We thank the reviewers for their helpful comments. We have addressed every comment, and believe the result is an improved manuscript. Reviewer comments are below, with our author responses indented and in bold.

Response to Reviewer 1:

The manuscript investigates ozone formation in Colorado, a region that consistently exceeds the 8-hour ozone standard. The authors' find that the region is transitioning to a NOx-limited regime, as well as observe temperature dependencies of ozone attributed to drought. Overall, I found this manuscript to be very informative and straightforward, and timely for a region that is relatively less-studied than other areas of the country. The manuscript is well-written and figures clear. Most of my comments are minor and relate to clarity. With minor revisions, I recommend this manuscript for publication in ACP.

General Comments (1) There is inconsistency in the statistics used. Figures 2 and 3 show 5th and 95th percentiles, while later figures show one siqma. Sometimes the standard deviation of the sample is shown (e.g., Figure 7) and other times the standard error of the mean (e.g., Figure 8). For clarity, I believe the authors should maintain consistency throughout the manuscript, and at a 95% confidence interval, needed to assess the statistical significance of results.

> **Thank you to the reviewer for pointing out the inconsistencies in the error reporting. We agree that this should be improved, and the figures and references to figures or data have been updated in the revised manuscript as follows:**
>
> **Figure 2b. The error bars are now the 95% confidence intervals around the reported ozone/year slopes.**
>
> **Figure 3b. We included an additional figure similar to Figure 2b to show the NO_2/year slopes for the 5th, 50th, and 95th percentiles with the error bars representing the 95% confidence intervals around the slopes.**
>
> **Figure 5 was updated with suggestions from comment 7 to show the weekday and weekend averages with the 95% confidence intervals.**
>
> **Figure 7a was updated and shows the average weekday minus weekend ozone for each year for the six sites. The solid grey line represents the aggregated average of the six sites with the shading representing the 95% confidence interval.**
>
> **Figure 7b was updated and shows the average weekday minus weekend NO_2 for each year for the CAMP and Welby sites. The error bars now represent the 95% confidence interval of the averages.**
>
> **Figures 8 and 9 were updated to include averages and 95% confidence intervals, and also to change the temperature binning approach as suggested by the second reviewer.**
>
> **Figure 8a. was updated with the new equal bin size approach suggested by reviewer 2, and the averages of those temperature bins for each year are displayed. The 95% confidence**

intervals for the O_3 bin averages were not included in the figure for clarity purposes, but are typically <8 ppb_v.

Figure 9 was updated with the new equal bin size approach suggested by reviewer 2, and the 95% confidence intervals around the yearly O_3/temperature slopes are included.

Specific Comments

(2) Lines 78-31. Do the authors mean *1980-1993* instead of “1980-2008”? Also, the ratio of VOC/NOx emissions has evolved with time in cities (Parrish et al., 2011; McDonald et al., 2013), which could also affect ozone trends. Parrish, D. D., H. B. Singh, L. Molina, and S. Madronich (2011), Air quality progress in North American megacities: A review, Atmos Environ, 45, 7015-7025, doi:10.1016/j.atmosenv.2011.09.039. McDonald, B. C., D. R. Gentner, A. H. Goldstein, and R. A. Harley (2013), Long-term trends in motor vehicle emissions in U.S. urban areas, Environ Sci Technol, 47, 10022-10031, doi:10.1021/es401034z.

We do mean “1980-2008”. Lefohn et. al (2010) compare trends at monitoring sites across the US for two overlapping time periods 1980-2008 and 1994-2008. They found that many sites had a decreasing O_3 trend for the longer 1980-2008 period, but most of the decreasing trends were not present during the 1994-2008 period indicating that O_3 decreases had slowed or stopped in the 1994-2008 period. We have revised the statement to try and clarify that point.

> **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, 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.**

We thank the reviewer for their comment and suggestion and have including the following reference as suggested;

> **McDonald et al. (2013) report decreased VOC, CO, and NO_x automobile emissions in major US urban centers, and more importantly decreasing VOC/NO_x trends from 1990 to 2007 with a turnaround and small increase after 2007, which would affect local O_3 chemistry within the city and at downwind receptor sites**

(3) Line 164. This is an example where I found the inconsistency in statistics confusing. The error bars shown would suggest that all these results are statistically significant, rather than only at the 95th percentile.

In this section Figures 2 and 3 were referenced, both of which have been updated per comment 1. The statistical significance of the long-term O_3 and NO_2 trends were determine from both an F-test and from the 95% confidence intervals around the slope.

(4) Lines 174 – 178. The authors’ qualify the AVOC emissions trend shown in Figure 4 as an inventory estimate. I think this paragraph could be strengthened by referencing studies that have assessed emission trends for key sectors of this analysis, e.g., motor vehicles (e.g., McDonald et al., 2013), and oil and gas (e.g., Duncan et al., 2016), as well as studies that have reported uncertainties in emissions (e.g.,

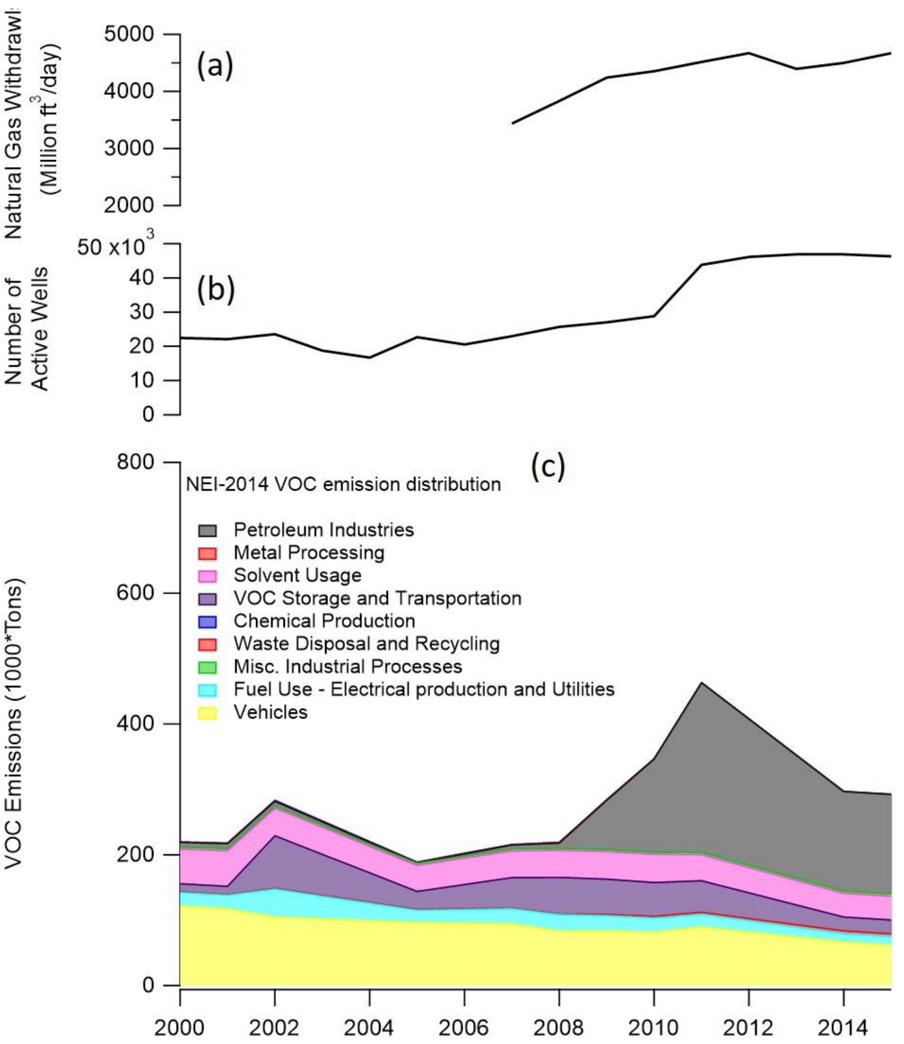
Petron et al., 2014). What explains the hump in VOC emissions from petroleum industries around 2011? Is this realistic, and comport with oil and natural gas production statistics from the Energy Information Administration? Such a rapid increase and decrease in VOC emissions would likely have some influence on observed ozone, as many of the points shown in Figure 6 are still on the NOx-saturated side of the curve. Also, McDuffie et al. (2016) suggested that maximum O3 was sensitive to NOx and reductions in VOCs in the Front Range.

Duncan, B. N., L. N. Lamsal, A. M. Thompson, Y. Yoshida, Z. F. Lu, D. G. Streets, M. M. Hurwitz, and K. E. Pickering (2016), A space-based, high-resolution view of notable changes in urban NOx pollution around the world (2005-2014), J Geophys Res-Atmos, 121, 976-996, doi:10.1002/2015jd024121.

Petron, G., A. Karion, C. Sweeney, B. R. Miller, S. A. Montzka, G. J. Frost, M. Trainer, P. Tans, A. Andrews, J. Kofler, D. Helmig, D. Guenther, E. Dlugokencky, P. Lang, T. Newberger, S. Wolter, B. Hall, P. Novelli, A. Brewer, S. Conley, M. Hardesty, R. Banta, A. White, D. Noone, D. Wolfe, and R. Schnell (2014), A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin, J Geophys Res-Atmos, 119, 6836-6852, doi:10.1002/2013jd021272.

McDuffie, E. E., P. M. Edwards, J. B. Gilman, B. M. Lerner, W. P. Dube, M. Trainer, D. E. Wolfe, W. M. Angevine, J. De Gouw, E. J. Williams, A. G. Tevlin, J. G. Murphy, E. V. Fischer, S. McKeen, T. B. Ryerson, J. Peischl, J. Holloway, K. Aikin, A. O. Langford, C. J. Senff, R. J. Alvarez II, S. R. Hall, K. Ullmann, K. O. Lantz, and S. S. Brown (2016), Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range, J Geophys Res-Atmos, 121, doi:10.1002/2016JD025265.

