NO_2 data was available for 2015, but not O_3. The La Casa site is <1 mile west of the I-70 and I-25 interstate junction. O_3 and NO_2 data were available for 2015. Temperature data was available for all sites for all years.

2.2 Ozone and NO_2 data treatment

Ambient NO_2 concentrations were measured by chemiluminescence monitors equipped with molybdenum oxide converters. These monitors are used as the EPA Federal Reference Method for monitoring ambient NO_2 concentrations, and have a known interference from nitric acid and organic nitrates (Dunlea et al., 2007). The true ambient NO_2 mixing ratio is a component of the reported values. NO_2* will be used in this manuscript to refer to the EPA NO_2 measurements, which includes the interference, and can be considered to be a proxy for total reactive nitrogen oxides (NO_y). While the absolute NO_2* concentration will be greater than NO_2 but less than NO_y, trends in NO_2* provided insight on trends in local NO_x emissions. The O_3 and NO_2* 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 ($R^2 = 0$). The null hypothesis was rejected with a confidence level ≥ 95% if the probability (p) associated with the F-statistics was low ($p \leq 0.05$).

3 Results and Discussion

3.1 Long term trends in O_3 and NO_2* in the Northern Front Range Metropolitan Area

Contrary to most other places in the U.S., O_3 in the NFRMA was either stagnant or increasing between 2000 and 2015, despite substantial decreases in NO_x emissions. At most sites in the eastern U.S. and some on the west coast, O_3 was decreasing at all percentiles. In the NFRMA, however, five out of six monitoring sites exhibited no change or increasing O_3 at the 50th and 95th percentiles in the 2000 – 2015 period (Fig. 2). The 5th percentile is often taken as background O_3. With the exception of the Greeley site, the 5th percentile of O_3 increased across the NFRMA between 2000 and 2015. However, only the downtown Denver CAMP site had statistically significant increases in O_3 of 2.6 ± 0.9, 2.3 ± 0.3, and 1.8 ± 0.7 ppb_v/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_v/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 O_3 from 1990 – 2010, contrary to what we found for 2000 – 2015 at the 95th percentile.

The increasing O_3 trends in the NFRMA occurred despite reductions in NO_x. NO_2* at the CAMP site decreased significantly from 2000 at a rate of 1.2 ± 0.2 and 1.5 ± 0.2 ppb_v/yr for the 50th and 95th percentiles for CAMP (Fig. 3). Welby exhibited a non-significant decreasing NO_2* trend at the 95th percentile of 0.5 ± 0.3 ppb_v/yr (Fig. 3). The increased O_3 may be due to increased summer temperatures in Colorado, increased regional baseline O_3, or increased local $P(O_3)$ 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 10^3 tons in 2000 to 2.6 x 10^5 tons in 2011 with a decrease to 1.5 x 10^5 tons in 2015 (Fig. 4). However, we note the NEI is only an estimate and does not include biogenic sources

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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_x with increasing VOC emissions concurrent with an increase in O_3 at both sites suggests that the downtown Denver sites were in a NO_x-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, O_3 can be higher on weekends than on weekdays if the system is in a NO_x-saturated regime because decreased NO_x 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_v in 2003 to 13 ppb_v 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 O_3 to be indicative of changes in $P(O_3)$ due to lower NO_x. Figure 6 follows the analysis of Pusede and Cohen (2012), presenting summer average weekday and weekend O_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 O_3 production in the Denver region in a transitional phase from NO_x-saturated to peak $P(O_3)$. Regions that have higher NO_x 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 O_3.

The average change in O_3 (ΔO_3) and NO_2* (ΔNO_2*) from weekend to weekday is plotted as a function of year for the two available NFRMA sites (Fig. 7a, Fig. 7b). A positive ΔO_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 ΔO_3. This is consistent with the decreased regional NO_x emissions, which would move the system from NO_x-saturated to peak $P(O_3)$. The CAMP site was the exception, and consistently had a larger ΔO_3 than the other sites. This was consistent with the CAMP site's higher NO_2* relative to Welby and the 30-50% decrease

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in NO_2* from weekdays to weekend. Measured NO_2* decreased at both CAMP and Welby (Fig. 3), although the ΔNO_2* at CAMP and Welby was unchanged, with average NO_2* of -11 ± 3 ppb_v and -1.7 ± 0.9 ppb_v, respectively. Thus while absolute NO_x emissions have changed, weekly traffic patterns have not. Applying a one-sided linear regression to the five-site ΔO_3 median for 2001-2015 yielded a statistically significant decreasing trend of -0.5 ± 0.1 ppb_v/yr with an $r^2 = 0.55$. The ΔO_3 decreased across the NFRMA outside of the highest traffic regions in Denver, again consistent with the hypothesis that the NFRMA $P(O_3)$ regime has transitioned from NO_x-saturated chemistry towards peak $P(O_3)$. Two specific sites, Greeley and Rocky Flats, show negative ΔO_3 values in recent years, suggesting that those sites have, at least in those specific years, transitioned to NO_x-limited chemistry.

