

**FRAPPÉ/DISCOVER-AQ (July/August 2014)
in perspective of multi-year ozone analysis**

Project Report #2: Monitoring network assessment for the City of Fort Collins

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Summary:

The analysis of long-term ozone concentration measurements revealed that since 2012 ozone MDA8 concentrations at Fort Collins CSU exceed the 75 ppbv NAAQS, on average, 0.5 times per month during summertime. At Fort Collins West the number of exceedances was 3 times per month. A weekend effect on the order of 10% with higher weekend versus weekday MDA8 ozone concentrations was observed at FC CSU with a decreasing trend since the 1990's when measurements started. This is indicative for a high NO_x influenced site (emission inventories suggest a contribution of over 50% from mobile emissions) and a shift towards a more NO_x limited ozone production regime. The summer 2014 (FRAPPE/DISCOVER-AQ) was both lower in absolute ozone concentration and the magnitude of the weekend effect compared to the long-term trend.

Over the last 10 years, FC West observed a statistically significant decrease in MDA8 ozone on the order of -0.24 ppbv/year. MDA8 at FC CSU experienced no significant trend in the last 10 years but experienced an increase on the order of 0.24 ppbv/year over the last 25 years.

1. EPA ozone network – multi-year dataset of hourly values

For this second project report, we analyzed hourly data from the EPA ozone network in the Colorado Front Range downloaded at http://aqhdr1.epa.gov/aqsweb/aqstmp/airdata/download_files.html#Raw in February 2017. Auxiliary data to this report such as hourly wind speed, wind direction and carbon monoxide concentrations were downloaded from the same webpage. When indicated, we analyze MDA8 (daily 8-hour maximum) ozone concentrations, e.g. for the multi-year trend analysis. The EPA

record of ozone measurements in Colorado starts in 1990 for early sites and more sites were added over the years. Some sites have data throughout all the years, some have substantial data gaps and some sites were discontinued. To make the available data in the Colorado Front Range (Figure 1) comparable, we selected data for those time periods only when data was available at all sites of interest and focus on the more recent years. This subset of data ranges from 1 January 2012 – 1 January 2016 (“2012-2015”). If not otherwise noted, the data shown is from this subset. For the trend analysis (section 4) we used all available data from each site.

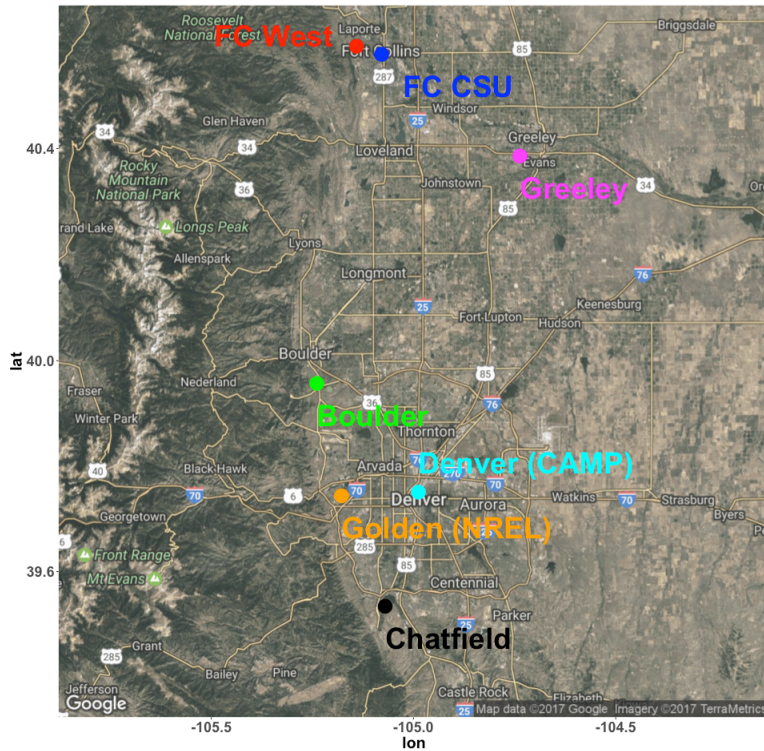


Figure 1: Map of the Colorado Front Range with analyzed long-term ozone measurement sites.