> **The reviewer's suggestion motivated us to include an updated Figure 4 to include the number of active oil and natural gas wells in Colorado from 2000 to 2015 and the yearly average natural gas withdrawal estimates from the Energy Information Administration, which show increases in both number of wells and the natural gas withdrawal in Colorado (see updated figure 4 below). We have included the following text for some more information regarding ONG in Colorado, changing VOC emissions around the country, and impacts on ozone in the Front Range.**
>
> > **The US Energy Information Administration (EIA) report a 2-fold increase in active ONG wells from ~25000 to ~40000 from 2010 to 2012 (Fig. 4c) (US-EIA, 2017). A number of VOC studies in the NFRMA since 2011 report enhanced C_2-C_5 alkanes relative to other urban/semi-urban regions (Abeleira et al., 2017;McDuffie et al., 2016;Pétron et al., 2012;Pétron et al., 2014;Swarthout et al., 2013). Pétron et al. (2014) reported that the state inventory for total VOCs emitted by ONG activities was at least 2x lower than May 2012, which indicates that the contribution of ONG related VOCs in figure 4 would increase substantially. McDonald et al. (2013) report decreases in both NO_x and VOC emissions from automobiles, and a steady reduction in the VOC/NO_x emission ratio in major cities from 1990 to 2008, with a possible trend reversal following 2008. McDuffie et al. (2016) reported that maximum O_3 at a site in the NFRMA was sensitive to NO_x and VOC reductions.**



(5) Line 172. The NEI is reported for a single year. I believe the authors mean the EPA Trends Report, which is now reported by state.

The reviewer is correct, and this mistake was revised in the manuscript. Thank you.

(6) Line 187. The weekday/weekend effect is really due to a drop-off in heavy-duty truck traffic (Marr et al., 2002; McDonald et al., 2014). Passenger cars drive similar amounts on weekends and weekdays.

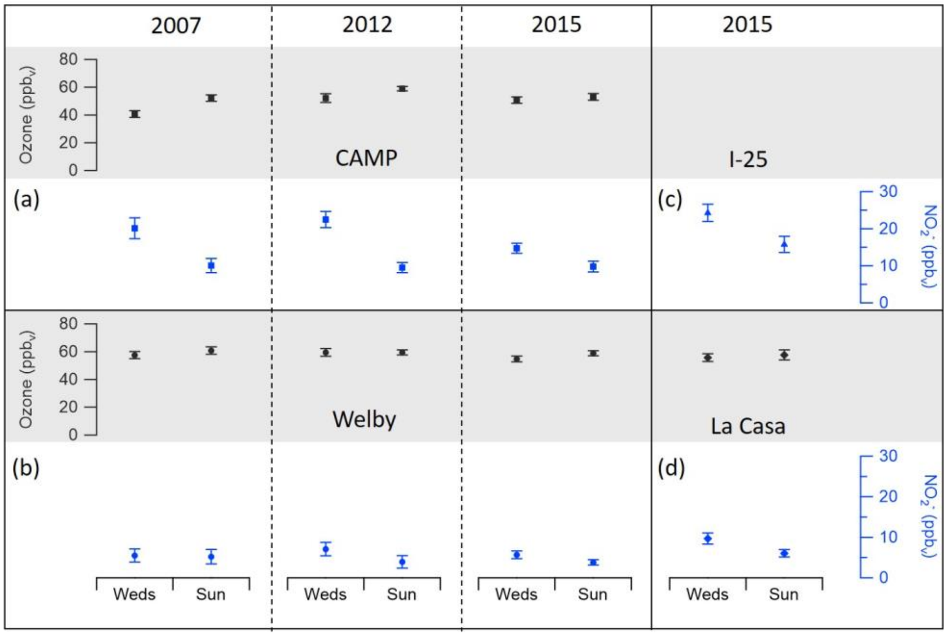
Marr, L. C., and R. A. Harley (2002), , Environ Sci Technol, 36, 4099-4106, doi:10.1021/Es020629x.
McDonald, B. C., Z. C. McBride, E. W. Martin, and R. A. Harley (2014), High-resolution mapping of motor vehicle carbon dioxide emissions, J Geophys Res-Atmos, 119, 5283- 5298, doi:10.1002/2013jd021219.

We agree with the reviewer, and have included the following revision;

> **Traffic patterns in urban regions are different between weekends and weekdays with a decrease in heavy-duty truck traffic on weekends (Marr and Harley, 2002). VOCs are expected to be stable across the week (Marr and Harley, 2002) as major VOC sources do not vary by day-of-week.**

(7) Line 209. I found the variability in concentrations across days, as shown in Figure 5, distracting for discerning weekday-weekend effects. I think this figure could be made clearer by showing a mean and confidence interval of weekdays (Mon-Friday), and of weekend days (Sa/Su) combined. Also, I think 95th confidence intervals should be shown, to make it easier for the reader to discern statistical significance.

The suggestion from the reviewer was used to clarify the data presented on Figure 5. Figure 5 was remade with average +/- 95% confidence interval for the same sites and years as the original figure. See updated figure below.



(8) Lines 212-213. Are these 24 hour averages or daytime averages? If it is the former, could nighttime chemistry affect the weekday-weekend effect?

All data presented in the manuscript is constrained to daytime (10:00am – 4:00pm local) values.

(9) Line 226-227. This sentence is confusing. Suggest revising.

This section was updated with new insight provided by updating the figures, and includes the following revisions.

> **Measured NO_2* decreased at both CAMP and Welby between 2001 and 2015 (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 site exhibited a statistically significant decrease of 0.6 ± 0.4 ppb_v/yr . The decreasing ΔNO_2* at the CAMP site appears to be converging with 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 thus reducing the measurable ΔNO_2* (Bishop et al., 2015).**

(10) Lines 281-287. On Line 283, I believe the authors mean *2002-03* instead of "2001-02". To my eye in Figure 9, it is clear that 2008 and 2011-12 are suppressed, but I found it harder to see for 2002-2003. For 2002-2003, it only looks like the Fort Collins and Welby sites are suppressed, and not the other locations.

We have updated the manuscript to reflect this observation.

Minor Comments (11) Line 211. Terminology switches from “weekday-weekend” to “weekend-weekday”. Suggest choosing one word ordering and sticking with it.

The terminology throughout the manuscript has been updated to “weekend-weekday”.

Response to Reviewer 2:

The authors investigate O3 trends in the Northern Front Range Metropolitan Area of Colorado, a region which has exhibited ongoing issues with O3 exceedances in spite of significant reductions in NOx emissions. In addition to examining overall trends over time, the authors use weekday/weekend comparisons of NOx and O3 to help explain features of local chemistry, and also compare O3 vs. temperature over time. Overall this paper is clear, well-organized, and represents a solid, if incremental addition to the existing air-pollution literature. I recommend publication, following improvements in a few areas.

First, and most importantly, I have concerns over the authors' use of binned temperatures as a preliminary step to linear regression. While I understand that this methodology has been utilized for similar purposes in the past, there are clear statistical flaws related to the practice that should be addressed before these results can be considered robust. Specific issues in the context of this paper include the following: • At relatively small sample sizes (n = 64-92 per summer), terms such as "95th percentile" become somewhat problematic. Dividing this already thin sample size into even smaller 3◦C temperature bins must have, I assume, resulted in some bins with observations in the single digits. What methodology was used to determine percentiles from such small sample sizes? • By choosing uniformly spaced bin widths (years, in the case of this paper's temporal analysis, and uniform 3◦C temperature widths in the case of the O3/T comparisons) information regarding sample sizes within each bin is lost completely. A bin containing more observations clearly should be weighted more heavily than a bin with fewer, but as written I see no indication that this kind of weighting was performed. This issue will be especially consequential for the temperature bins, since the relatively sparse temperature extremes will be incorrectly given weights equal to those of the middle bins, most likely exaggerating the resulting slopes. See Wasco and Sharma, 2014 for a description of how evenly spaced bins can produce exaggerated slopes as a result of this bias. Two methods that could correct this bias are equal number bins (with variable temperature widths based on the frequency distribution) and quantile regression (Koenker and Bassett, 1978). I think either of these would be superior to the current "equal distance bin" approach, with quantile regression also having the benefit of simultaneously addressing the small sample size issue. Wasko C, Sharma A. Quantile regression for investigating scaling of extreme precipitation with temperature. Water Resour Res 2014;50:3608–14. Koenker R, Bassett Jr G. Regression Quantiles. Econometrica 1978;46:33– 50. Further examples of this technique applied specifically to similar air-quality questions may be found elsewhere in the literature.

Thank you to the reviewer for a detailed explanation of the issues with uniformly spaced temperature bins, and the suggestion of weighting the yearly trends. We will address both topics below:

1) **Temporal trends and weighting of years: The EPA ozone, NO_2, and temperature data are available at an hourly time resolution. For the temporal trends of ozone and NO_2 we calculated daily averages for 10:00 am – 4:00 pm for summer data (Jun-Aug). To determine the percentiles for each summer at a site we aggregated the daily averages and applied the Tukey method to find the 5th, 33rd, 50th, 67th, and 95th percentiles (figure 2a, figure 3a). As the reviewer noted relatively small sample sizes can be problematic when calculating high or low percentiles (95th and 5th). We believe that the reviewer is referring to the tendency for the percentile calculations at the 5th or 95th to be skewed by low and high outliers, which**

becomes more problematic as the sample size decreases. As the sample size becomes sufficiently small the 5th and 95th percentiles will tend to equal the minimum and maximum values of the data, which can be outliers. We went back through the yearly trends to investigate the influence of outliers on the percentiles and found that only 1 year at 2 sites (Welby and Carriage 2004) exhibited 1 day of unrealistically low ozone (<5 ppbv), which is lower than typical background ozone, and were removed as outliers to not skew the 5th percentile values. Below is a table summarizing the number of daily average points for each year used in the percentile calculations.