Collectively, this weekend-weekday analysis suggested that the region is NOx-saturated, but transitioning to a NOx-limited region. Increases in O_3 are likely due to a combination of decreasing NO_x 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 O_3-temperature penalty in the NFRMA

Increasing temperature can increase $P(O_3)$ by enhancing biogenic and evaporative VOC emissions, but has variable impacts on the weekday-weekend effect as a result of changing NO_x emissions (Pusede et al., 2014). We showed that while O_3 increased with temperature in the NFRMA, consistent with a NO_x-saturated regime, this relationship was variable year to year. Ambient O_3 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 O_3 allowed us to investigate the extent to which biogenic VOCs influenced $P(O_3)$ in the NFRMA and the interannual variability in those temperature-dependent VOC sources, as well as the shift from a NO_x-saturated to NO_x-limited $P(O_3)$ regime. NO_x-saturated regimes should be sensitive to changes in VOC reactivity, while NO_x-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).

O_3 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 NO_x-saturated or near peak $P(O_3)$ for all years, consistent with temperature dependent biogenic emissions having large impacts on ambient local O_3. The variance in the O_3-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 O_3 events in Colorado (Reddy and Pfister, 2016), but those parameters should not affect the O_3 temperature relationship.

Figure 8a shows daytime, summer O_3 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, O_3 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 O_3 because it was downwind of both NO_x (Boulder, Denver) and VOC sources (forested regions in the neighboring foothills), had fewer nearby fresh NO_x sources and thus less NO+O_3 titration, and experienced enhanced $P(O_3)$ due to the region being near at the cross-over point between NO_x-saturated and NO_x-limited (Fig. 6).

Bloomer et al. (2009) reported average O_3-temperature relationships of 2.2 – 2.4 ppb_v/°C for the Northeast, Southeast, and Great Lakes regions of the U.S. across all O_3 percentiles. In contrast, the Southwest region, including Colorado, had an average relationship of 1.4 ppb_v/°C (Bloomer et al., 2009). We find that O_3 was indeed correlated with temperature at all NFRMA sites, with relationships that ranged from 0.07 to 1.95 ppb_v/°C with an average of 1.0 ± 0.4 ppb_v/°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 O_3 percentiles showed greater variability and larger uncertainties in the slopes than the 50th percentile. This indicated that baseline O_3 and high O_3 events in the region were less dependent on temperature. Baseline O_3 was likely tied to the transport of O_3 and O_3 precursors from the west coast (Cooper et al., 2012), while the high O_3 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 O_3 was typically influenced by local temperature dependent, and likely biogenic, VOC emissions.

Unlike ambient O_3 and the weekend to weekday ΔO_3, we noted no clear long-term trend in the O_3-temperature relationship. The O_3-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 O_3-temperature slopes for the 50th percentile. Reddy and Pfister (2016) reported high 500 hPa heights and O_3 for 2002-2003, 2006, and 2012 while 2004 and 2009 had low 500 hPa heights and low O_3, 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 O_3 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 O_3-temperature dependence in NO_x-saturated regimes, a trend that was observed in the NFRMA (Fig. 9).

The suppressed O_3-temperature relationship during drought years in the NFRMA demonstrated the importance of temperature dependent VOCs in driving $P(O_3)$ 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 O_3 concentrations) are indeed different between the drought and non-drought years at the 95% confidence limit. If NO_x emissions continue to decrease, and the NFRMA continues its trend towards a NO_x-limited regime (Fig. 7), the O_3-temperature dependence should also decrease and temperature-dependent VOCs will play a smaller role in driving O_3 production. However, this would require substantial decreases in NO_x for the heavily trafficked Denver to become fully NO_x-limited, so temperature-dependent VOCs will likely remain important in at least some regions of the NFRMA.

4. Conclusions

O_3 was decreasing across most of the country as NO_x and VOC emissions continue to be reduced, with the exception of background O_3 in the west (Cooper et al., 2012). In contrast, five out of six sites in the NFRMA showed no change or increasing O_3 at the 50th and 95th percentiles between 2000 and 2015. While NO_x 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 NO_x-saturated, but are transitioning to, and in one case may already have reached, the peak $P(O_3)$ cross-over point between NO_x-saturated and NO_x-limited regimes. Some of the more rural NFRMA sites may already be in or near a NO_x-limited system. This transition suggests that increasing anthropogenic VOC emissions will have less of an effect on $P(O_3)$ in the region if NO_x 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 NO_x in a NO_x-saturated system are likely culprits for the increasing O_3 trends within the NFRMA over the past 15 years. Although the median NO_2* has decreased at the CAMP site from 37 ppb_v in 2003 to 13 ppb_v in 2015, the site remains on the steep transitional part of the $P(O_3)$ curve between NO_x-saturated and peak $P(O_3)$ chemistry (Fig. 6). Continued reductions in NO_x emissions alone could lead to increased O_3 in the downtown Denver area until the $P(O_3)$ chemistry passed the peak production region, although concurrent reductions in VOCs could mitigate the increase in $P(O_3)$. As sources of VOCs and NO_x 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_v 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.

