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

Andrew A. Abeleira[1], Delphine K. Farmer[1]

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 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 due to a combination of decreasing NO_x emissions in a NO_x-saturated environment, and increased anthropogenic VOC emissions in the NFRMA. Further investigation of the weekend-weekday 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. In contrast to anthropogenic VOCs, 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, albeit smaller than many other U.S. locations, 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 coupled to temperature-dependent VOCs, this relationship is suppressed in drought years. We attribute this drought year suppression to decreased biogenic isoprene emissions due to long-term drought stress. Thus, while anthropogenic NO_x and VOCs likely dominate ozone production regimes in the NFRMA, biogenic VOCs may also impact regional ozone and its temperature dependence.

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:

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

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 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).

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

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. Alkoxy (RO) radicals form carbonyl-containing compounds and HO_2 (R7).

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

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

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

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

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

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

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

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 when comparing O_3 at the same sites for a longer period of 1980-2008 and shorter period of 1994-2008 that the predominant pattern was a change from a negative trend (decreasing O_3) during the longer period to no trend (stagnant O_3) in the shorter period, indicating that O_3 reductions 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. McDonald et al. (2013) report decreased VOC, CO, and NO_x automobile emissions in major US urban centers, and decreasing VOC/NO_x trends from 1990 to 2007 with a turnaround and small increase after 2007. This will affect local O_3 chemistry within the city and at downwind receptor sites. Lefohn et al. (2010) reported that the distributions of high 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. 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.

The intermountain West is an intriguing environment with potentially increasing background O_3 (Cooper et al., 2012). 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 (Brilli et al., 2007;Fortunati et al., 2008;Guenther, 2006). 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 levels (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), stratospheric intrusions (Lin et al., 2015), 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 weekend-weekday 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 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 likely 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, and studies have shown that background O_3 in the Western US has increased (Cooper et al., 2010;Parrish et al., 2004;Pfister et al., 2011;Weiss-Penzias et al., 2006). However, only the CAMP and Welby sites in Denver exhibit significant increasing O_3 with trends of 1.3 ± 1.0 ppb$_v$/year and 1.1 ± 1.0 ppb$_v$/year respectively at the 5th percentile with significance determined by passing an F-Test (section 2.2). The CAMP and Welby sites also exhibit statistically significant increases at the 50th (CAMP: 1.2 ± 0.4, Welby: 0.7 ± 0.5 ppb$_v$/year) and 95th (CAMP: 1.0 ± 0.9, Welby: 0.7 ± 0.5 ppb$_v$/year) percentiles. 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 95^{th} percentile, which could be a result of changing VOC and NO_2^* emissions in the 2010 - 2015 period.

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 -1.0 ± 0.6 and -1.4 ± 0.6 ppb_v/yr for the 50^{th} and 95^{th} percentiles for CAMP (Fig. 3). Welby exhibited a non-significant decreasing NO_2* trend at the 95^{th} percentile of -0.7 ± 0.8 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 per the EPA state average annual emissions trend (Fig. 4). To the best of our knowledge, the NFRMA does not have any long-term VOC datasets, but the EPA state average annual emissions trend 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). The US Energy Information Administration (EIA) report a 2-fold increase in active ONG wells from ~25,000 to ~40,000 from 2010 to 2012 (Fig. 4c) (US-EIA, 2017). However, we note the state average annual emissions 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_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 Weekend-Weekday effect in Denver, CO

The 'weekend-weekday effect' describes how anthropogenic emissions of O_3 precursors 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 weekends and weekdays from a decrease in heavy-duty truck traffic on weekends (Marr and Harley, 2002). VOCs are expected to be stable across the week, as major VOC sources do not vary by day-of-week. Despite this reduction in heavy-duty trucking 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 weekend-weekday 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 is located roughly 8-miles northeast from the three other sites, and borders a large lake and the Rocky Mountain Arsenal open space. Welby is 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 weekend-weekday effect in NO_2* existed for all years at the CAMP site, and most years at the Welby site with intermittent years with that do not have a clear difference in weekday and weekend NO_2^*. 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 $P(O_3)$. This analysis suggests that continued reductions 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 six available O_3 NFRMA sites and the two NO_2^* sites (Fig. 7a, 7b). A positive ΔO_3 reflects a higher O_3 concentration on the weekend than weekday, consistent with a NO_x-saturated system. A negative ΔO_3 is consistent with a NO_x-limited system in which O_3 decreases when NO_x decreases. The weekend-weekday effect exhibits a non-significant decreasing trend from 2000 to 2015 for yearly averages of the six sites. This is consistent with the decreased regional NO_x emissions, which would move the system from NO_x-saturated to peak $P(O_3)$ in the absence of large changes in VOC reactivity. 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 in NO_2* from weekdays to weekend. Measured NO_2* decreased at both CAMP and Welby (Fig. 3b), but with larger decreases at the CAMP site. The ΔNO_2* at Welby remained stable with an average value of -1.7 ± 0.9 ppb_v, while ΔNO_2* at the CAMP exhibited a statistically significant decrease of 0.6 ± 0.4 ΔNO_2* ppb_v/yr . The decreasing ΔNO_2* at the CAMP site appears to be converging with the ΔNO_2* at the Welby site. It is unlikely that traffic patterns are assimilating between the two sites, and a more plausible explanation is that emission control technologies on heavy duty commercial fleet vehicles are reducing the impact on emissions of those specific vehicles, and are reducing the measurable ΔNO_2* (Bishop et al., 2015). 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 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 suggests that the region is NO_x-saturated, but transitioning to a NO_x-limited region. Increases in O_3 may thus be 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 state average annual emissions suggested that petroleum-related VOCs have increased. However, we note that large increases in VOC reactivity shift the transition point between NO_x-limited and NO_x-saturated regions to higher NO_x concentrations. The clear regional decrease in the weekend-weekday effect, as evidenced by the decreasing ΔO_3 trend, indicates that the region is transitioning, and that any increases in VOC reactivity have not been so large as to dramatically inhibit this effect.

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 weekend-weekday 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 at the BAO site (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 allows us to investigate the extent to which biogenic VOCs influenced $P(O_3)$ in the NFRMA and the interannual variability of 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 impacting ambient 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 non-uniform temperature bins with bin size dictated by maintaining an equal number of data points in each temperature bin 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 the cross-over point between NO_x-saturated and NO_x-limited chemical regimes (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 do not dominate, VOC reactivity in the NFRMA (McDuffie et al., 2016;Abeleira et al., 2017). However, the six NFRMA sites exhibited significant variability in the 5^{th}, 50^{th}, and 95^{th} percentiles among the sites both within a given year and across years (Fig. 9). The 5^{th} and 95^{th} O_3 percentiles showed greater variability and larger uncertainties in the slopes than the 50^{th} 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), stratospheric intrusions (Lin et al., 2015), and local, temperature independent VOC emissions. In contrast, the 50^{th} 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 50^{th} percentile (Fig. 9). Specifically, years 2008, and 2011-2012 have suppressed O_3-temperature slopes for the 50^{th} 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 (2008, and 2011-2012) did correspond to years in which Colorado was in moderate-severe drought with little soil moisture (NOAA, 2017). Years 2002-2003 also exhibited moderate to severe drought conditions in Colorado, and some but not all sites exhibited suppressed O_3-temperature slopes.