	Number of points in long term ozone trend daily averages						NO$_2$ trends	
Year	Welby	Rocky Flats	Greeley	Fort Collins	Carriage	CAMP	CAMP	Welby
2000	90	88		89	91			
2001	89	90		91	90		89	89
2002	88	85	87	91	91		85	78
2003	86	91	91	91	91		74	
2004	87	91	91	91	85		80	81
2005	91	91	91	91	89	63	91	91
2006	90	91	91	91	88	91	82	
2007	91	89	91	91	86	90	89	91
2008	90	91	87	91	91			90
2009	84	91	91	91	91			
2010		89	91	77	90		91	78
2011	91	91	91	91	91		71	86
2012	87	91	90	90	80	91	90	71
2013	86	90	91	75		91	91	86
2014	91	91	90	78		91	91	91
2015	90	91	91	91		90	90	84

The reviewer suggests weighting the yearly trends by the number of data points to correct for differences in the number of points in different years. However, we note that >90% of the years for all sites with available data have 80-92 daily averages, and we thus expect a negligible effect on the analysis from weighting based on the number of data points.

2) **Uniformly spaced temperature bins versus temperature bins with the same number of data points: The reviewer suggests redoing the ozone-temperature analysis using temperature bin widths dictated by a constant number of data points in a bin instead of using uniform temperature bins. As the reviewer noted we were dividing an already small sample size of 80-90 daily averages into temperature bins, some of which contained <10 data points for the high and low temperature bins. Applying the percentile calculations to such small sample sizes was not statistically robust, and tended to only yield the minimum and maximum values for those temperature bins. To increase the number of data points for a more robust statistical analysis we used the hourly ozone and temperature data. For a full 92-day summer data set we are now working with 552 data points (10:00am – 4:00pm, 6 hours per day). The 552 data points were split into 5 temperature bins with 110 data points each, with the two extra points disregarded. Due to missing data, the smallest number of**

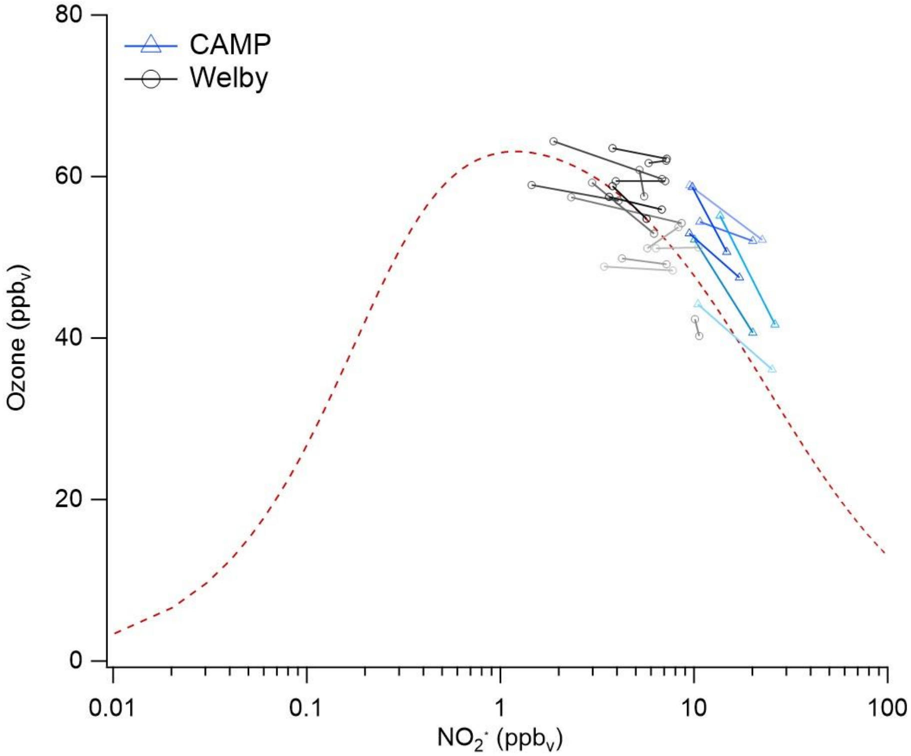
data points for a single temperature bin was 51 (CAMP 2005), but >90% of bins contained 100-110 data points. Due to the scarcity of bins with <100 data points we did not weight the ozone-temperature relationships by the number of points in each bin. We have updated figures 8 and 9 with this improved analysis. Below are summary tables of the number of ozone points in each temperature bin for each site and year. We note that this has no substantive effect on the interpretation of the data, nor conclusions drawn, but does make for a more robust analysis.

	Number of Points in Welby temperature bins					Number of Points in Rocky Flats temperature bins					Number of Points in Greeley temperature bins				
Year	**Bin 1**	**Bin 2**	**Bin 3**	**Bin 4**	**Bin 5**	**Bin 1**	**Bin 2**	**Bin 3**	**Bin 4**	**Bin 5**	**Bin 1**	**Bin 2**	**Bin 3**	**Bin 4**	**Bin 5**
2000	104	110	110	110	110	103	105	107	107	110					
2001	106	108	109	105	110	107	107	108	110	110					
2002	105	106	107	109	102	102	98	99	96	101					
2003	97	96	104	110	106	109	104	110	109	109					
2004	96	108	105	105	104	107	109	108	108	105					
2005	108	107	110	110	109	110	110	108	110	110					
2006	109	105	106	109	100	109	109	108	107	110					
2007	110	110	110	108	108	110	107	108	109	98					
2008	104	103	106	110	109	107	110	105	110	110					
2009	102	93	99	92	103	109	110	109	109	109					
2010						110	108	102	103	96					
2011	109	107	105	108	110	106	110	110	110	110					
2012	106	106	110	110	62	110	110	110	108	108	110	109	109	109	107
2013	110	109	106	108	72	106	110	110	110	105	110	110	103	108	109
2014	110	110	109	110	109	110	110	110	110	110	108	109	108	108	104
2015	103	108	110	107	109	107	110	110	110	108	108	105	108	108	108

	Number of Points in Fort Collins temperature bins					Number of Points in Carriage temp bins					Number of Points in Camp temp bins				
Year	**Bin 1**	**Bin 2**	**Bin 3**	**Bin 4**	**Bin 5**	**Bin 1**	**Bin 2**	**Bin 3**	**Bin 4**	**Bin 5**	**Bin 1**	**Bin 2**	**Bin 3**	**Bin 4**	**Bin 5**
2000	104	109	108	107	107	90	94	95	90	91					
2001	77	90	91	93	96	109	103	109	109	109					
2002	81	88	98	93	72	105	108	110	109	110					
2003	107	106	107	109	104	106	105	110	109	110					
2004	110	110	108	110	105	109	109	108	108	108					
2005	70	89	102	108	108	109	105	104	101	94	51	74	70	74	103
2006	107	107	110	110	110	92	109	109	104	105	110	109	108	107	107
2007	109	107	108	108	110	106	98	105	109	110	108	104	108	109	110
2008	109	109	108	107	110	90	103	104	100	107					
2009	105	110	110	109	110	107	110	109	110	110					
2010	104	110	110	110	110	109	110	109	110	110					
2011	110	110	108	108	110	108	106	109	110	104					
2012	110	108	105	108	100	108	108	110	110	108	108	107	109	110	109
2013	110	108	108	109	109						108	107	110	110	109
2014	109	110	110	110	110						109	110	110	110	110
2015	95	108	110	109	105						110	110	109	108	105

2. Figure 6: While I appreciate the attempt to use many symbols to distinguish years, I think the end result just doesn't work. The dense area around 10 ppb NO2 in particular is nearly impossible to interpret easily. I suggest either abandoning the symbols entirely, and using shaded dots to represent different years, or else zooming in on the data to create more whitespace in this concentrated region.

> **We have revised this figure to minimize the visual interference and clustering of the symbols. The revised figure is below:**



3. The usage of "standard deviation" in several figure captions seems unclear. For example, on Figure 9 it seems to suggest that this is a standard deviation of many regression slopes. Is this the standard error of a single regression? Was bootstrapping performed, leading to many regression coefficients?

> **We have revised and updated most of the figures per a suggestion from reviewer 1 to be more consistent with the error analysis. The updates are as follows;**
>
> **Figure 2b. The error bars are now the 95% confidence intervals around the reported ozone/year slopes.**

Figure 3b. We included an additional figure similar to Figure 2b to show the NO_2/year slopes for the 5th, 50th, and 95th percentiles with the error bars representing the 95% confidence intervals around the slopes.

Figure 5 was updated with suggestions from reviewer 1 comment 7 to show the weekday and weekend averages with the 95% confidence intervals.

Figure 7a was updated and shows the average weekday minus weekend ozone for each year for the six sites. The solid grey line represents the aggregated average of the six sites with the shading representing the 95% confidence interval.

Figure 7b was updated and shows the average weekday minus weekend NO_2 for each year for the CAMP and Welby sites. The error bars represent the 95% confidence interval of the averages.

Figure 8a was updated with the new equal bin size approach, and the averages of those temperature bins for each year are displayed. The 95% confidence intervals for the O_3 bin averages were not included in the figure for clarity purposes, but are typically <8 ppb_v.