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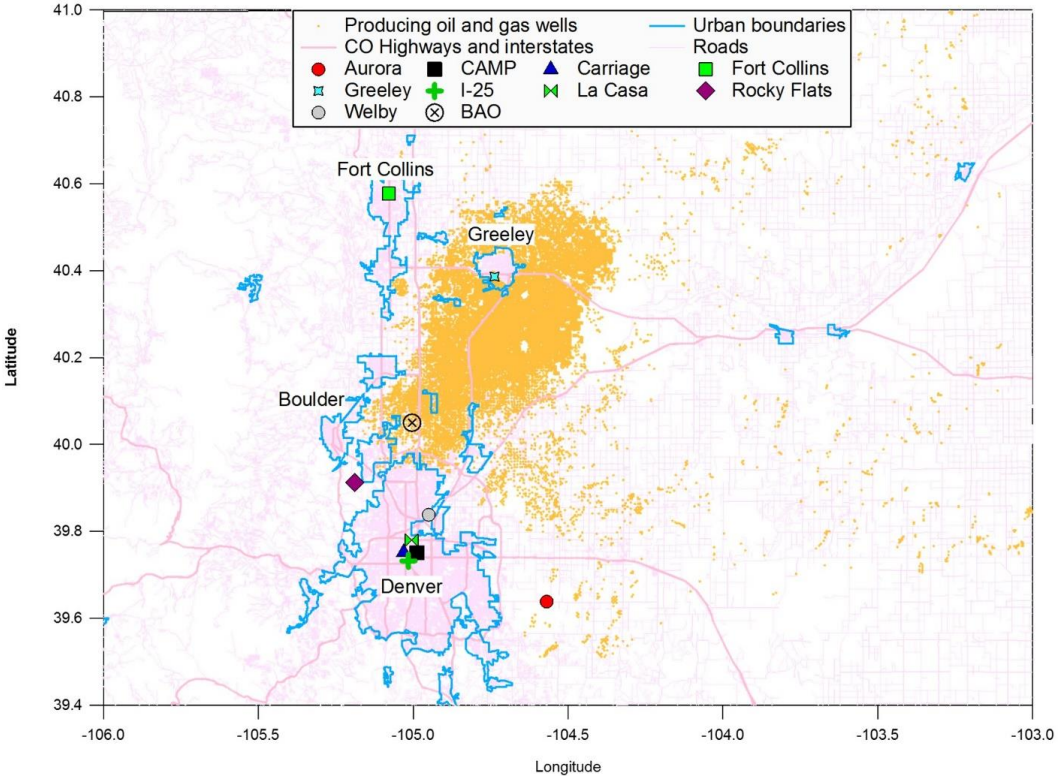

Figure 1. Site map for O_3 and NO_2 measurements in the NFRMA identified by shapes and colors. Producing oil and gas wells as of 2012 are identified on the map with gold dots. Urban areas are outlined with thick light-blue lines. Major interstates and state highways are identified by thick pink lines.