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 2-4 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 50^{th} percentile – but not at the baseline 5^{th} percentile. A standard t-test showed that the 50^{th} and 95^{th} 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 heavy traffic region of 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 decreased across most of the country as anthropogenic NO_x and VOC emissions were 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 50^{th} and 95^{th} 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 two cases 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 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. Two time periods exhibit a clearly suppressed O_3-temperature dependence at the 50^{th} percentile (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. However, we emphasize that this effect is most clearly observed at the 50^{th} percentile, rather than the 5^{th} or 95^{th} percentiles, suggesting that biogenic VOCs have a greater influence on mean O_3 than on background or high O_3 events in the NFRMA. 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 (IPCC, 2014). The work herein suggests that drought can temporarily suppress the O_3-temperature penalty in the NFRMA and perhaps other NO_x-saturated regions by reducing temperature dependent biogenic VOC emissions.

Acknowledgements

We thank the National Oceanic and Atmospheric Administration for funding this work (Award# NA14OAR4310148).

Figures

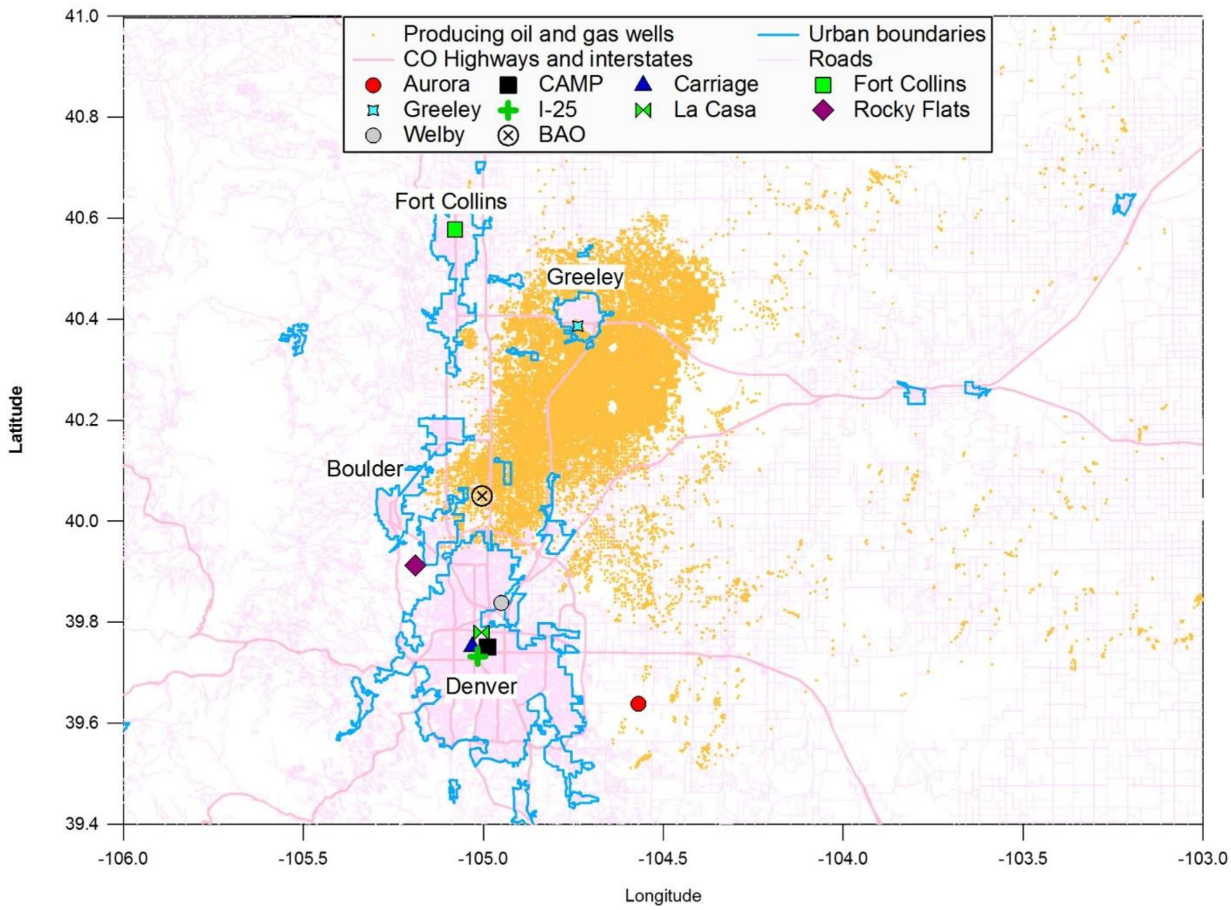

Figure 1. Site map for O_3 and NO_2 measurements in the NFRMA identified by shapes and colors. Producing oil and gas wells as of 2012 are identified on the map with gold dots. Urban areas are outlined with thick light-blue lines. Major interstates and state highways are identified by thick pink lines.