Figure 9 was updated with the new equal bin size approach suggested, and the 95% confidence intervals around the yearly O_3/temperature slopes are included.

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.

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.

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.

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.

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.

Pétron, G., Karion, A., Sweeney, C., Miller, B. R., Montzka, S. A., Frost, G. J., Trainer, M., Tans, P., Andrews, A., and Kofler, J.: A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin, Journal of Geophysical Research: Atmospheres, 119, 6836-6852, 2014.

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.

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

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 due to a combination ~~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-~~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~~ 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:

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

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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).

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

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).

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

$$RO_2 + NO \rightarrow RONO_2 \qquad \text{(R2b)}$$

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

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

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

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

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

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. ~~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. McDonald et al. (2013) report decreased VOC, CO, and NO_x automobile emissions in major US urban centers, and ~~more importantly~~ decreasing VOC/NO_x trends from 1990 to 2007 with a turnaround and small increase after 2007. This will ~~7, which would~~ 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. ~~A number of~~ M~~m~~odeling 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~~ 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 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), 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 ~~weekday~~weekend-~~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 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 $\geq 95\%$ 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.~~ 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 95th percentile, which could be a result of changing VOC and NO_2^* emission in the 2000 – 2015 period..~~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 -1.0 ± 0.6 and -1.4 ± 0.6 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 -0.7 ± 0.8 ppb_v/yr (Fig. 3). ~~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 state average annual emissions trend~~NEI 2014~~. To the best of our knowledge, the NFRMA does not have any long-term VOC datasets, but the EPA state average annual emissions trend ~~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). 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 NEI is only an estimate and does not include biogenic sources of VOCs, which can contribute substantially to VOC reactivity in the region, but vary substantially from year to year (Abeleira et al., 2017). The increased O_3 is thus unsurprising for the 2000 – 2015 timeframe. The long-term reduction in NO_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-~~Weekend~~ Weekday effect in Denver, CO

The '~~weekday~~weekend-~~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).~~–~~ ~~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 reduction in heavy-duty trucking traffic~~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-~~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 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 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 $NO_2{}^*$. ~~An observable weekday~~weekend~~-weekend~~ ~~weekday~~ ~~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~~weekend-~~weekday~~ 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 six available O_3 NFRMA sites and the two $NO_2{}^*$ 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. A negative ΔO_3 is consistent with a NO_x-limited system in which O_3 decreases when NO_x decreases. The week~~end~~end-week~~day~~day 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 ~~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. ~~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 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~~weekend-~~weekday~~ weekday analysis suggested that the region is NO$_x$-saturated, but transitioning to a NO$_x$-limited region. Increases in O$_3$ ~~are likely~~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 ~~NEI~~ 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 ~~weekday~~weekend-~~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$_3$ ~~allowed~~ allows us to investigate the extent to which biogenic VOCs influenced P(O$_3$) in the NFRMA and the interannual variability ~~in~~ 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 ~~having large~~ impact~~s~~ing ~~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$_3$~~ 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. ~~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~~ do not dominate, ~~the~~ VOC reactivity

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Formatted: Not Superscript/ Subscript 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), stratospheric intrusions (Lin et al., 2015) 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). 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 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 ~~heavy ~~trafficked ~~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 ~~was ~~decreas~~ing~~ed across most of the country as anthropogenic NO_x and VOC emissions were ~~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~~weekend-~~weekday ~~weekday analysis demonstrated that most sites in the NFRMA were NO_x-saturated, but are transitioning to, and in ~~one ~~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 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 5th and 95th 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~~ Two time periods exhibit a clearly suppressed O_3-temperature dependence at the 50th percentile (~~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. However, we emphasize that this effect is most clearly observed at the 50th percentile, rather than the 5th or 95th 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). ~~Our~~ The work herein suggests that drought can temporarily suppress the O_3-temperature penalty in the NFRMA and ~~potentially~~ perhaps other NO_x-saturated regions by reducing temperature dependent biogenic VOC emissions.

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Acknowledgements

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

Figures

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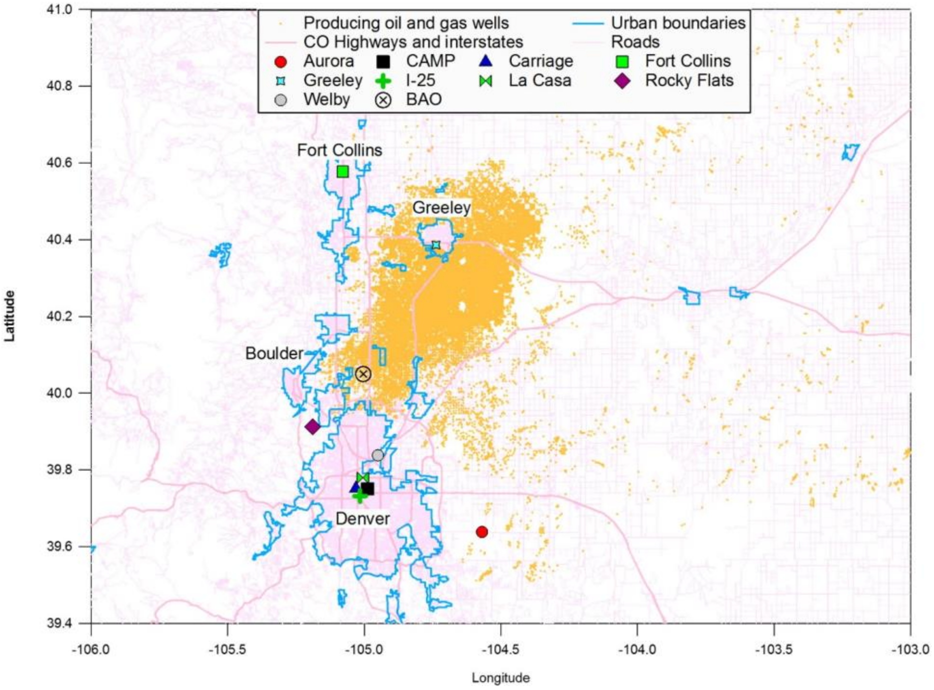
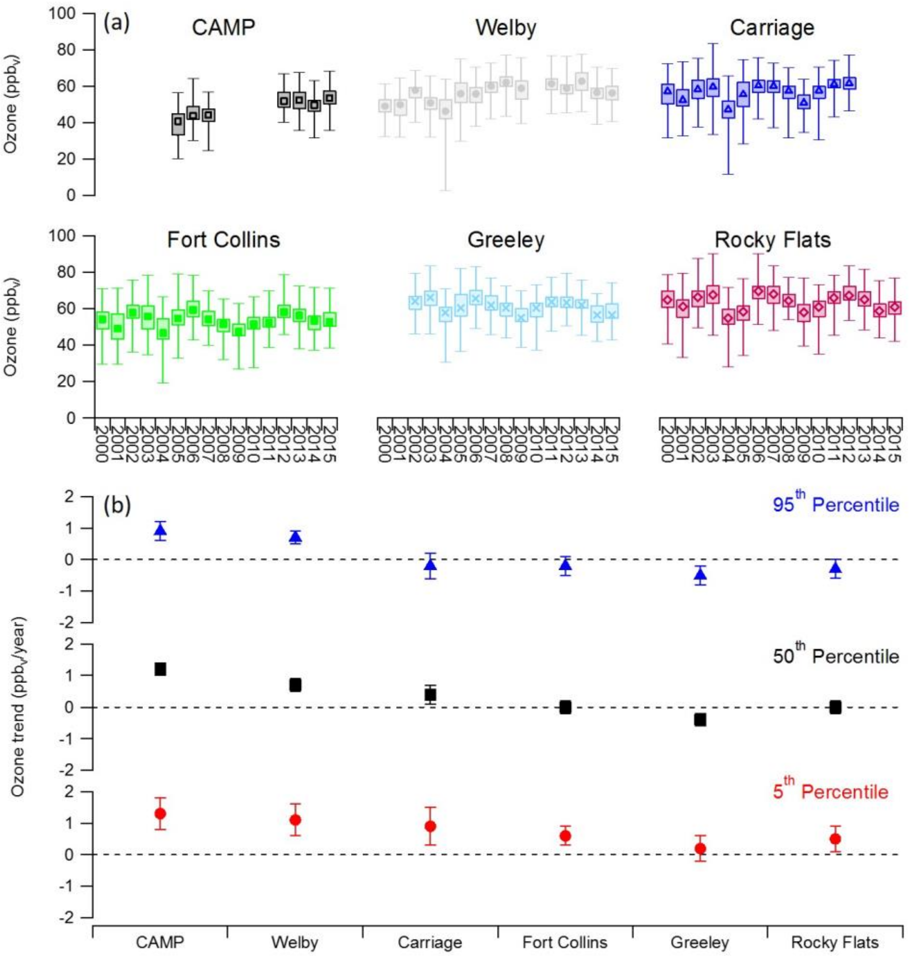


Figure 1. Site map for O_3 and NO_2 measurements in the NFRMA identified by shapes and colors. Producing oil and gas wells as of 2012 are identified on the map with gold dots. Urban areas are outlined with thick light-blue lines. Major interstates and state highways are identified by thick pink lines.