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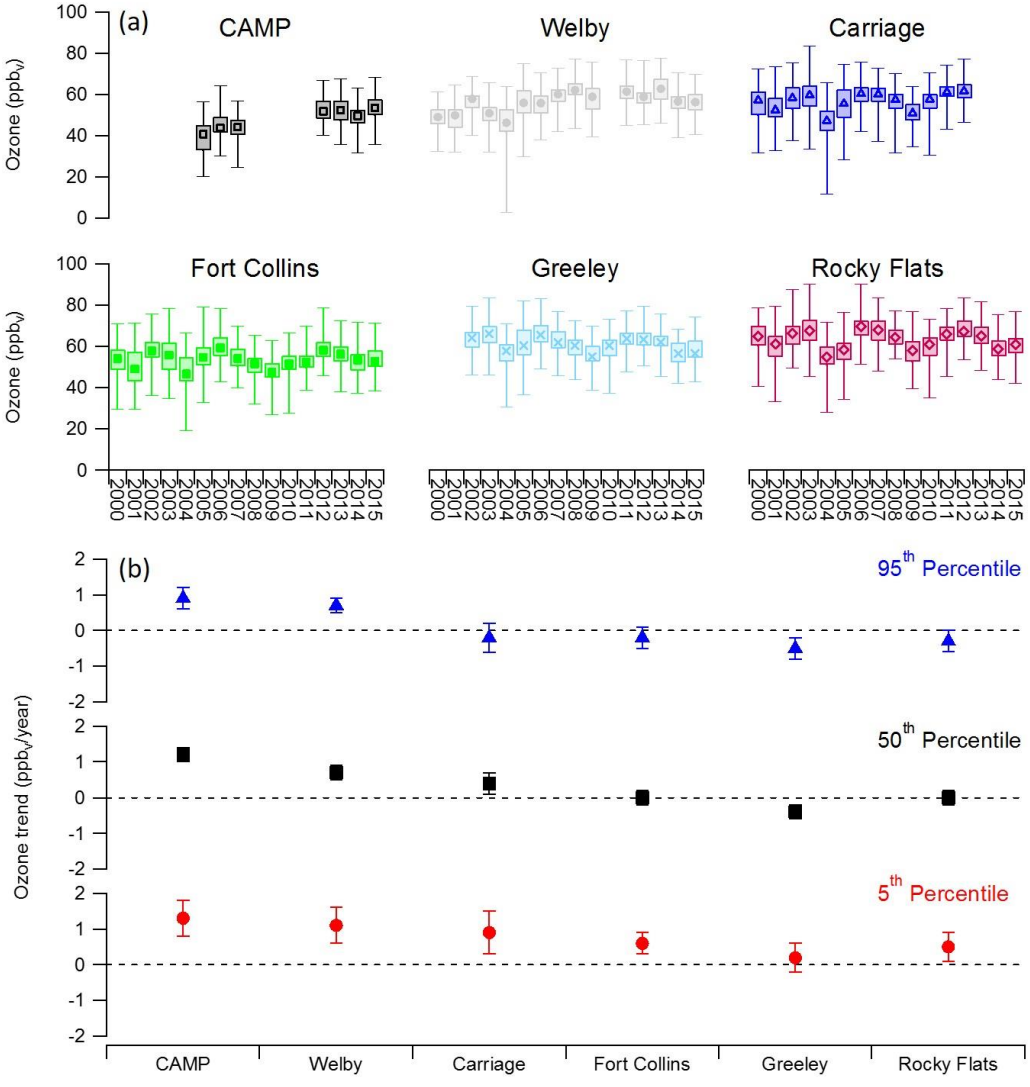

Figure 2. a) Trends in summer (June 1 – August 31) daytime (10:00 am – 4:00 pm) O_3 for six sites in the NFRMA between 2000 and 2015. Whiskers correspond to 5th and 9th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the marker corresponds to the 50th percentile. Percentiles 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_v O_3/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.

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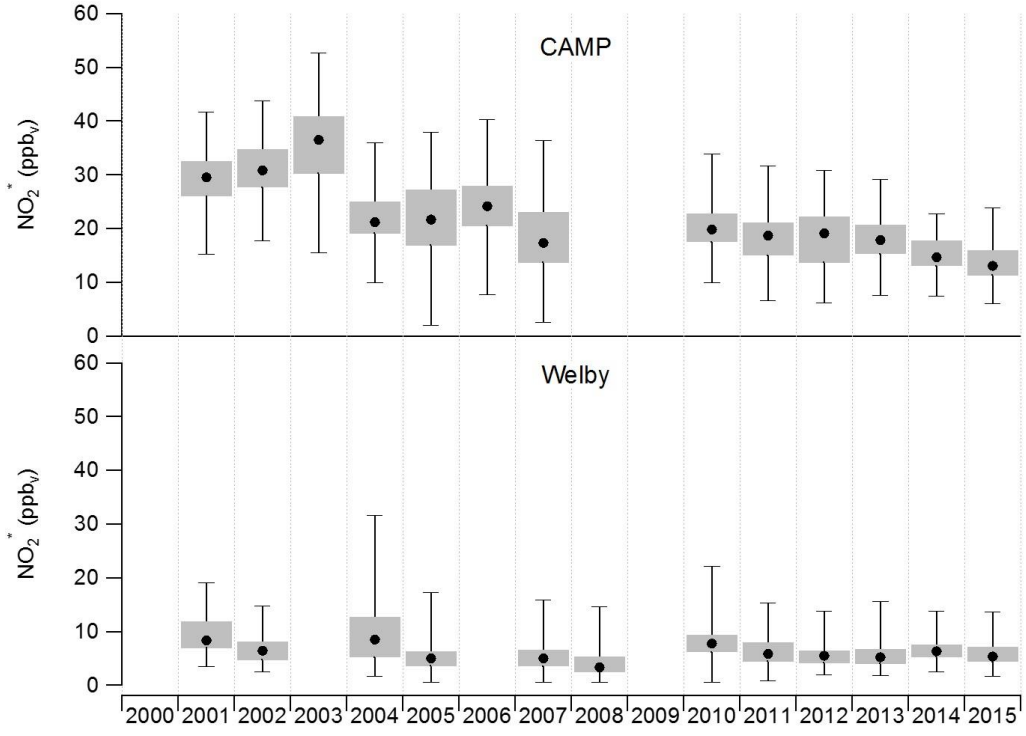

Figure 3. Box and whisker plots of NO_2* for the CAMP and Welby sites in Denver for all available data from 2000 – 2015. Whiskers correspond to 5th and 95th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the black marker corresponds to the 50th percentile.