2. Ozone long-term analysis

For seven surface ozone monitoring sites in the Colorado Front Range including FC West, FC CSU, Boulder, Golden (NREL), Denver (CAMP) and Greeley we selected hourly measurements only where all sites are reporting data. As mentioned above this includes the years 2012-2015. The average diurnal, monthly and weekly cycle for ozone at all seven sites is plotted in Figure 2A for hourly values and in Figure 2B for MDA8. Average diurnal and annual cycles can be roughly divided into two groups. One group, including FC West, Boulder, Golden (NREL) and Chatfield, shows overall higher concentrations during all times of the day and all times of the year and their diurnal and annual cycles are very similar to each other. The second group including FC CSU and Denver (CAMP) has lower concentrations likely due to being located in urban centers with higher NO_x concentrations. The latter sites also show a strong weekend effect (see Attachment 1 for a definition on the weekend effect) with higher average ozone concentrations on Saturday and Sunday. Greeley falls somewhere in between the two groups

resembling Denver more during nighttime and in the winter, whereas reaching higher ozone concentrations similar to FC West, Boulder, Chatfield and Golden (NREL) during daytime and in the summer.

MDA8 ozone concentrations for different seasons and for July/August for the years 2012-2015 as well as only for July/August 2014 (the time period coinciding with FRAPPÉ/DISCOVER-AQ) are listed for all sites in Table 1.

Average MDA8 during July/August of 2014 (FRAPPÉ/DISCOVER-AQ) was at all sites lower by about 2-5 ppbv compared to the long-term observations for the same months. Similarly, for the average number of exceedance days (in reference to a NAAQS of 75ppbv) per month (Table 2), July/August 2014 is lower than the long-term average at all sites but Boulder. Over the years 2012-2015, FC CSU observes MDA8>75ppbv exceedances in July/August less than once per month and FC West close to three times a month. For a lower NAAQS of 70 ppbv, the number of violations at FC CSU increases to, on average, 3 days per month during July/August and at FC West to 6 days per month.

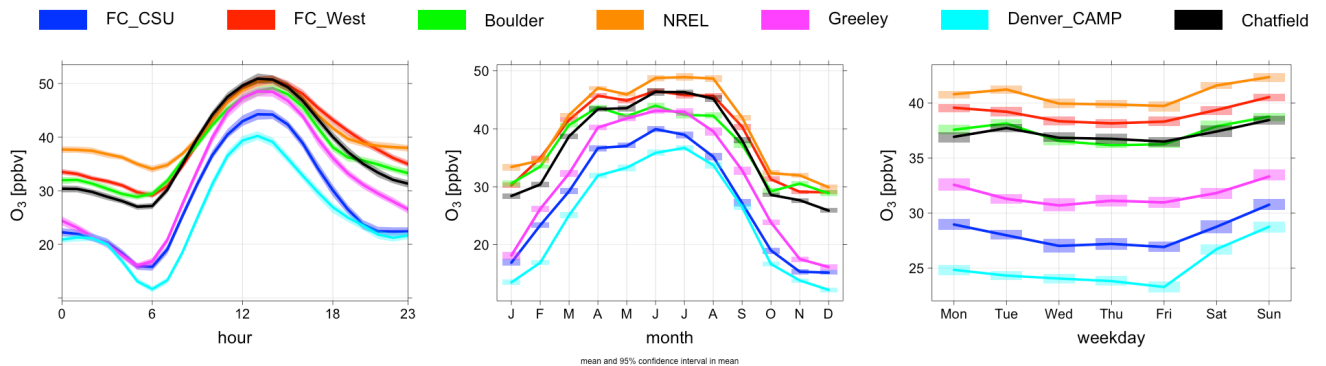


Figure 2A: Long-term (2012-2015) ozone analysis of hourly averaged concentrations from seven different sites in the Colorado Front Range. Note that the scales vary between the graphs.