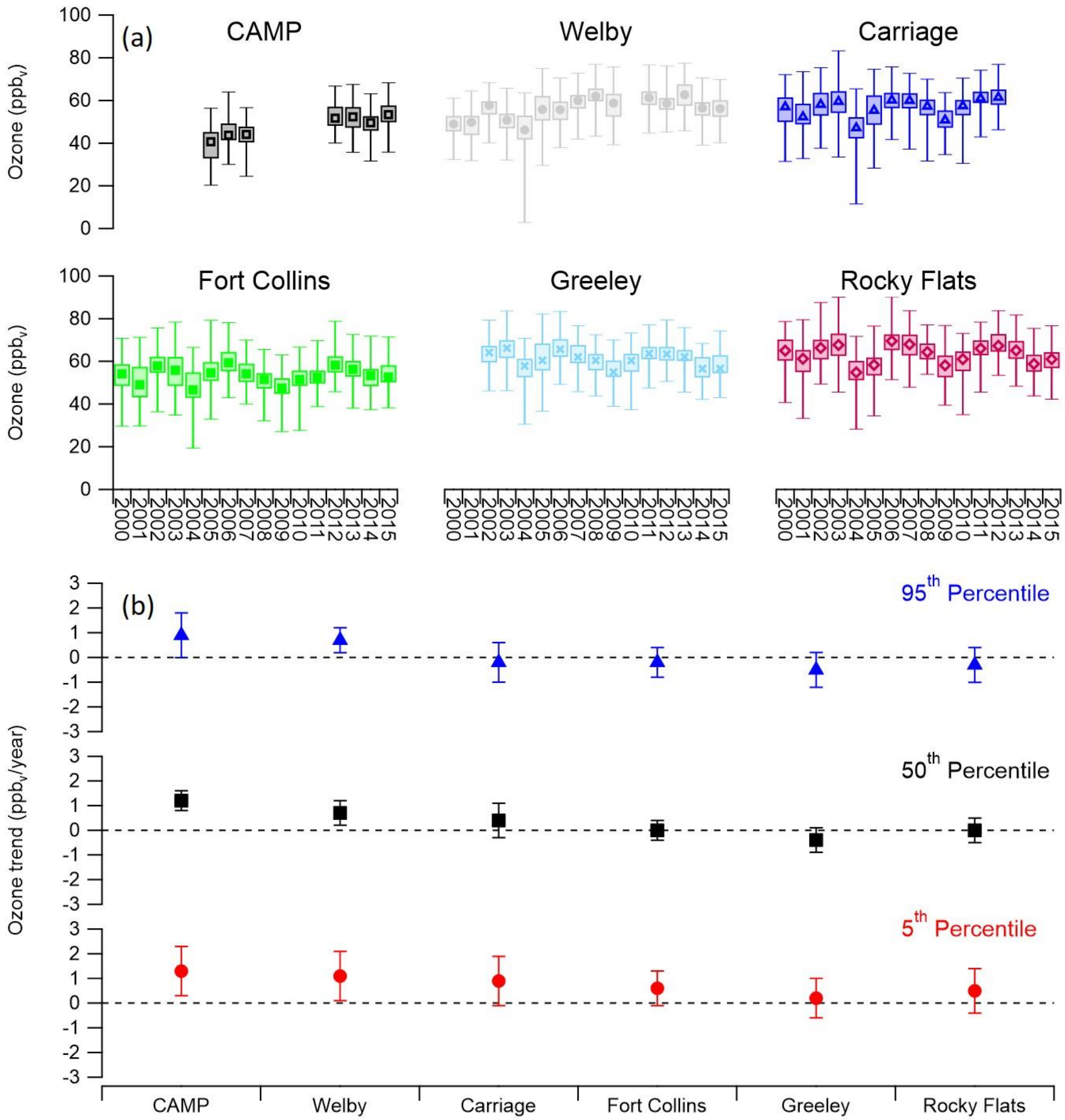

Figure 2. (a) Trends in summer (June 1 – August 31) daytime (10:00 am – 4:00 pm) O_3 for six sites in the NFRMA between 2000 and 2015. Whiskers correspond to 5th and 9th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the marker corresponds to the 50th percentile. Percentiles were calculated from daily daytime averages of hourly 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 represent the 95% confidence interval around the ozone/year linear regression slope.

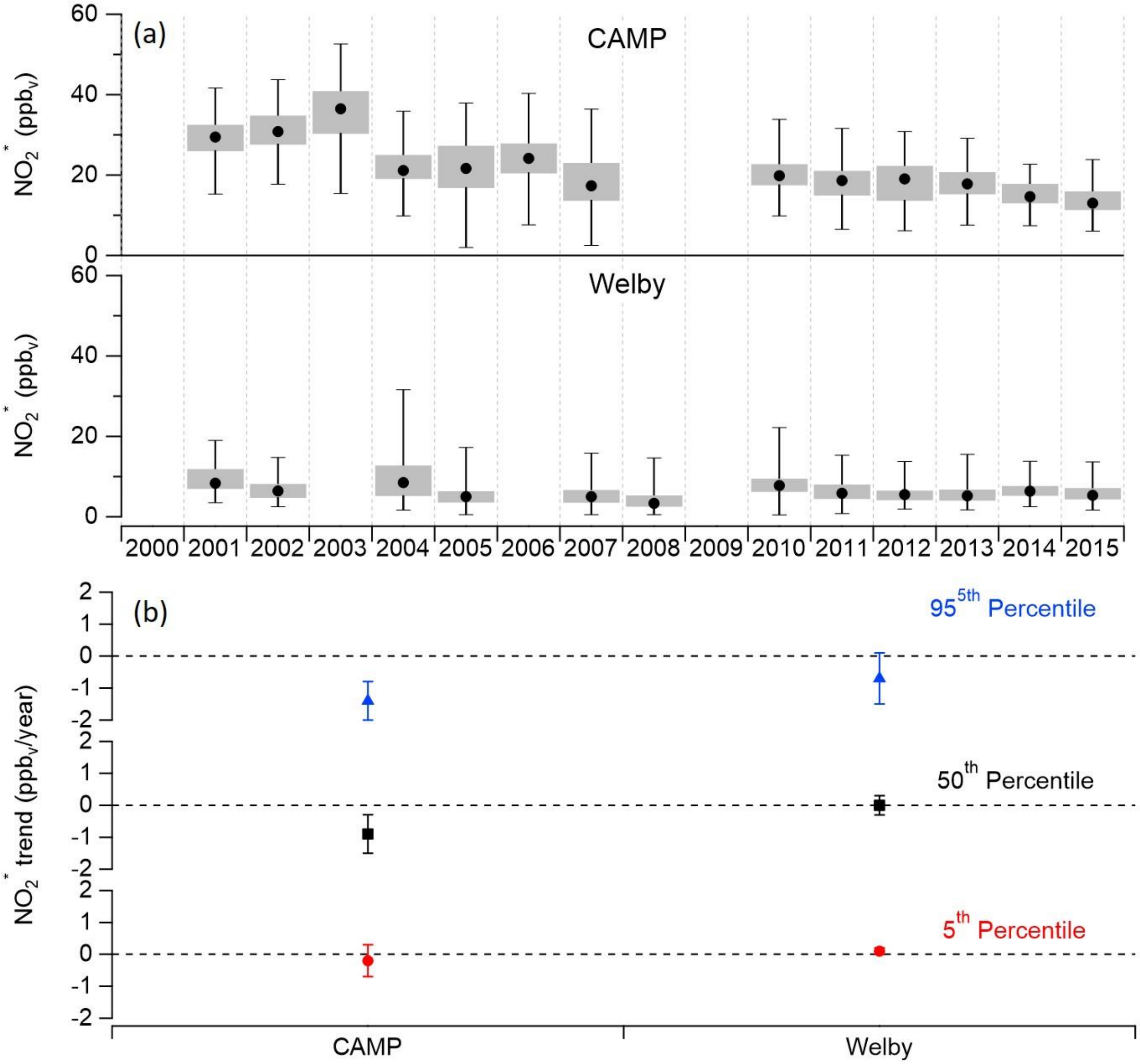

Figure 3. (a) Trends in summer (June 1 – August 31) daytime (10:00 am – 4:00 pm) NO_2* for the CAMP and Welby sites in Denver for all available data from 2000 – 2015. Whiskers correspond to 5th and 95th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the black marker corresponds to the 50th percentile. (b) NO_2^* temporal trends were determined as the slope from annual trends (ppb$_v$ NO_2/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 represent the 95% confidence interval around the NO_2*/year linear regression slope.