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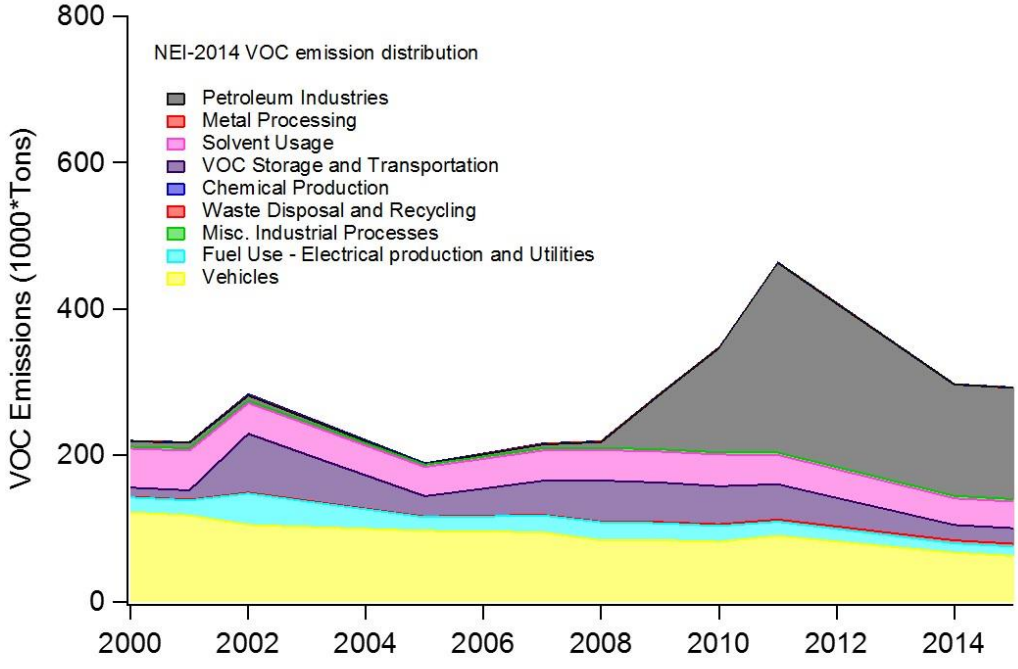

Figure 4: VOC emission estimates from EPA National Emissions Inventory 2014 (NEI-2014) for Colorado. Emission sources are separated by color, and are added to give the total VOC emission estimates for anthropogenic VOCs. Biogenic VOCs and VOCs from biomass burning (controlled fires and wildfires) are not included.

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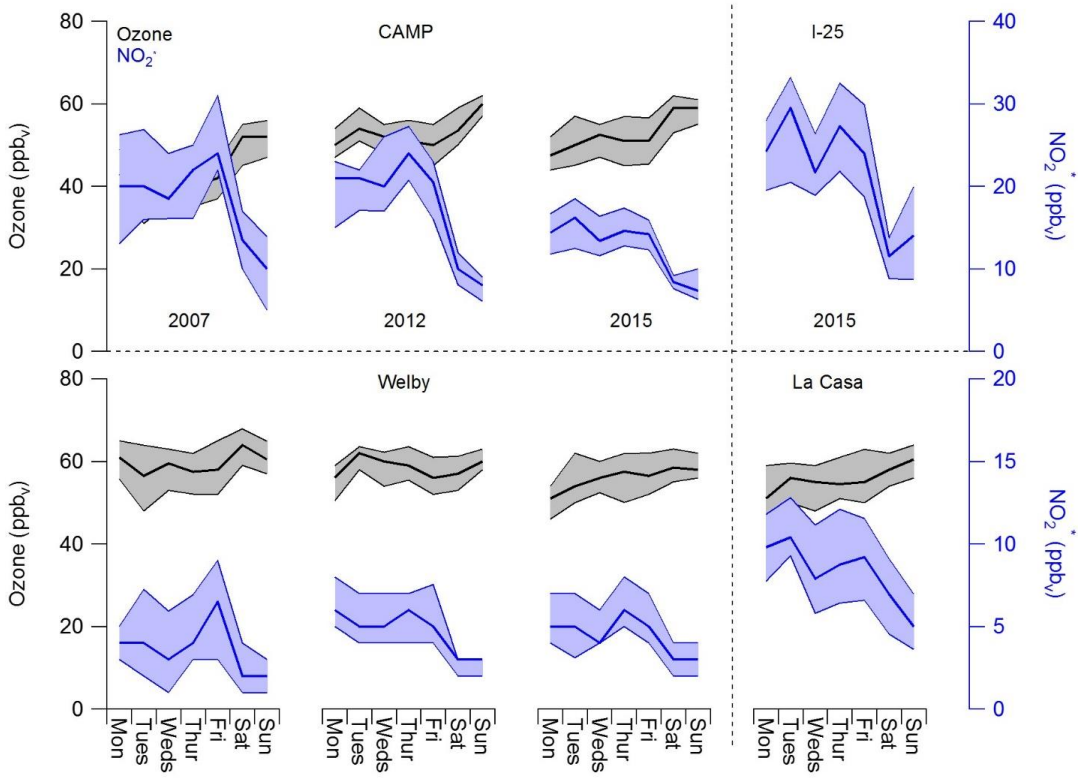