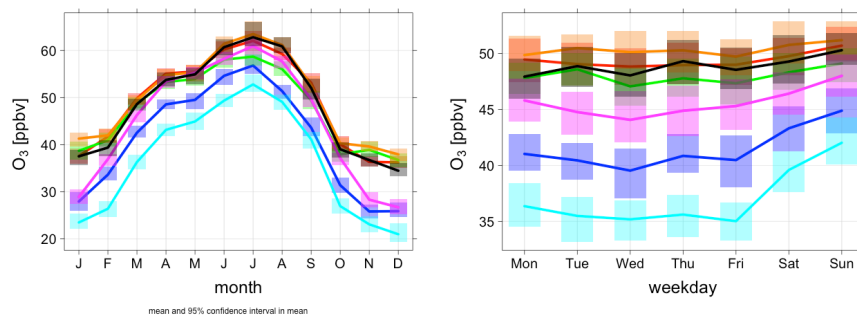


Figure 2B: Long-term (2012-2015) ozone analysis of MDA8 concentrations from seven different sites in the Colorado Front Range. Note that the scales vary between the graphs.

sites / MDA8 [ppbv]	DJF	MAM	JJA	SON	July/August (2012- 2015)	July/August 2014
FC CSU	29	46	54	33	53	52
FC West	38	53	60	42	60	57
Boulder	38	51	57	41	57	53
Golden (NREL)	40	53	61	43	62	58
Greeley	30	51	58	38	59	54
Denver (CAMP)	23	41	50	30	50	47
Chatfield	36	52	61	42	61	56

Table 1: Average MDA8 ozone concentrations for the 4 different seasons (DJF = December, January & February; MAM = March, April & May; JJA = June, July, August; SON = September, October, November), July/August (2012-2015) and July/August 2014 (FRAPPÉ/DISCOVER-AQ).

sites / # of exceedance days	DJF	MAM	JJA	SON	July/August (2012- 2015)	July/August 2014
FC CSU	0.0 (0.0)	0.0 (0.2)	0.4 (2.2)	0.0 (0.1)	0.4 (2.8)	0.0 (3.2)
FC West	0.0 (0.0)	0.1 (1.0)	2.1 (5.5)	0.2 (0.4)	2.8 (6.0)	1.3 (3.8)
Boulder	0.0 (0.0)	0.1 (0.9)	1.1 (2.6)	0.0 (0.3)	1.3 (3.0)	1.3 (1.3)
Golden (NREL)	0.0 (0.0)	0.0 (0.7)	3.0 (6.4)	0.0 (0.5)	3.8 (6.9)	1.9 (5.1)
Greeley	0.0 (0.0)	0.1 (0.4)	0.6 (2.5)	0.0 (0.1)	0.7 (2.8)	0.0 (0.0)
Denver (CAMP)	0.0 (0.0)	0.0 (0.0)	0.2 (0.4)	0.0 (0.0)	0.1 (0.5)	0.0 (0.0)
Chatfield	0.0 (0.0)	0.2 (0.5)	2.6 (5.5)	0.1 (0.3)	2.9 (6.6)	0.6 (2.6)

Table 2: Number of days per month exceeding MDA8 75 ppbv for the 4 different seasons (DJF = December, January & February; MAM = March, April & May; JJA = June, July, August; SON = September, October, November), July/August (2012-2015) and July/August 2014 (FRAPPÉ/DISCOVER-AQ). The number in parenthesis is for number of exceedances for a 70 ppbv standard.

3. Weekend effect by season for ozone

In our first report and in the previous section, we showed that during the FRAPPÉ/DISCOVER-AQ period in July/August 2014 both sites in Fort Collins observed an indication of a weekend effect in ozone. To further investigate this, we looked at seasonal weekday trends (Figure 3) for the multiple year spanning data (2012-2015). The strongest weekend effect for ozone in the Colorado