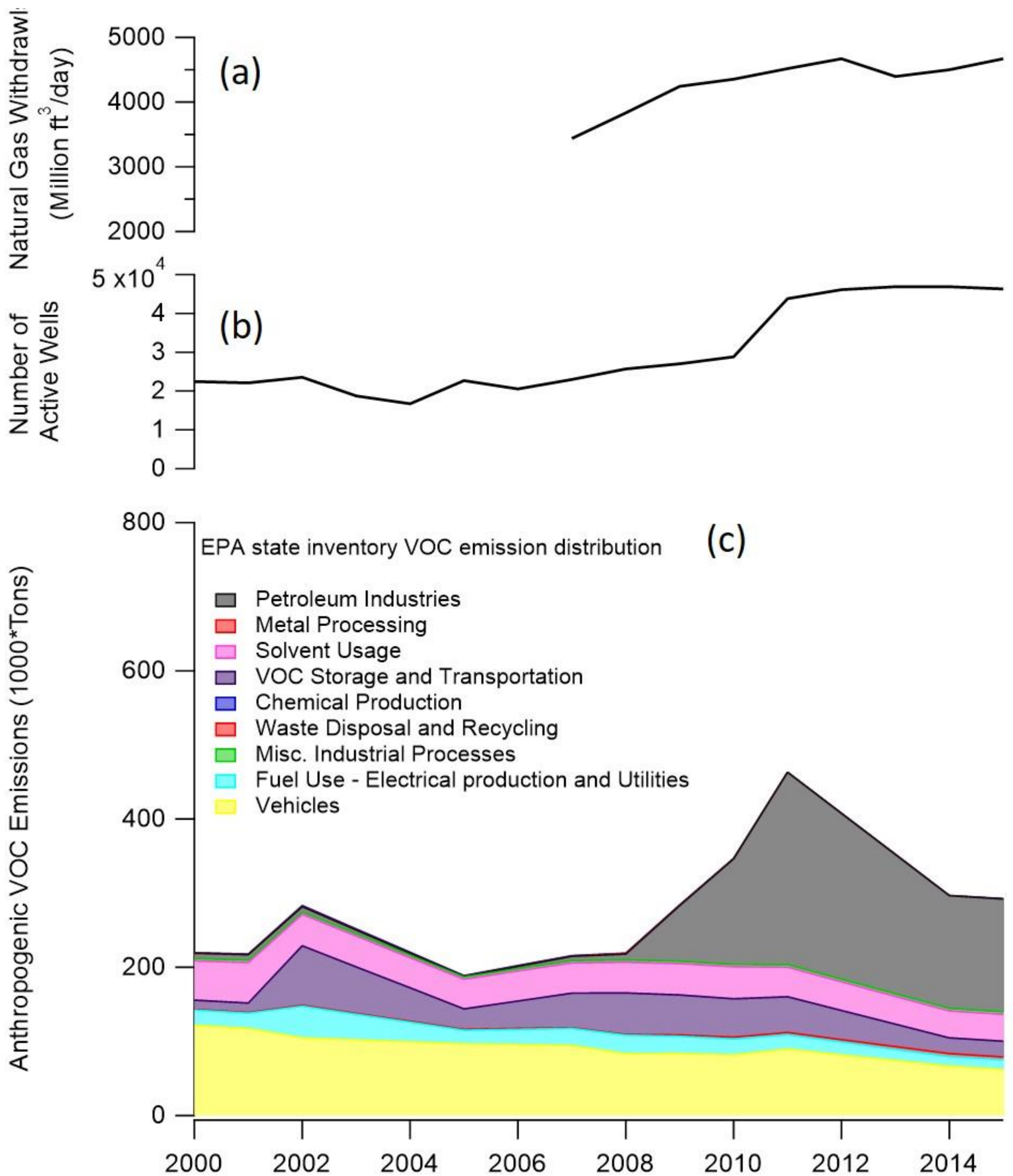

Figure 4: (a) Estimated yearly averaged natural gas withdrawals in Colorado (US-EIA, 2017), (b) Yearly average number of active ONG well operations (US-EIA, 2017). (c) Anthropogenic VOC emission estimates from the EPA state average annual emissions trend for Colorado. Emission sources are separated by 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.

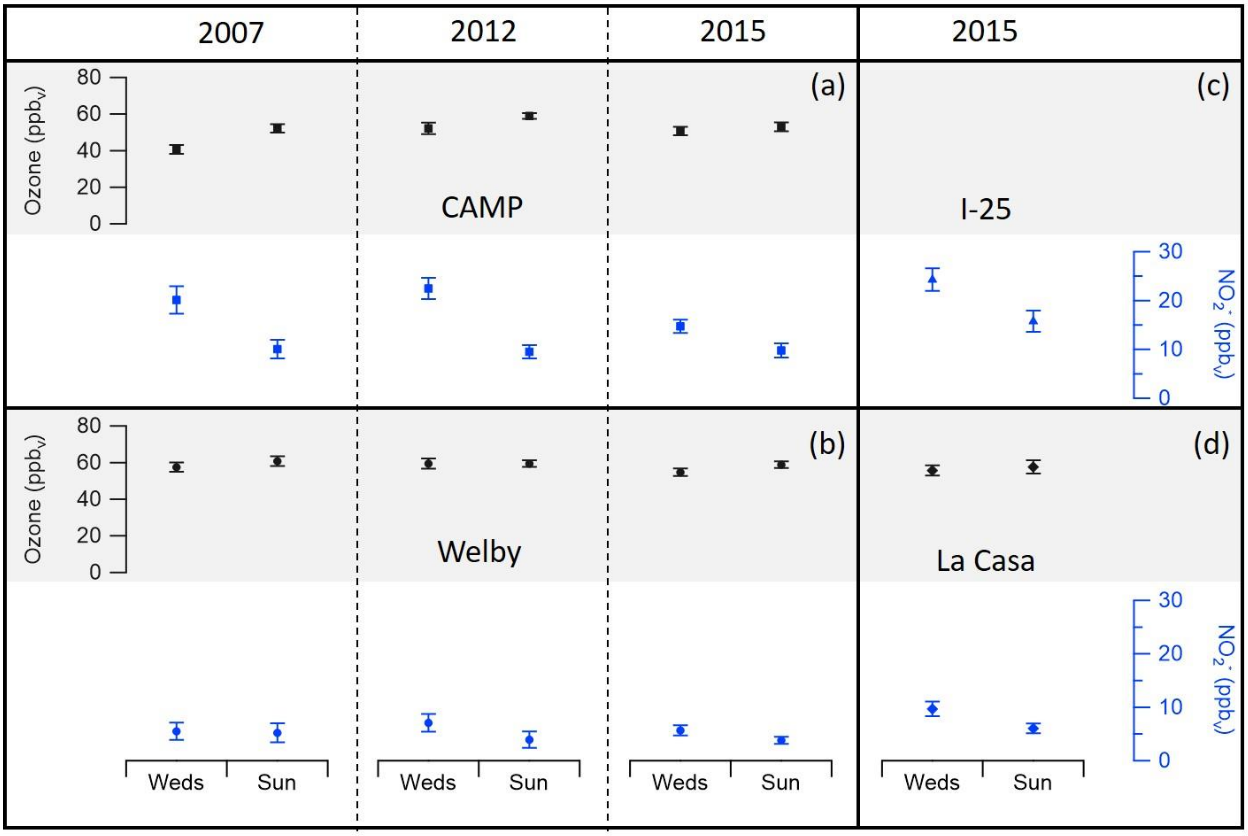

Figure 5. Weekend-Weekday analysis (Sunday vs Wednesday) for O_3 (black with shading) and NO_2* (blue) for the CAMP (a, squares), Welby (b, circles), and the La Casa (c, diamonds) sites in Denver. I-25 (d, triangles) is limited to NO_2^* due to data availability. All sites have plots for 2015, but only CAMP (a) and Welby (b) are additionally plotted for 2007 and 2012 due to data availability. Wednesday is representative of weekday NO_2^* and typically is not different than the average of Tuesday, Wednesday and Thursday at a 95% confidence for this dataset. Monday, Friday, and Saturday are considered carry-over or "mixed" days between weekdays and weekends and are ignored. Error bars represent a 95% confidence intervals around the summertime mean of Wednesday or Sunday O_3 or NO_2^*.