Figure 5. O_3 and NO_2* as a function of day of week for the CAMP, Welby, La Casa, and I-25 sites in Denver. All sites have plots for 2015, but only CAMP and Welby are plotted for 2007 and 2012 due to data availability. Solid lines are the 50th percentile for daytime hourly NO_2* (blue) and O_3 (black) 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.

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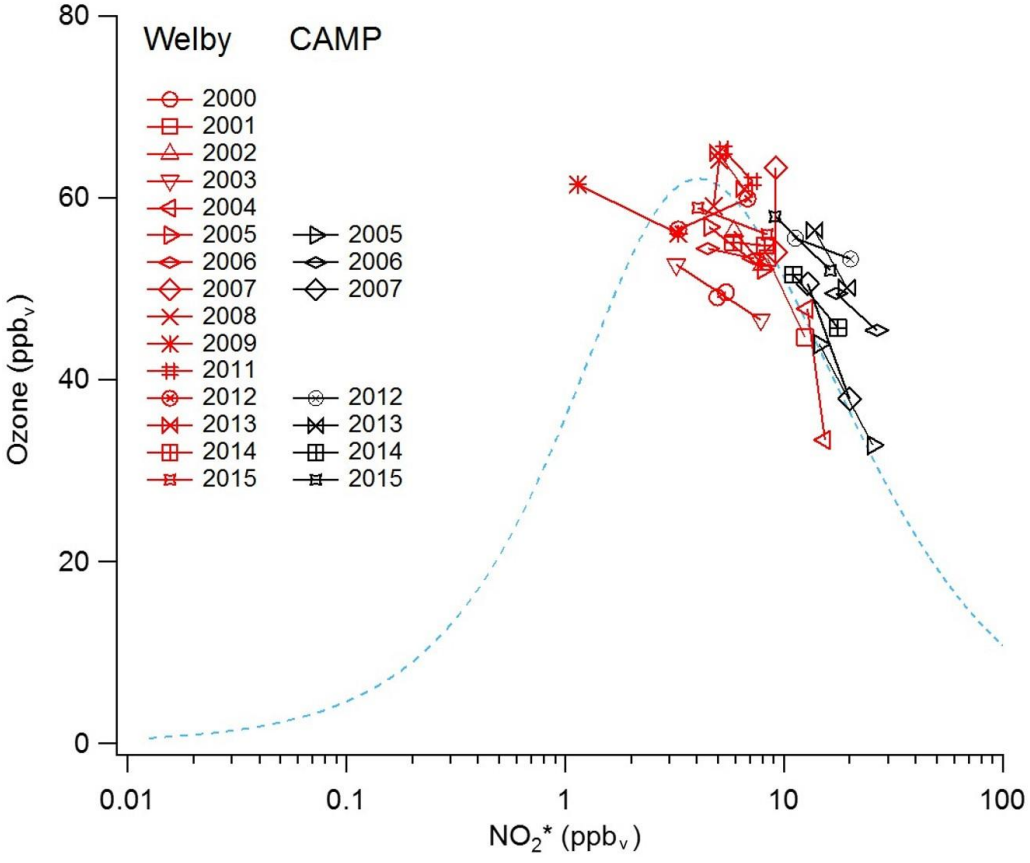

Figure 6. Weekday and weekend O_3 versus NO_2* for Welby (red) and CAMP (black) sites. Tethered symbols correspond to averages of Wednesday values for weekdays, and average Sunday values for weekends for each year depending on data availability. Standard errors of means for each year are <4 ppb_v for O_3 and <2 ppb_v for NO_2*. The dashed blue line is a visual aid to guide the readers eye to the non-linear O_3 curve, and was generated from the simple analytic model described by Farmer et al. (2011).