Front Range is found in Denver (CAMP) followed by FC CSU. These are the two most urban sites that also show the lowest overall ozone concentrations indicating that these two sites are most impacted by high NO_x emitted from nearby sources. This results in titration of ozone at night and suppresses initial ozone production on high photochemistry days. First analysis of available emission inventories suggests a major contribution from traffic emissions in the Fort Collins area, and reduced traffic on weekends leads to a decrease in NO_x causing less titration and a potential to shift towards a more efficient ozone production regime. The weekend effect is lowest in winter and highest in spring and fall. In spring and fall the weekend effect is visible at all sites, but in winter and summer only Denver and FC CSU show a clear weekend effect. One reason for this could be the more stable weather in spring/fall compared to summer, when thunderstorms frequently interrupt daily buildup of ozone and a more homogenous distribution of pollutants. Figure 4A shows the annual trend of the weekend effect of MDA8 for the available data period for each site. All MDA8 ozone concentrations for each season, year and site are averaged for weekdays and weekends separately and then the difference is calculated. Figure 4B shows the relative weekend effect (difference between weekend and weekday ozone divided by weekday ozone). The most statistically significant trend is observed in summer for Denver CAMP with a decrease of 0.3 ppbv/year of the weekend effect. In the 1990's summertime MDA8 ozone was 40% higher on the weekends than on weekdays at the measurement site in Denver (CAMP). In recent years, the difference has decreased to 10%. In summer, FC CSU also shows a significant decreasing trend in the weekend effect on the order of 0.15 ppbv/year, indicating a decrease in NO_x emissions and a shift towards a more NO_x limited regime. Golden (NREL) shows a statistical significant decrease in weekend effect in spring and winter of about 0.15 ppbv/year. Most other sites and seasons do not show a significant trend of the weekend effect, but it should be noted that the weekend effect, similarly as ozone concentrations, can strongly vary for year to year specifically the trend analysis for shorter time periods is influenced by this. In summer 2014 (FRAPPE/DISCOVER-AQ) we observed at all sites an overall smaller weekend effect compared to other years.

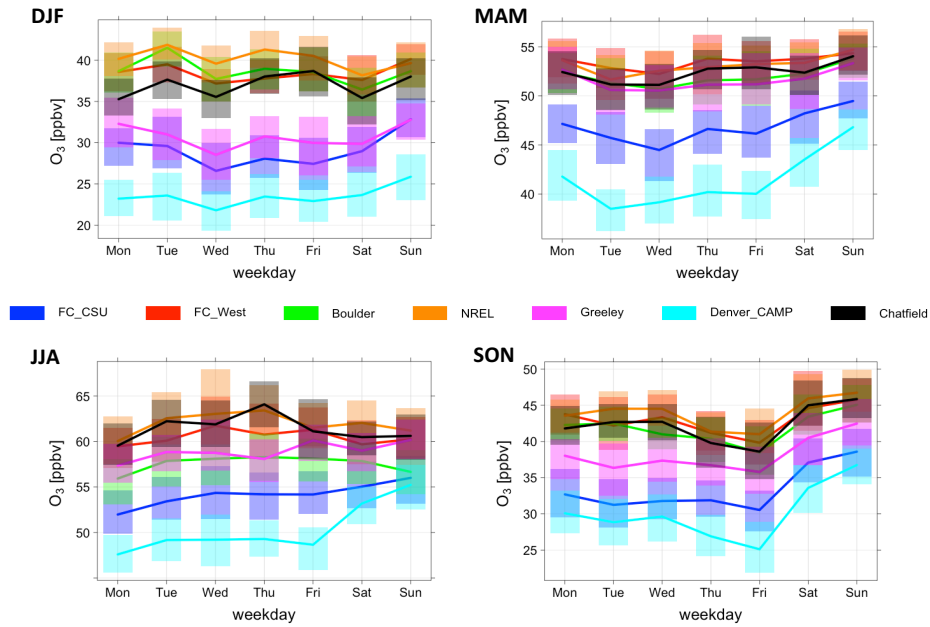


Figure 3: Seasonal weekly cycle of MDA8 ozone concentrations (2012-2015) in the Colorado Front Range split by season. Note that the scales vary between the graphs.