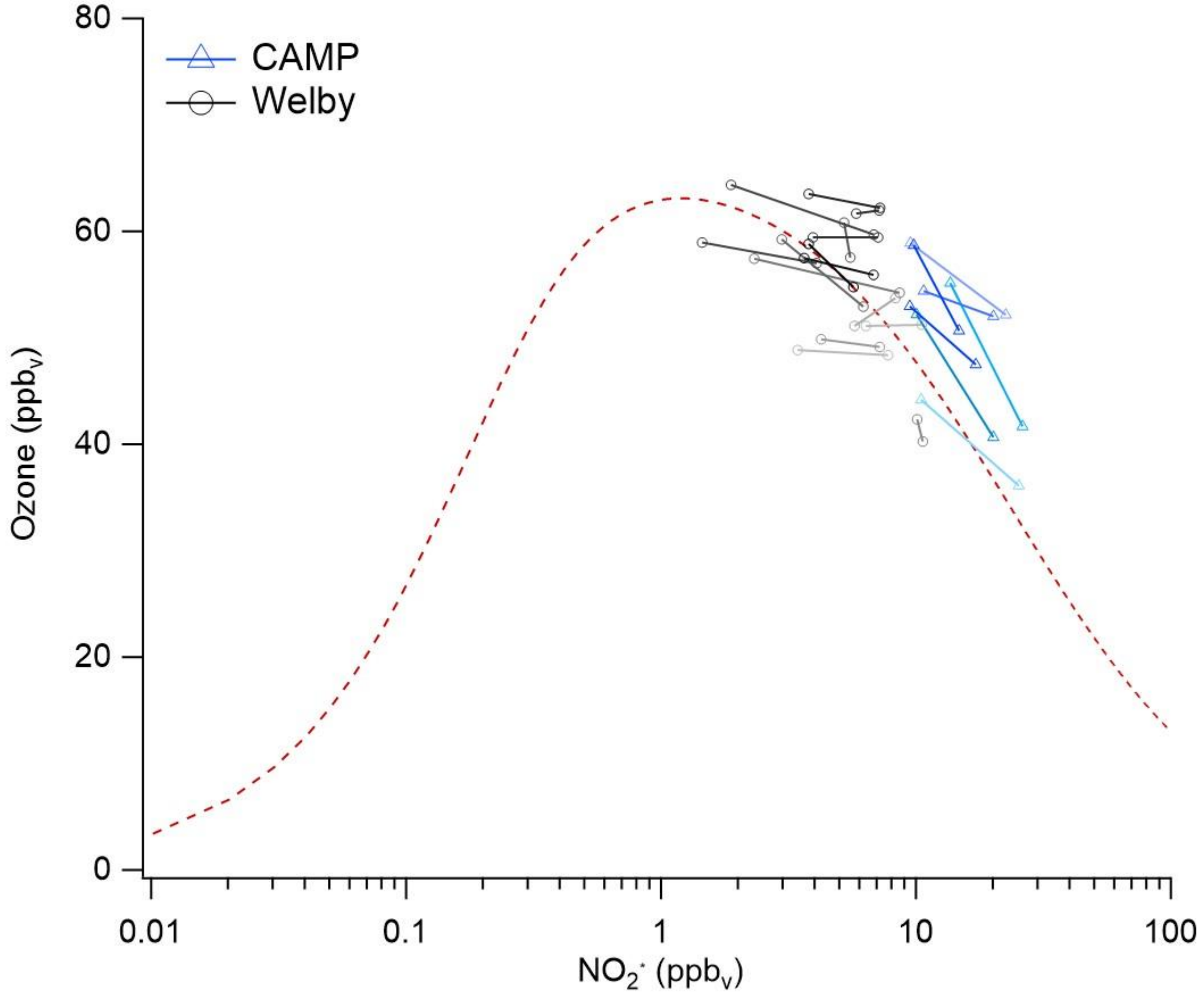

Figure 6. Weekday and weekend O_3 versus NO_2* for Welby (black) and CAMP (blue) sites. Tethered symbols correspond to average Wednesday values for weekdays, and average Sunday values for weekends for each year depending on data availability. The colour shading corresponds to year, with the lightest shade corresponding to the earliest year (2000 for Welby, 2005 for CAMP) and 2015 as the darkest shade. The 95% confidence intervals for each year are <5 ppb_v for O_3 and <2.5 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).

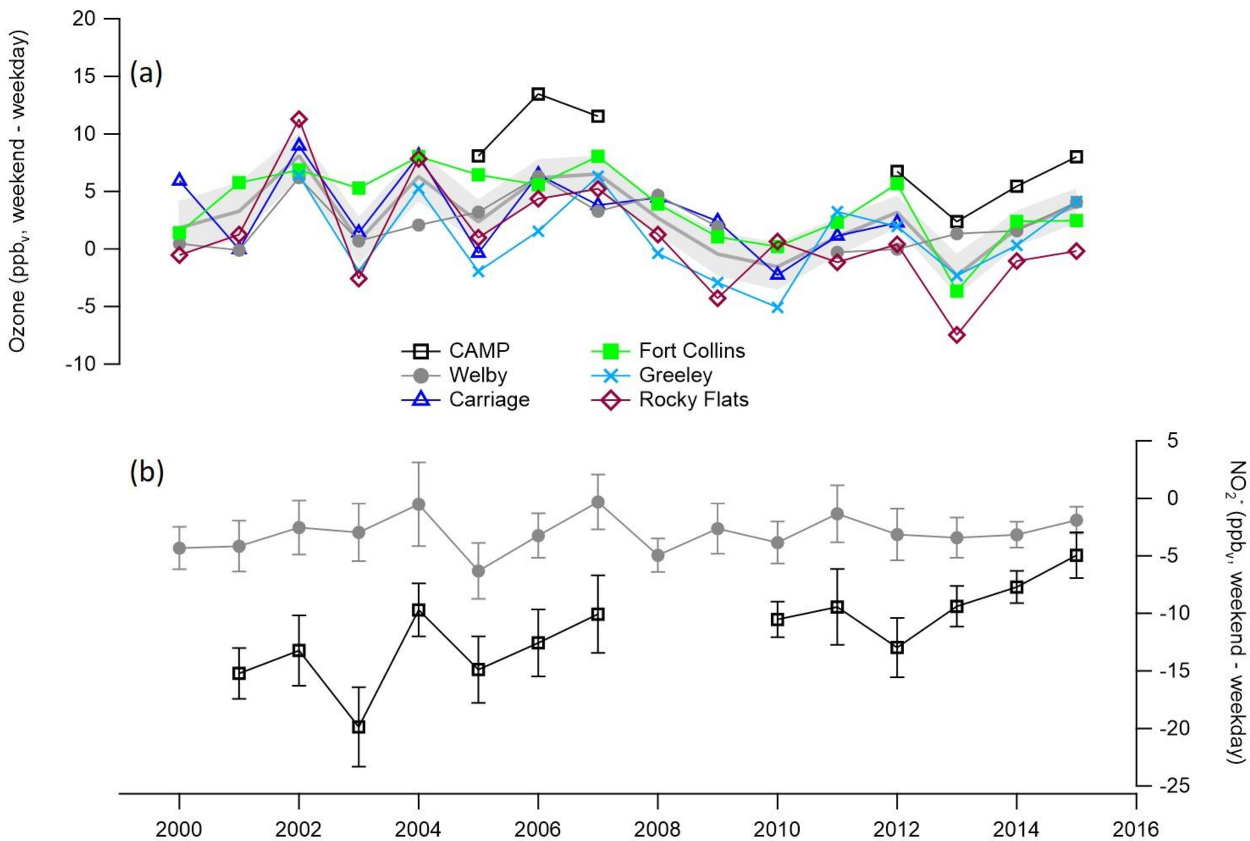

Figure 7: (a) The change in O_3 calculated as average weekend (Sunday) minus weekday (Wednesday) O_3 for the six NFRMA sites identified by color and marker. The solid grey line is the average of the sites. The inclusion of a site in the averaging for a given year was dependent on available data for that year. The light grey shading represents ± the 95% confidence interval of all Wednesday and Sunday hourly values for each year for sites with available data. (b) The change in NO_2* is calculated identically to O_3 in (a) for the CAMP and Welby sites, and the error bars represent the 95% confidence interval of the averages.