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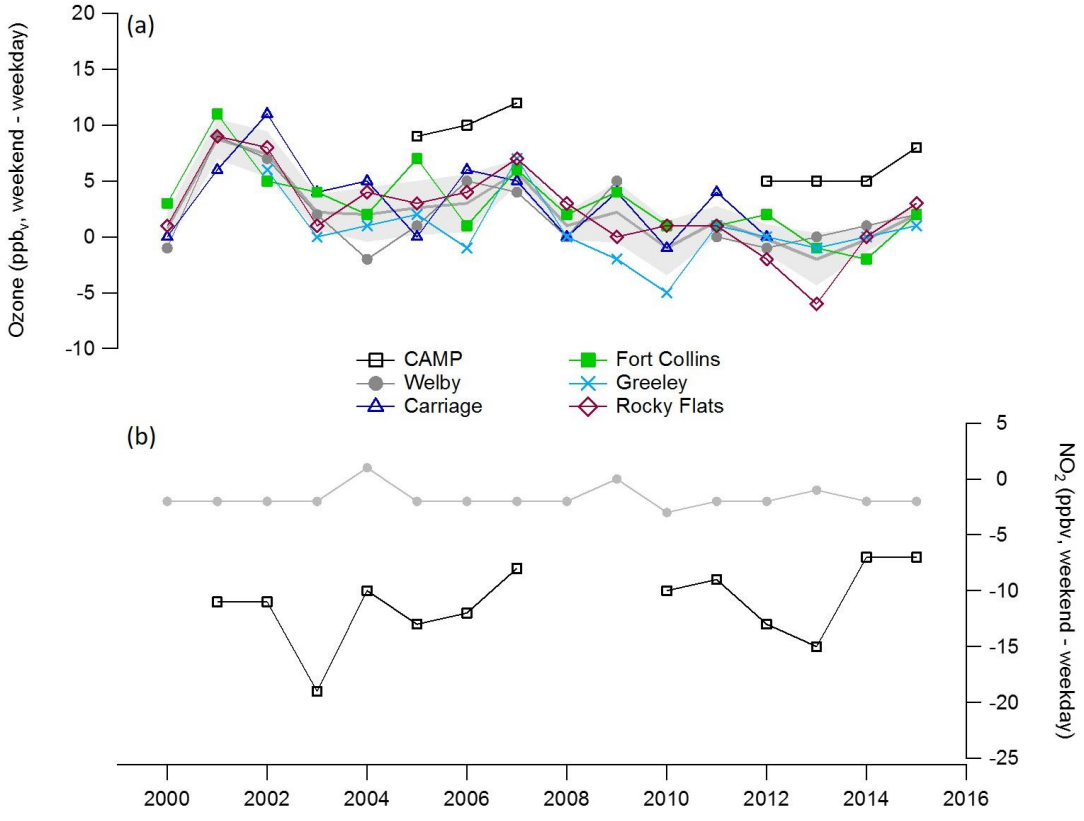

Figure 7: (a) The change in O_3 calculated as median weekend (Saturday to Sunday) minus summer weekday (Tuesday to Thursday) for the six NFRMA sites identified by color and marker for each year of available data. The solid grey line is the average median of the sites with the exception of CAMP. The inclusion 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.

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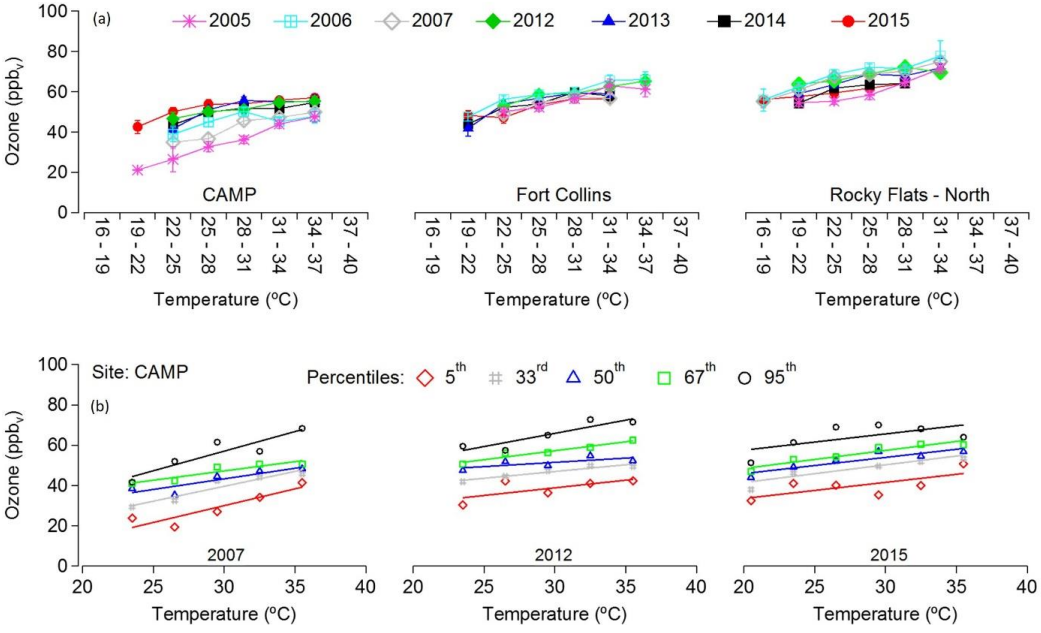