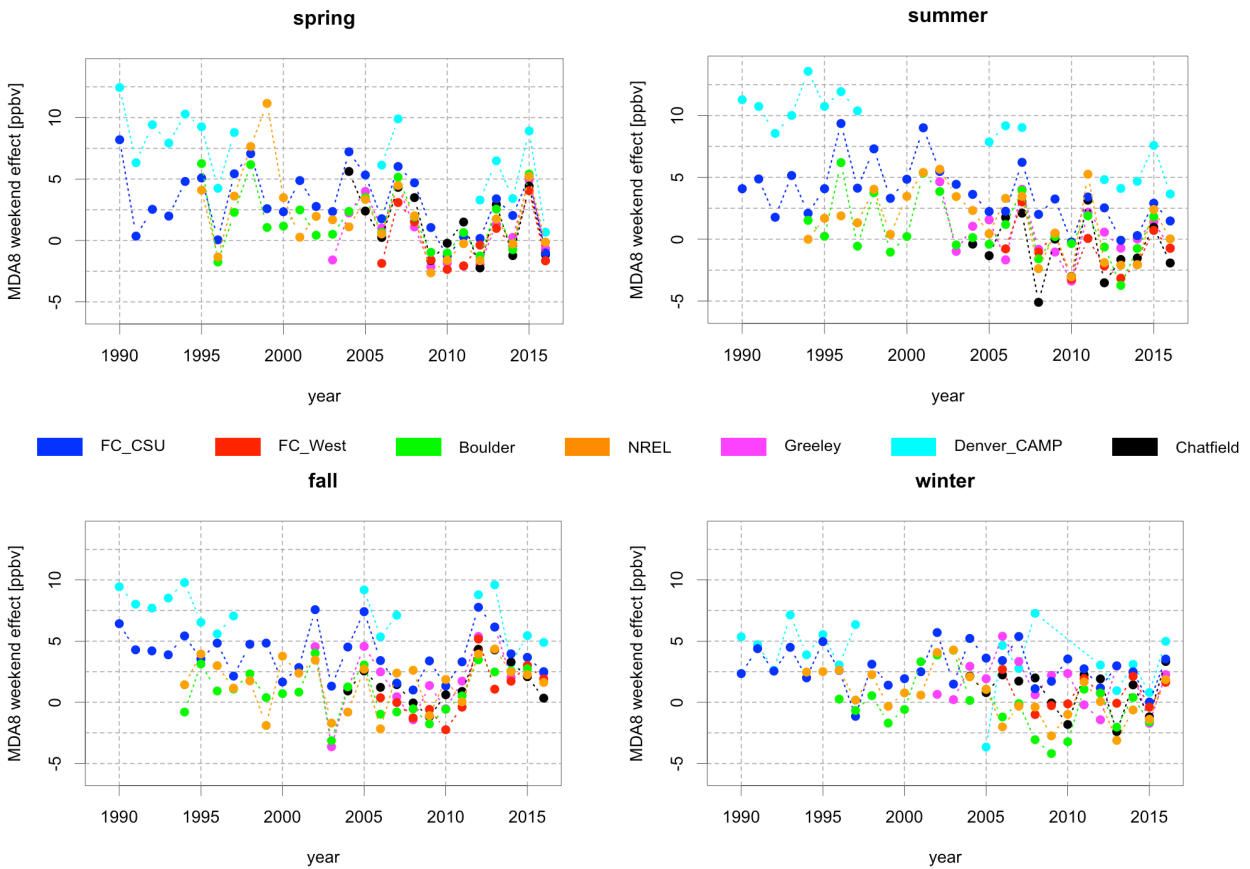


Figure 4A: Weekend effect in MDA8 ozone concentrations in the Colorado Front Range split by season.