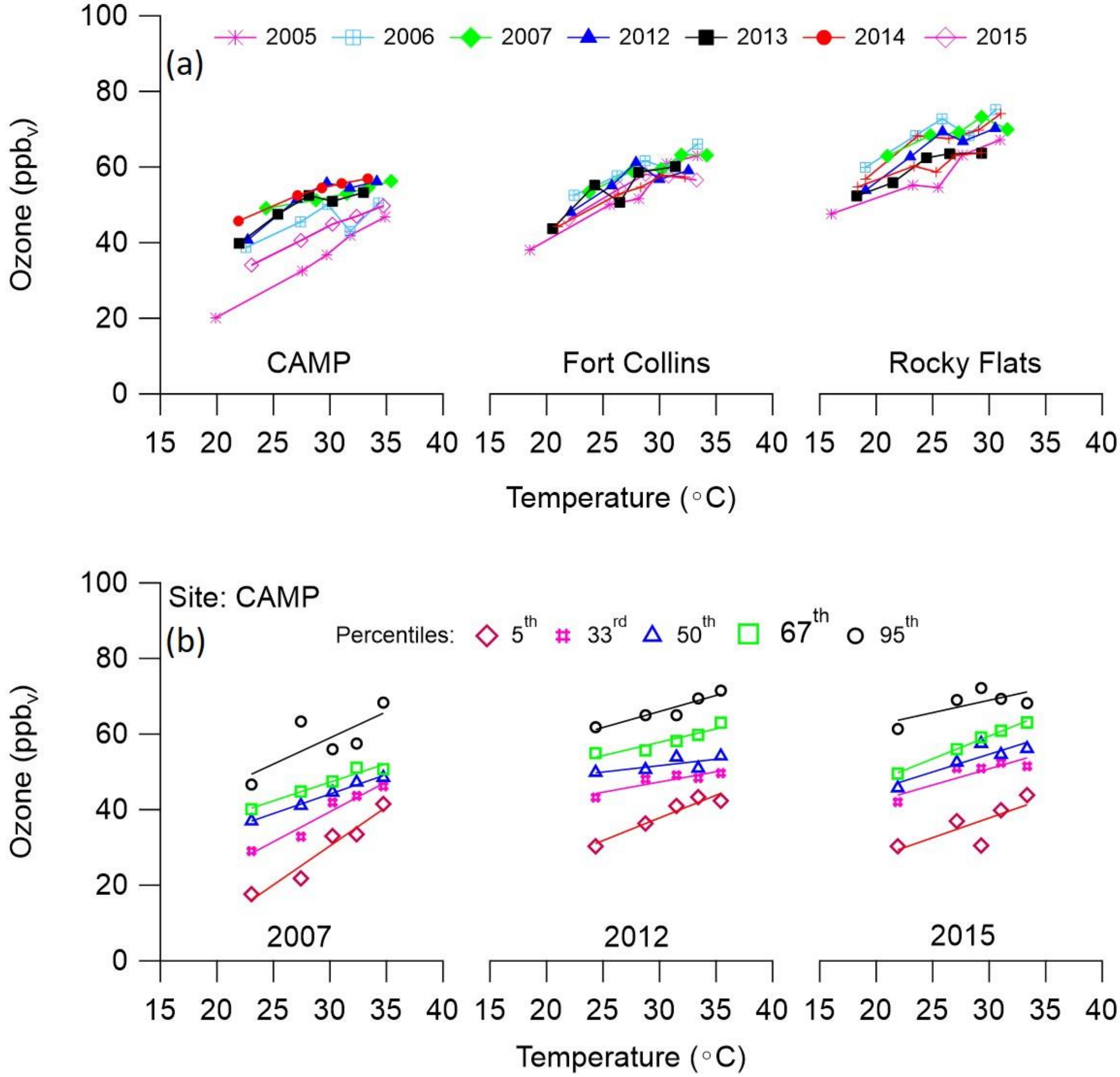

Figure 8. a) O_3 versus temperature for CAMP, Fort Collins, and Rocky Flats. Hourly O_3 is binned by hourly temperature with bins containing 51 - 110 points for O_3 and temperature depending on data availability at a site. The temperature bins typically contained 100 – 110 data points (>90% of temperature bins for all sites in all available years). Average O_3 of each bin is plotted versus the average temperature of each bin. Markers and colors represent yearly averages for each site. Error bars were left off for visual clarity, but the 95% confidence interval around the yearly bin averages are typically <8 ppb_v. Years were selected based on availability of overlapping data for multiple sites. b) One-sided linear regressions of equal point temperature bins for the 5th (red open diamond), 33rd (pink hash), 50th (green open triangle), 67th (blue open square), and 95th (black open circle) percentiles for the CAMP site for 2007 (left), 2012 (middle), and 2015 (right).