(a)
CAMP
Welby
Carriage
Fort Collins
Greeley
Rocky Flats
Ozone (ppbv)
100
80
60
40
20
0
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
(b)
95th Percentile
50th Percentile
5th Percentile
Ozone trend (ppbv/year)
2
1
0
-1
-2
CAMP
Welby
Carriage
Fort Collins
Greeley
Rocky Flats

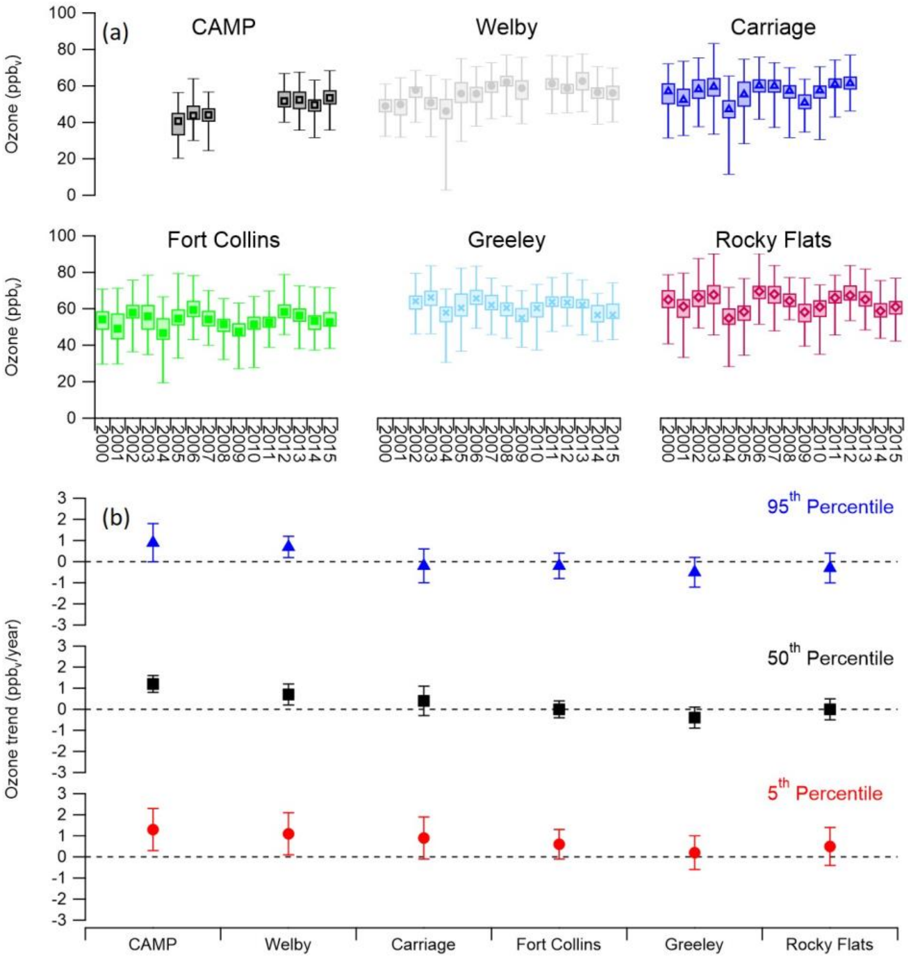
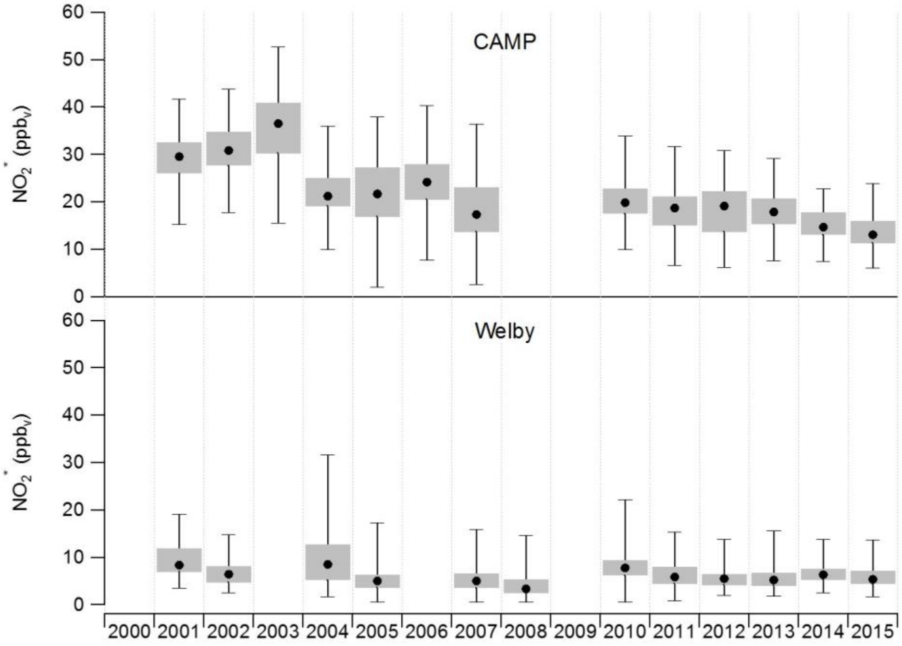


Figure 2. (a) Trends in summer (June 1 – August 31) daytime (10:00 am – 4:00 pm) O_3 for six sites in the NFRMA between 2000 and 2015. Whiskers correspond to 5th and 9th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the marker corresponds to the 50th percentile. Percentiles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


CAMP
Welby
NO2* (ppbv)
NO2* (ppbv)
0
10
20
30
40
50
60
2000
2001
2002
2003
2004
2005
2006
2007
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2014
2015

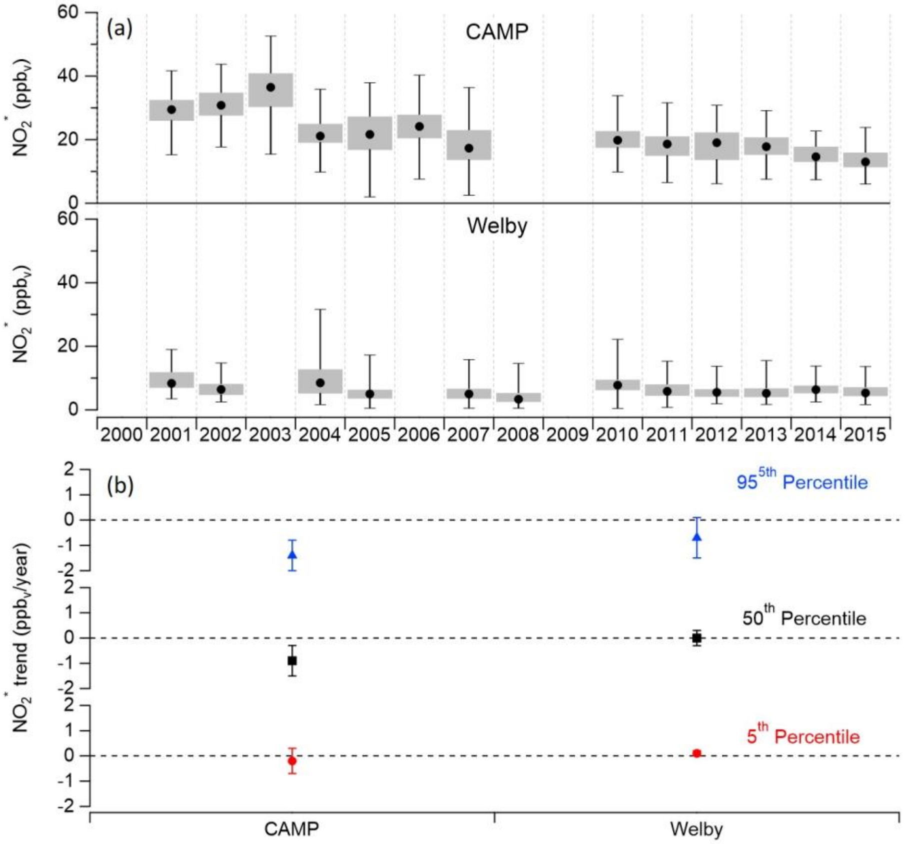

Figure 3. (a) Trends in summer (June 1 – August 31) daytime (10:00 am – 4:00 pm) NO_2* for the CAMP and Welby sites in Denver for all available data from 2000 – 2015. Whiskers correspond to 5th and 95th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the black marker corresponds 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 ~~ozone~~NO_2*/year linear regression slope.

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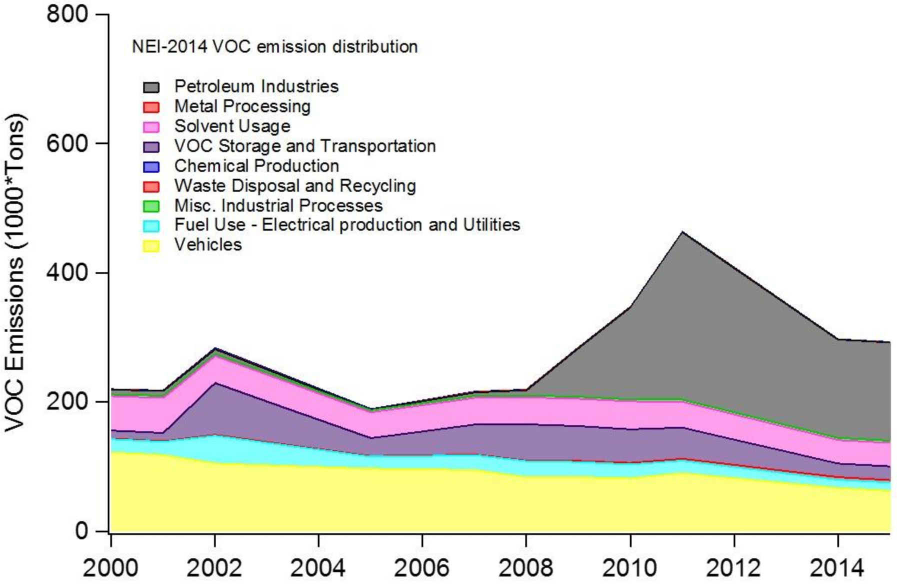
~~Figure 3. Box and whisker plots of NO_2* for the CAMP and Welby sites in Denver for all available data from 2000 – 2015. Whiskers correspond to 5th and 95th percentiles, box thresholds correspond to 33rd and 67th percentiles, and the black marker corresponds to the 50th percentile.~~