Figure 8. a) O_3 versus temperature for CAMP, Fort Collins, and Rocky Flats. O_3 is binned into 3°C temperature bins. Markers and colors represent yearly averages for each site. Error bars represent ± 1 standard error of the mean. Years were selected based on availability of overlapping data for multiple 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).

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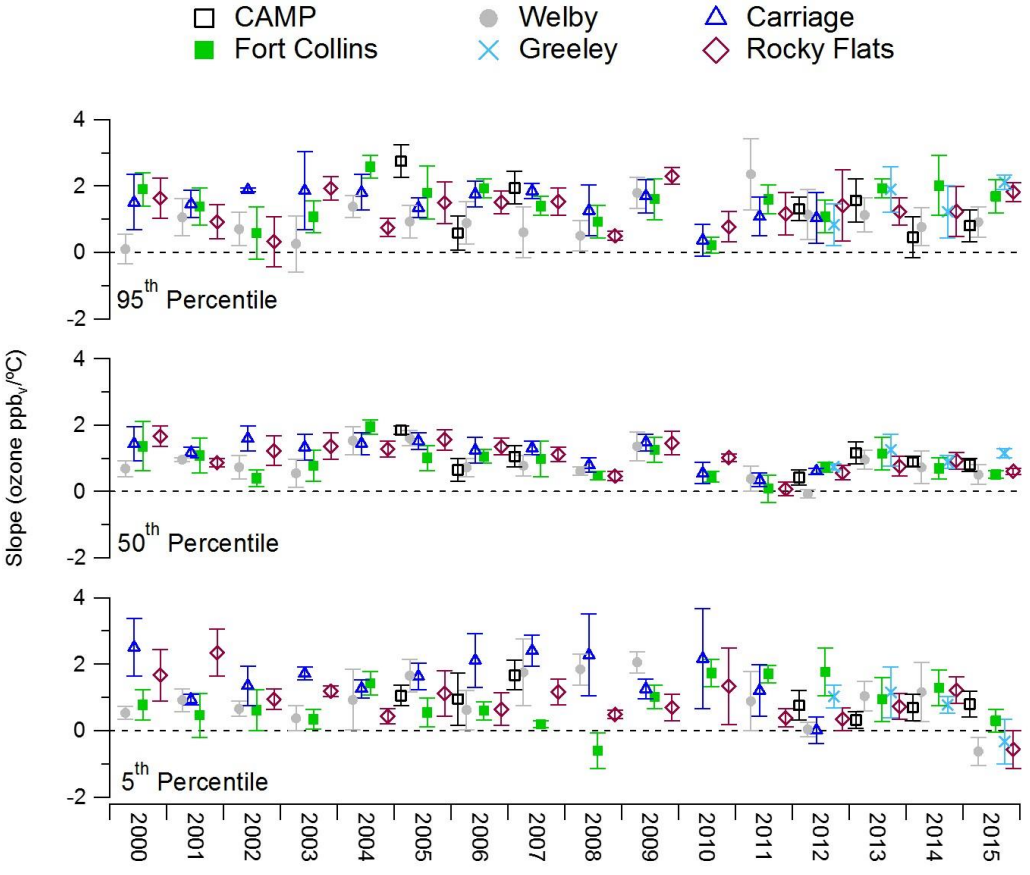

Figure 9. Slopes from one-sided linear regression of O_3 versus temperature (i.e. the temperature dependence of O_3) are binned into 5° Celsius bins for daytime (10:00 am – 4:00 pm) data at the 5th, 50th, and 95th percentiles for O_3. Data are shown for CAMP (black squares), Welby (grey solid circles), 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.

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Site	Latitude	Longitude	Elevation (m)	Measurements
CAMP	39.7512	-104.988	1591	O_3 & NO_2^*
Welby	39.8382	-104.955	1554	O_3 & NO_2^*
Carriage	39.7518	-105.031	1619	O_3
Fort Collins	40.5775	-105.079	1523	O_3
Greeley	40.3864	-104.737	1476	O_3
Rocky Flats	39.9128	-105.189	1784	O_3
I-25	39.7321	-105.015	1586	NO_2^*
La Casa	39.7795	-105.005	1601	O_3 & NO_2^*

Table 1. Summary of Measurements sites used in this analysis. Note that NO_2^* refers to the NO_2 detected by the EPA reference method, and thus includes a fraction of NO_y species.