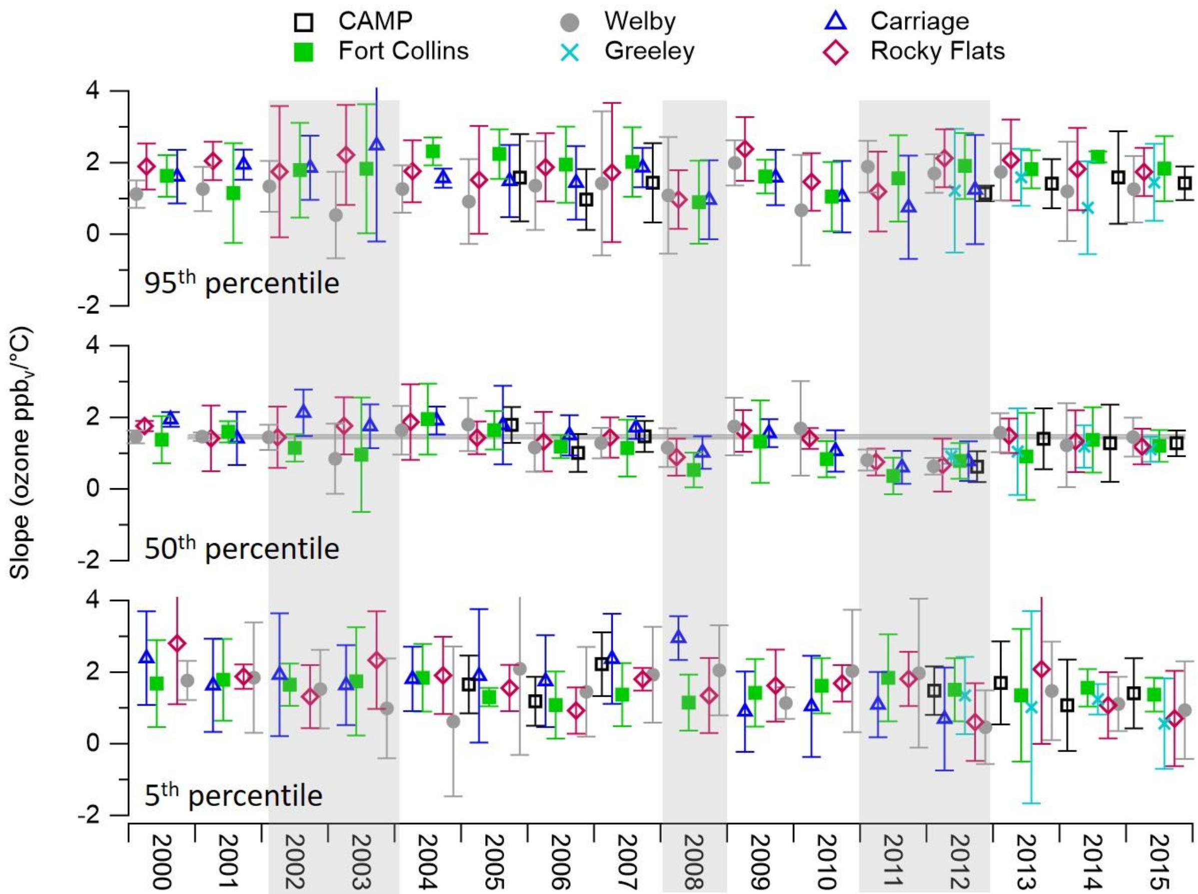

Figure 9. Slopes from one-sided linear regression of O_3 versus temperature (i.e. the temperature dependence of O_3). Hourly O_3 (10:00 am – 4:00 pm) is binned by hourly temperature with bins containing 51 - 110 points for O_3 and temperature depending on data availability at a site. The temperature bins typically contained 100 – 110 data points (>90% of temperature bins for all sites in all available years). The slopes of O_3 versus temperature for the 5th, 50th, and 95th percentiles for the O_3-tempetature bins are shown. 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 ± 95% confidence interval of the slopes. Faint grey line across the 50th percentile is the average slope bounded by the 95% confidence interval for years excluding 2008, 2011, and 2012.

References

Abeleira, A., Pollack, I., Sive, B. C., Zhou, Y., Fischer, E. V., and Farmer, D.: Source Characterization of Volatile Organic Compounds in the Colorado Northern Front Range Metropolitan Area during Spring and Summer 2015, Journal of Geophysical Research, In Press, 2017.

AMA: State of the Air 2015, in, edited by: Association, A. L., Chicago, IL, 2015.

Avnery, S., Mauzerall, D. L., Liu, J., and Horowitz, L. W.: Global crop yield reductions due to surface ozone exposure: 1. Year 2000 crop production losses and economic damage, Atmospheric Environment, 45, 2284-2296, 2011.

Bishop, G. A., Hottor-Raguindin, R., Stedman, D. H., McClintock, P., Theobald, E., Johnson, J. D., Lee, D.-W., Zietsman, J., and Misra, C.: On-road Heavy-duty Vehicle Emissions Monitoring System, Environmental Science & Technology, 49, 1639-1645, 10.1021/es505534e, 2015.

Bloomer, B. J., Stehr, J. W., Piety, C. A., Salawitch, R. J., and Dickerson, R. R.: Observed relationships of ozone air pollution with temperature and emissions, Geophysical Research Letters, 36, 2009.

Brilli, F., Barta, C., Fortunati, A., Lerdau, M., Loreto, F., and Centritto, M.: Response of isoprene emission and carbon metabolism to drought in white poplar (Populus alba) saplings, New Phytologist, 175, 244-254, 2007.

CARB: The Ozone Weekend Effect in California, California Air Reasearch Board Planning and Technical Support Division, 2003.

CDPHE: Denver Metro Area & North Front Range Ozone Action Plan., in, Denver, CO, 2008.

CDPHE: For Recommended 8-Hour Ozone Designations, in, edited by: Environment, C. D. o. P. H. a., CDPHE, Denver, Colorado, 2009.

CDPHE: Control of Ozone Via Ozone Precursors and Control of Hydocarbons Via Oil and Gas Emissions., in, Denver, CO, 2014.

CDPHE: Moderate area ozone SIP for the Denver Metro and North Front Range nonattaiment area., in, Denver, CO, 2016.

Cleveland, W. S., Graedel, T. E., Kleiner, B., and Warner, J.: Sunday and workday variations in photochemical air pollutants in New Jersey and New York, Science, 186, 1037-1038, 1974.

Cooper, O., Parrish, D., Stohl, A., Trainer, M., Nédélec, P., Thouret, V., Cammas, J.-P., Oltmans, S., Johnson, B., and Tarasick, D.: Increasing springtime ozone mixing ratios in the free troposphere over western North America, Nature, 463, 344-348, 2010.

Cooper, O. R., Gao, R. S., Tarasick, D., Leblanc, T., and Sweeney, C.: Long-term ozone trends at rural ozone monitoring sites across the United States, 1990–2010, Journal of Geophysical Research: Atmospheres, 117, 2012.

Davis, J., Cox, W., Reff, A., and Dolwick, P.: A comparison of CMAQ-based and observation-based statistical models relating ozone to meteorological parameters, Atmospheric environment, 45, 3481-3487, 2011.

Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos Villegas, C. R., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys., 7, 2691-2704, 10.5194/acp-7-2691-2007, 2007.

Ek, M., and Holtslag, A.: Influence of soil moisture on boundary layer cloud development, Journal of hydrometeorology, 5, 86-99, 2004.

EPA: National Ambient Air Quality Standards for Ozone; Propose Rule, in, edited by: EPA, 2014.

Ozone Trends: https://www.epa.gov/air-trends/ozone-trends, access: 1/19, 2016a.

Air Pollutants Emission Trends: https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data, access: 1/19, 2016b.