800
600
400
200
0
VOC Emissions (1000*Tons)
NEI-2014 VOC emission distribution
Petroleum Industries
Metal Processing
Solvent Usage
VOC Storage and Transportation
Chemical Production
Waste Disposal and Recycling
Misc. Industrial Processes
Fuel Use - Electrical production and Utilities
Vehicles
2000
2002
2004
2006
2008
2010
2012
2014

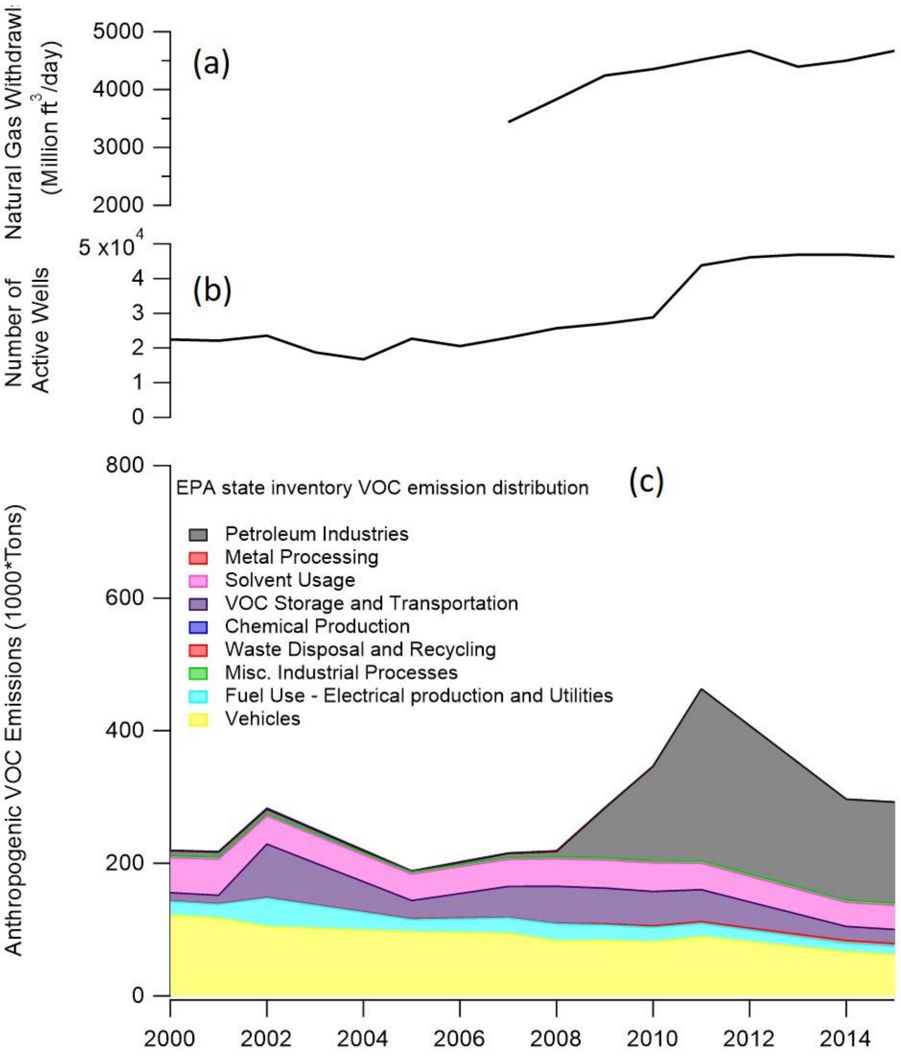
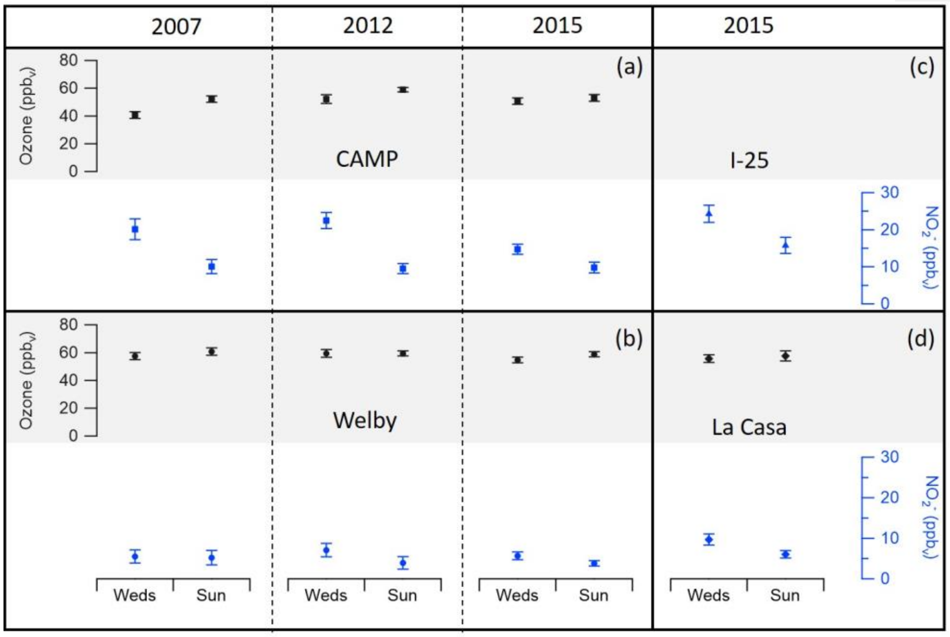


Figure 4: (a) Estimated yearly averaged natural gas withdrawals in Colorado (US-EIA, 2017), (b) Yearly average number of active ONG well operations (US-EIA, 2017). (c) VOC emission estimates from the EPA *state average annual emissions trend* ~~National Emissions Inventory 2014 (NEI-2014)~~ for Colorado. 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.


2007
2012
2015
2015
(a)
(c)
(b)
(d)
Ozone (ppb$_v$)
80
60
40
20
0
CAMP
I-25
Welby
La Casa
NO$_2$ (ppb$_v$)
30
20
10
0
Weds
Sun
Weds
Sun
Weds
Sun
Weds
Sun

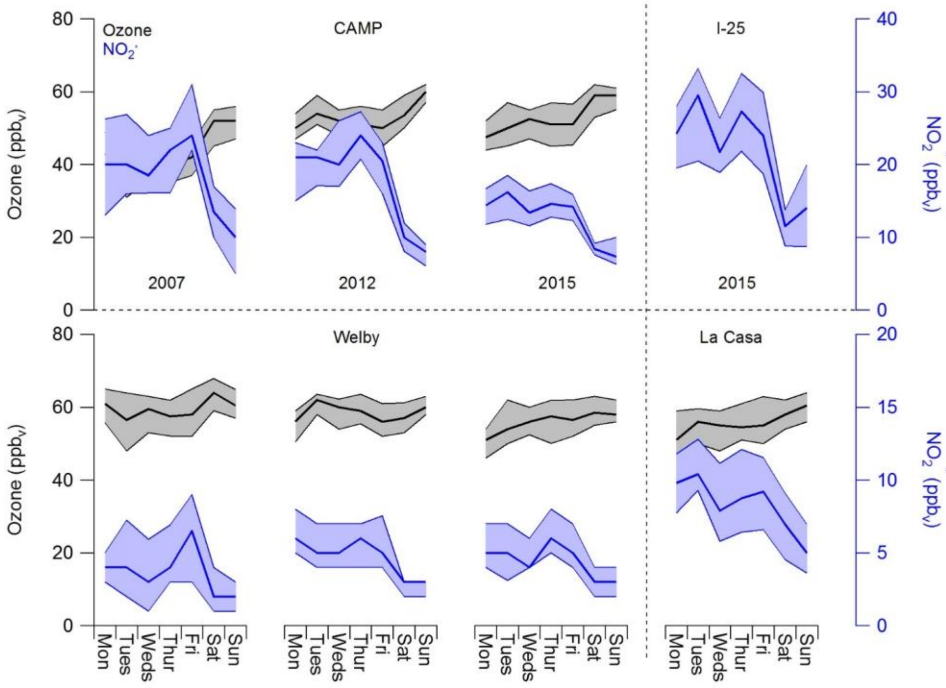
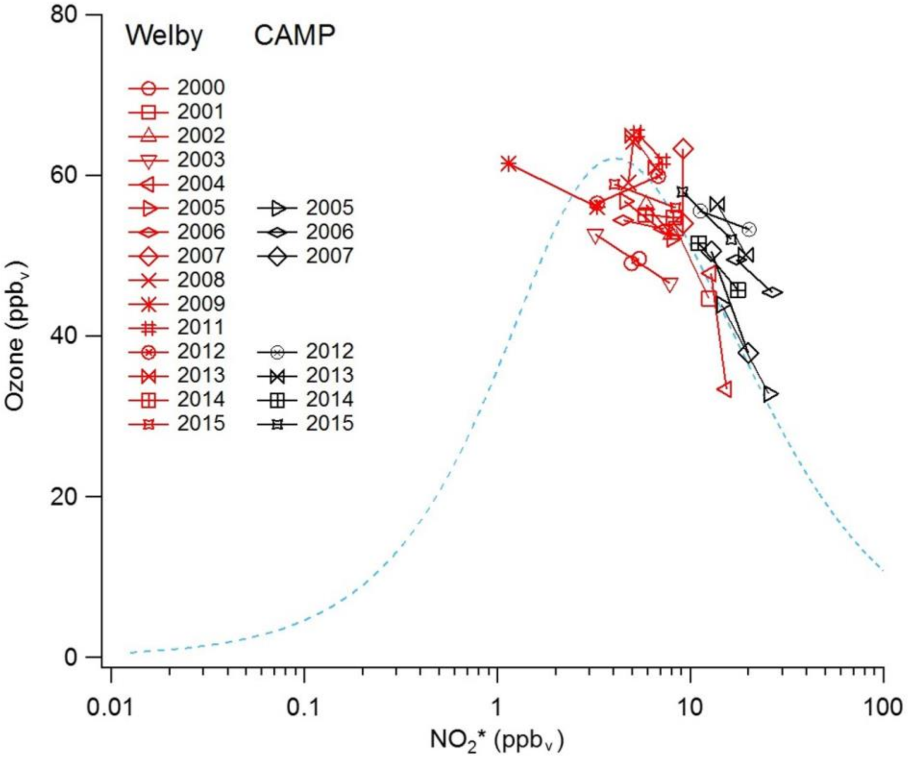