Farmer, D., Perring, A., Wooldridge, P., Blake, D., Baker, A., Meinardi, S., Huey, L., Tanner, D., Vargas, O., and Cohen, R.: Impact of organic nitrates on urban ozone production, Atmospheric Chemistry and Physics, 11, 4085-4094, 2011.
Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., Paulot, F., Singh, H. B., Roiger, A., Ries, L., Talbot, R. W., Dzepina, K., and Pandey Deolal, S.: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, Atmos. Chem. Phys., 14, 2679-2698, 10.5194/acp-14-2679-2014, 2014.
Fortunati, A., Barta, C., Brilli, F., Centritto, M., Zimmer, I., Schnitzler, J. P., and Loreto, F.: Isoprene emission is not temperature-dependent during and after severe drought-stress: a physiological and biochemical analysis, The Plant Journal, 55, 687-697, 2008.
Fujita, E. M., Stockwell, W. R., Campbell, D. E., Keislar, R. E., and Lawson, D. R.: Evolution of the magnitude and spatial extent of the weekend ozone effect in California's South Coast Air Basin, 1981–2000, Journal of the Air & Waste Management Association, 53, 802-815, 2003.
Gilman, J. B., Lerner, B. M., Kuster, W. C., and de Gouw, J. A.: Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado, Environ Sci Technol, 47, 1297-1305, 10.1021/es304119a, 2013.
Guenther, A., Zimmerman, P., Klinger, L., Greenberg, J., Ennis, C., Davis, K., Pollock, W., Westberg, H., Allwine, G., and Geron, C.: Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements, Journal of Geophysical Research: Atmospheres, 101, 1345-1359, 1996.
Guenther, A.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmospheric Chemistry and Physics, 6, 2006.
Heuss, J. M., Kahlbaum, D. F., and Wolff, G. T.: Weekday/weekend ozone differences: what can we learn from them?, Journal of the Air & Waste Management Association, 53, 772-788, 2003.
IPCC: Climate Change 2014–Impacts, Adaptation and Vulnerability: Regional Aspects, in, edited by: Change, I. P. o. C., Cambridge University Press, 2014.
Jacob, D. J., and Winner, D. A.: Effect of climate change on air quality, Atmospheric environment, 43, 51-63, 2009.
Lefohn, A. S., Shadwick, D., and Oltmans, S. J.: Characterizing changes in surface ozone levels in metropolitan and rural areas in the United States for 1980–2008 and 1994–2008, Atmospheric Environment, 44, 5199-5210, 2010.
Lin, M., Fiore, A. M., Horowitz, L. W., Langford, A. O., Oltmans, S. J., Tarasick, D., and Rieder, H. E.: Climate variability modulates western US ozone air quality in spring via deep stratospheric intrusions, Nature communications, 6, 2015.
Lindas, J., Farmer, D., Pollack, I., Abeleira, A., Flocke, F., Roscioli, R., Herndon, S. C., and Fischer, E. V.: The impact of aged wildfire smoke on atmospheric composition and ozone in the Colorado Front Range in summer 2015, Atmospheric Chemistry and Physics, in preparation, 2017.
Marr, L. C., and Harley, R. A.: Modeling the Effect of Weekday− Weekend Differences in Motor Vehicle Emissions on Photochemical Air Pollution in Central California, Environmental science & technology, 36, 4099-4106, 2002.
McDonald, B. C., Gentner, D. R., Goldstein, A. H., and Harley, R. A.: Long-term trends in motor vehicle emissions in US urban areas, Environmental science & technology, 47, 10022-10031, 2013.
McDuffie, E. E., Edwards, P. M., Gilman, J. B., Lerner, B. M., Dubé, W. P., Trainer, M., Wolfe, D. E., Angevine, W. M., deGouw, J., and Williams, E. J.: Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range, Journal of Geophysical Research: Atmospheres, 121, 8712-8729, 2016.
Murphy, J. G., Day, D. A., Cleary, P. A., Wooldridge, P. J., Millet, D. B., Goldstein, A. H., and Cohen, R. C.: The weekend effect within and downwind of Sacramento–Part 1: Observations of ozone, nitrogen oxides, and VOC reactivity, Atmospheric Chemistry and Physics, 7, 5327-5339, 2007.

North American Drought Monitor: https://www.ncdc.noaa.gov/temp-and-precip/drought/nadm/maps, access: 2/1, 2017.

Palut, M. P. J., and Canziani, O. F.: Contribution of working group II to the fourth assessment report of the intergovernmental panel on climate change, in, Cambridge University Press, 2007.

Parrish, D., Dunlea, E., Atlas, E., Schauffler, S., Donnelly, S., Stroud, V., Goldstein, A., Millet, D., McKay, M., and Jaffe, D.: Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions, Journal of Geophysical Research: Atmospheres, 109, 2004.

Pétron, G., Frost, G., Miller, B. R., Hirsch, A. I., Montzka, S. A., Karion, A., Trainer, M., Sweeney, C., Andrews, A. E., Miller, L., Kofler, J., Bar-Ilan, A., Dlugokencky, E. J., Patrick, L., Moore, C. T., Ryerson, T. B., Siso, C., Kolodzey, W., Lang, P. M., Conway, T., Novelli, P., Masarie, K., Hall, B., Guenther, D., Kitzis, D., Miller, J., Welsh, D., Wolfe, D., Neff, W., and Tans, P.: Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study, Journal of Geophysical Research: Atmospheres, 117, n/a-n/a, 10.1029/2011jd016360, 2012.

Pfister, G., Parrish, D., Worden, H., Emmons, L., Edwards, D., Wiedinmyer, C., Diskin, G., Huey, G., Oltmans, S., and Thouret, V.: Characterizing summertime chemical boundary conditions for airmasses entering the US West Coast, Atmospheric Chemistry and Physics, 11, 1769-1790, 2011.

Pollack, I., Ryerson, T., Trainer, M., Parrish, D., Andrews, A., Atlas, E. L., Blake, D., Brown, S., Commane, R., and Daube, B.: Airborne and ground-based observations of a weekend effect in ozone, precursors, and oxidation products in the California South Coast Air Basin, Journal of Geophysical Research: Atmospheres, 117, 2012.

Pusede, S., Gentner, D., Wooldridge, P., Browne, E., Rollins, A., Min, K.-E., Russell, A., Thomas, J., Zhang, L., and Brune, W.: On the temperature dependence of organic reactivity, nitrogen oxides, ozone production, and the impact of emission controls in San Joaquin Valley, California, Atmospheric Chemistry and Physics, 14, 3373-3395, 2014.

Pusede, S. E., and Cohen, R. C.: On the observed response of ozone to NO_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.

Reddy, P. J., and Pfister, G. G.: Meteorological factors contributing to the interannual variability of mid-summer surface ozone in Colorado, Utah, and other western US states, Journal of Geophysical Research: Atmospheres, 2016.

Singh, H. B., and Hanst, P. L.: Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides, Geophysical Research Letters, 8, 941-944, 1981.

Swarthout, R. F., Russo, R. S., Zhou, Y., Hart, A. H., and Sive, B. C.: Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources, Journal of Geophysical Research: Atmospheres, 118, 10,614-610,637, 10.1002/jgrd.50722, 2013.

Tai, A. P., Martin, M. V., and Heald, C. L.: Threat to future global food security from climate change and ozone air pollution, Nature Climate Change, 4, 817-821, 2014.

Thompson, C. R., Hueber, J., and Helmig, D.: Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado, Elementa: Science of the Anthropocene, 2, 000035, 10.12952/journal.elementa.000035, 2014.

Thompson, M. L., Reynolds, J., Cox, L. H., Guttorp, P., and Sampson, P. D.: A review of statistical methods for the meteorological adjustment of tropospheric ozone, Atmospheric environment, 35, 617-630, 2001.

Natural Gas - Data: https://www.eia.gov/, access: 4/15, 2017.

Warneke, C., Gouw, J. A., Edwards, P. M., Holloway, J. S., Gilman, J. B., Kuster, W. C., Graus, M., Atlas, E., Blake, D., and Gentner, D. R.: Photochemical aging of volatile organic compounds in the Los Angeles basin: Weekday-weekend effect, Journal of Geophysical Research: Atmospheres, 118, 5018-5028, 2013.

Weiss-Penzias, P., Jaffe, D. A., Swartzendruber, P., Dennison, J. B., Chand, D., Hafner, W., and Prestbo, E.: Observations of Asian air pollution in the free troposphere at Mount Bachelor Observatory during the spring of 2004, Journal of Geophysical Research: Atmospheres, 111, 2006.
White, A., Darby, L., Senff, C., King, C., Banta, R., Koermer, J., Wilczak, J., Neiman, P., Angevine, W., and Talbot, R.: Comparing the impact of meteorological variability on surface ozone during the NEAQS (2002) and ICARTT (2004) field campaigns, Journal of Geophysical Research: Atmospheres, 112, 2007.
Zhou, X., and Geerts, B.: The influence of soil moisture on the planetary boundary layer and on cumulus convection over an isolated mountain. Part I: observations, Monthly Weather Review, 141, 1061-1078, 2013.

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.