Figure 5. Week~~day~~end-Week~~end~~day analysis (Wednesday vs Sunday) for O_3 (black with shading) and NO_2* (blue) for the CAMP (a, squares), Welby (b, circles), and the La Casa (c, diamonds) sites in Denver. I-25 (d, triangles) is limited to NO_2^* due to data availability. All sites have plots for 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 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.~~


Welby
CAMP
2000
2001
2002
2003
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2007
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2009
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2005
2006
2007
2012
2013
2014
2015
Ozone (ppb$_v$)
NO$_2$* (ppb$_v$)
0
20
40
60
80
0.01
0.1
1
10
100

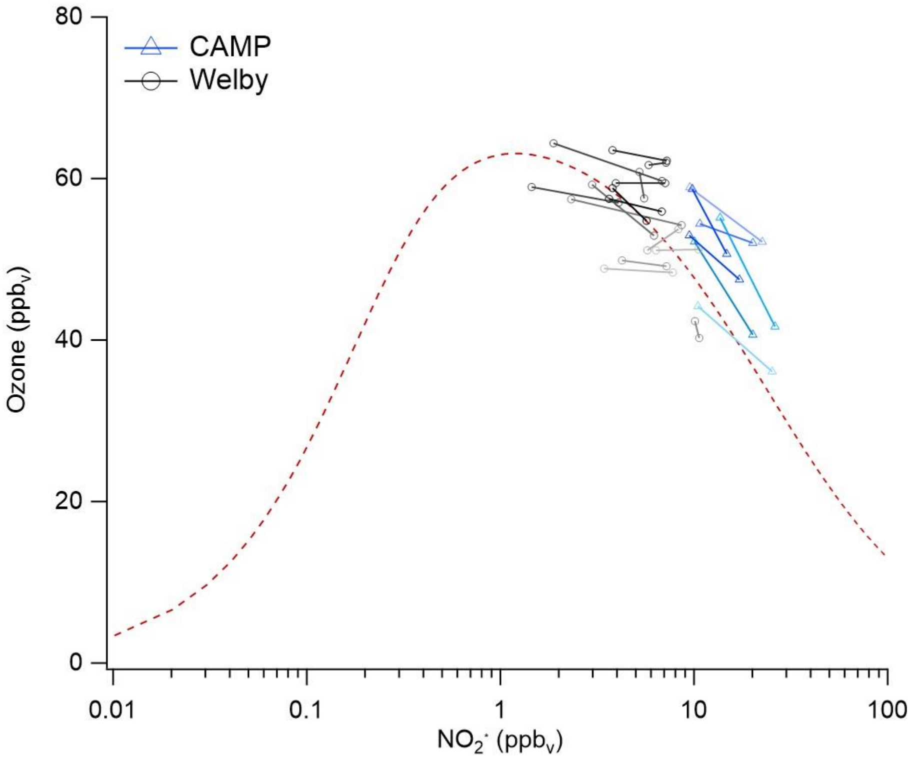
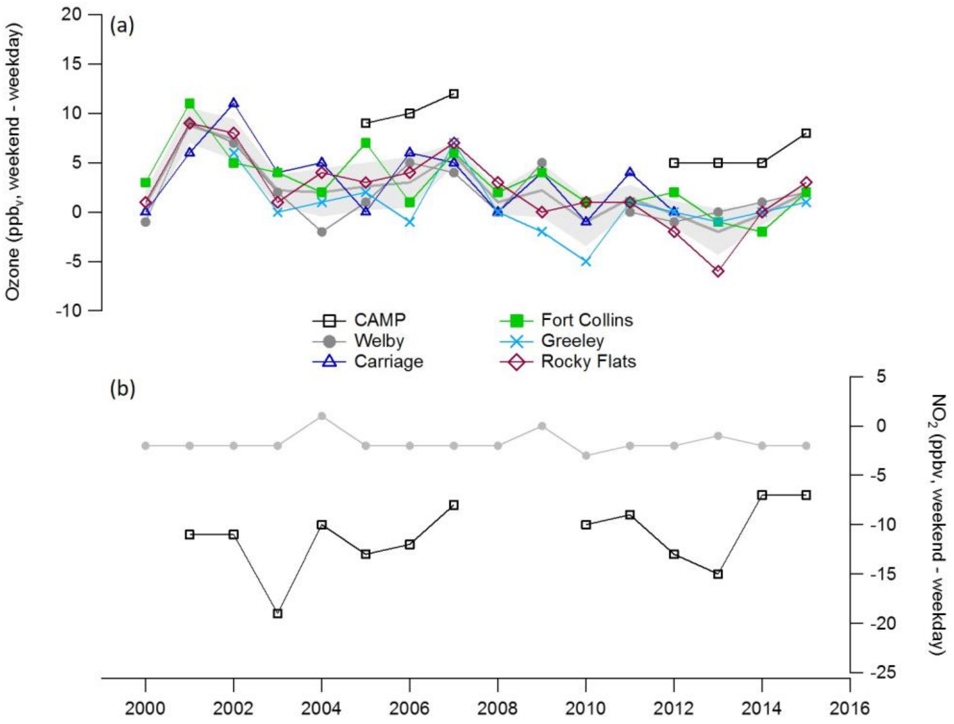


Figure 6. Weekday and weekend O_3 versus NO_2* for Welby (black) and CAMP (blue) sites. Tethered symbols correspond to average Wednesday values for weekdays, and average Sunday values for weekends for each year depending on data availability. The colour shading corresponds to year, with the lightest shade corresponding to the earliest year (2000 for Welby, 2005 for CAMP) and 2015 as the darkest shade~~Light shades correspond to early years in the dataset, and darker shades to later years~~. 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 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).~~



~~Figure 7: (a) The change in O_3 calculated as median weekend (Saturday to Sunday) minus summer weekday (Tuesday to Thursday) for the six NFRMA sites identified by color and marker for each year of available data. The solid grey line is the average median of the sites with the exception of CAMP. The inclusion of a site in the averaging for a given year was dependent on available data for that year. The light grey shading represents ± 1 standard deviation of the five site average. (b) The change in NO_2* calculated as median summer weekend (Saturday to Sunday) minus summer weekday (Tuesday to Thursday) for the CAMP and Welby sites.~~

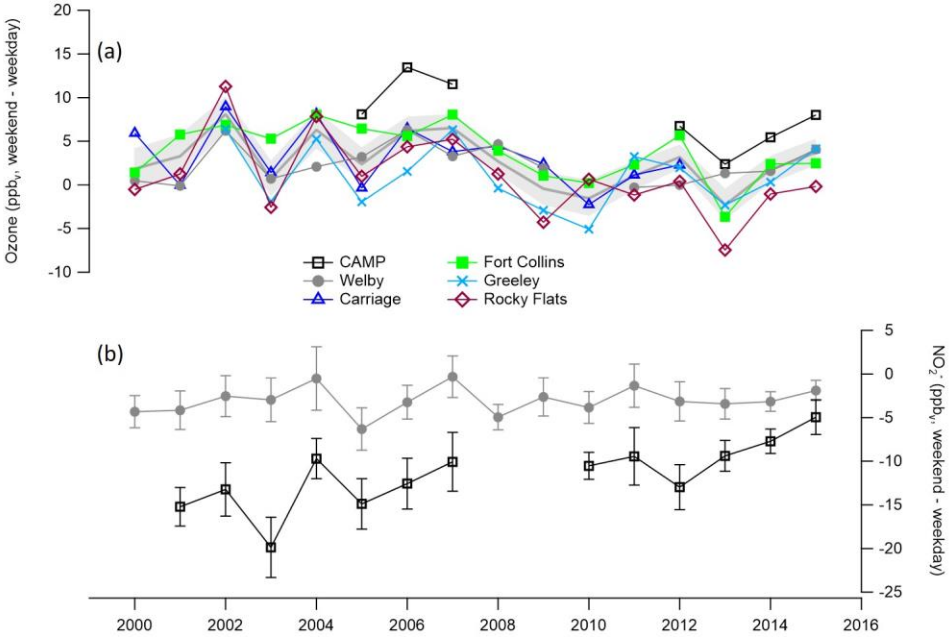


Figure 7: (a) The change in O_3 calculated as average weekend (Sunday) minus weekday (Wednesday) O_3 for the six NFRMA sites identified by color and marker. The solid grey line is the average of the sites. The inclusion of a site in the averaging for a given year was dependent on available data for that 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.

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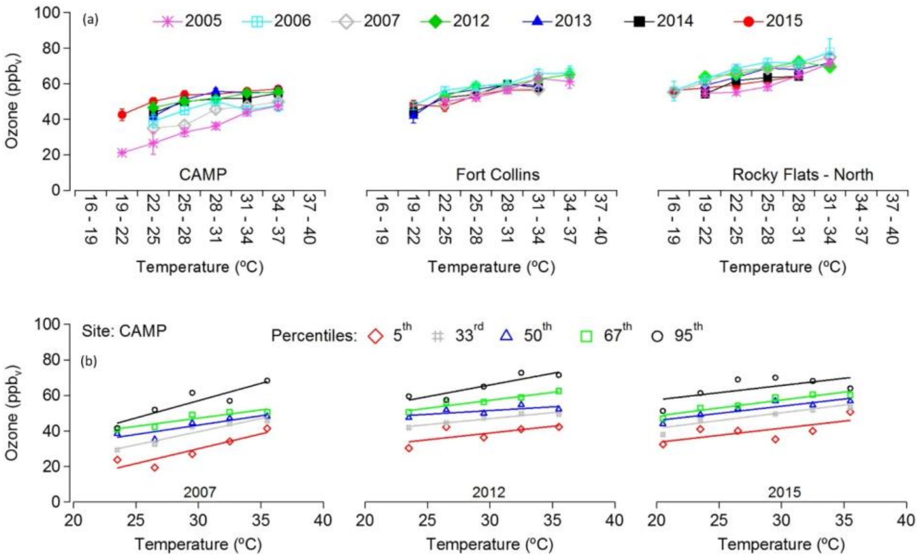

~~Figure 8. a) O_3 versus temperature for CAMP, Fort Collins, and Rocky Flats. O_3 is binned into 3°C temperature bins. Markers and colors represent yearly averages for each site. Error bars represent ± 1 standard error of the mean. Years were selected based on availability of overlapping data for multiple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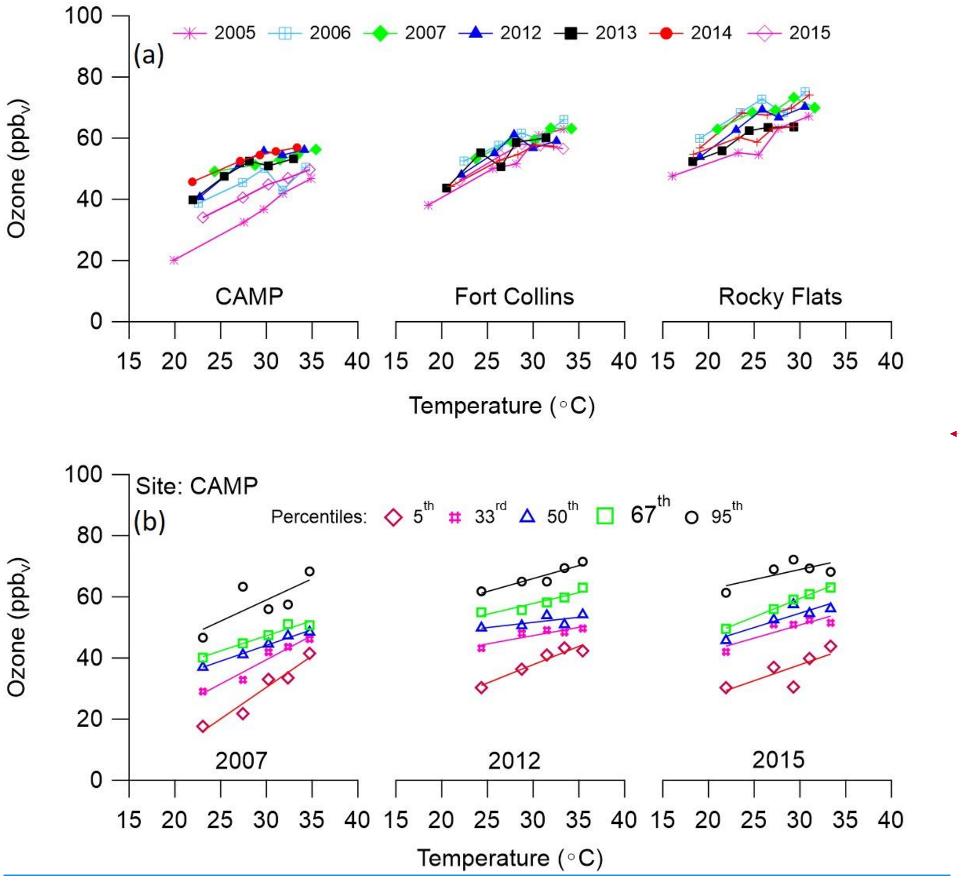
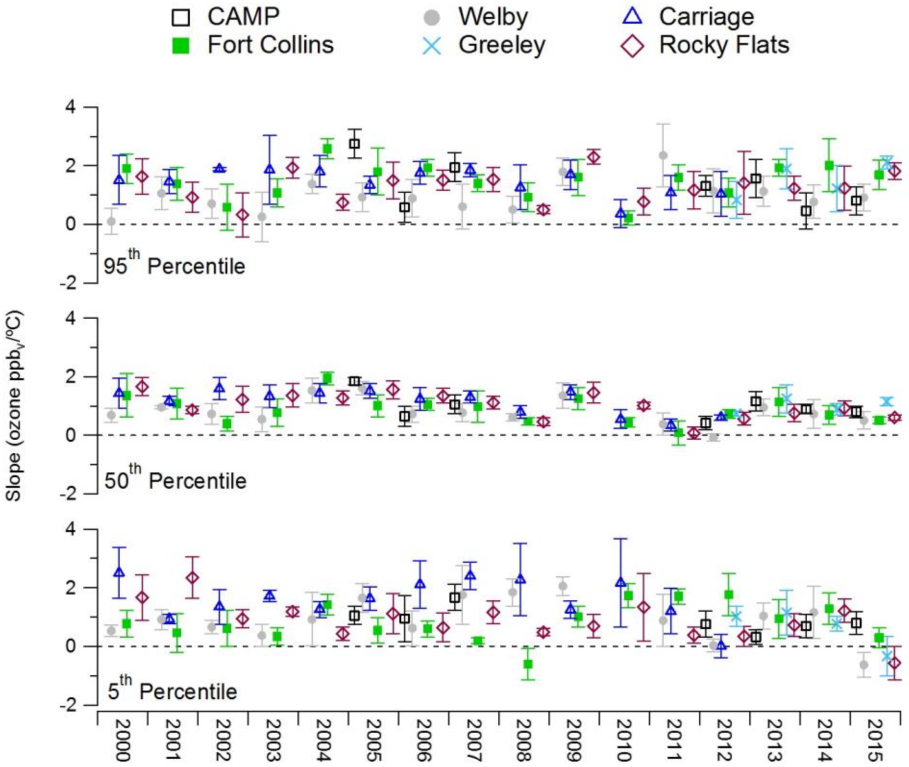


Figure 8. a) O_3 versus temperature for CAMP, Fort Collins, and Rocky Flats. Hourly O_3 is binned by hourly temperature with bins containing 51 - 110 points for O_3 and temperature depending on data availability at a site. The temperature bins typically contained 100 – 110 data points (>90% of temperature 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) 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.~~

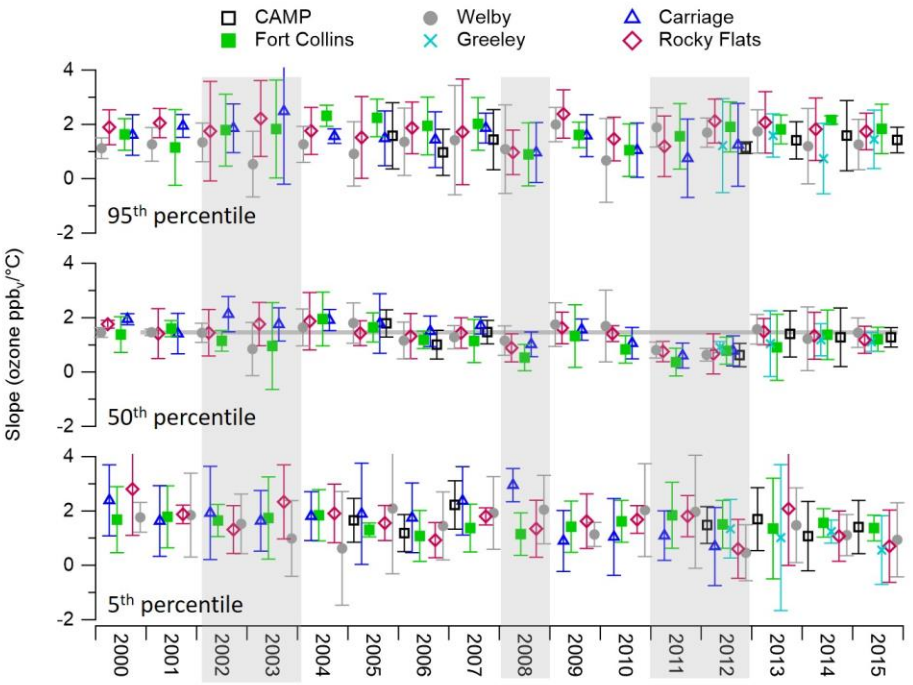


Figure 9. Slopes from one-sided linear regression of O$_3$ versus temperature (i.e. the temperature dependence of O$_3$). Hourly O$_3$ (10:00 am – 4:00 pm) is binned by hourly temperature with bins containing 51 - 110 points for O$_3$ and temperature depending on data availability at a site. The temperature 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

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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.