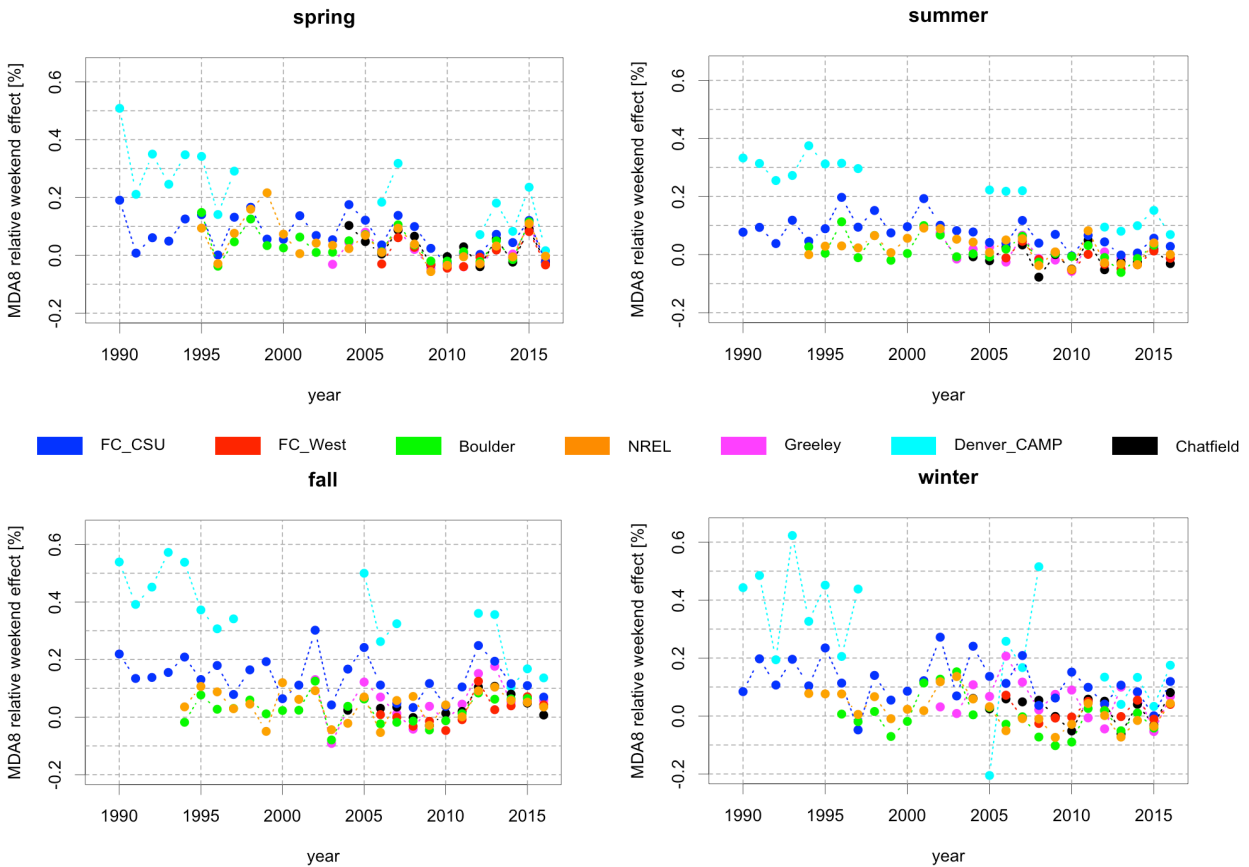


Figure 4B: Relative weekend effect in MDA8 in the Colorado Front Range split by season.

4. Seasonal and annual wind roses (FC CSU)

At FC CSU together with the multi-year ozone measurements also multi-year wind measurements are available. This allows the analysis of seasonal wind roses and polar plots (similar to Report #1 Figures 2 & 4) averaged over all years and for each year individually and puts the summer of 2014 (FRAPPÉ/DISCOVER-AQ) in perspective. Figure 5A shows seasonal wind roses during daytime (9AM-5PM) and Figure 5B shows seasonal wind roses during nighttime (8PM-7AM) for the entire available time period. During summer (JJA), daytime winds are predominately from the S and SSE, similarly to what was observed during FRAPPÉ/DISCOVER-AQ in July-August 2014. All other seasons have overall higher wind speeds with winds arriving both from S-SSE and NNW-N. During nighttime, the predominant wind direction is N-NNE for all seasons. The long-term record is very similar to the FRAPPÉ time period. Night-time wind speeds in winter, spring and fall are also higher than in summer. The analysis of annual summertime (July and August only for direct comparison of the FRAPPÉ/DISCOVER-AQ period) wind directions (Figure 6) shows that 2013 and 2015 have significantly different wind patterns compared to other years. Figure 7 shows the average summer (JA) daytime winds during all years but 2013 & 2015 (left) and only for 2013 & 2015 (right). Most years experienced summer daytime winds from the S-SSE but the years 2013 &

2015 experienced more variable winds with a significant influence from NNW. There is no reason why these two years should have such different transport patterns and we suspect that the reason behind might lie in faulty wind measurements. In March 2012, the meteorological tower was relocated from a freestanding tower on the west side of the shelter to a shelter mounted tower on the south side of the shelter due to the Mason Street Redevelopment Project. Potentially, construction activities or other factors might have caused interferences. In the following, 2013 and 2015 are treated separately from others or omitted in the analysis.

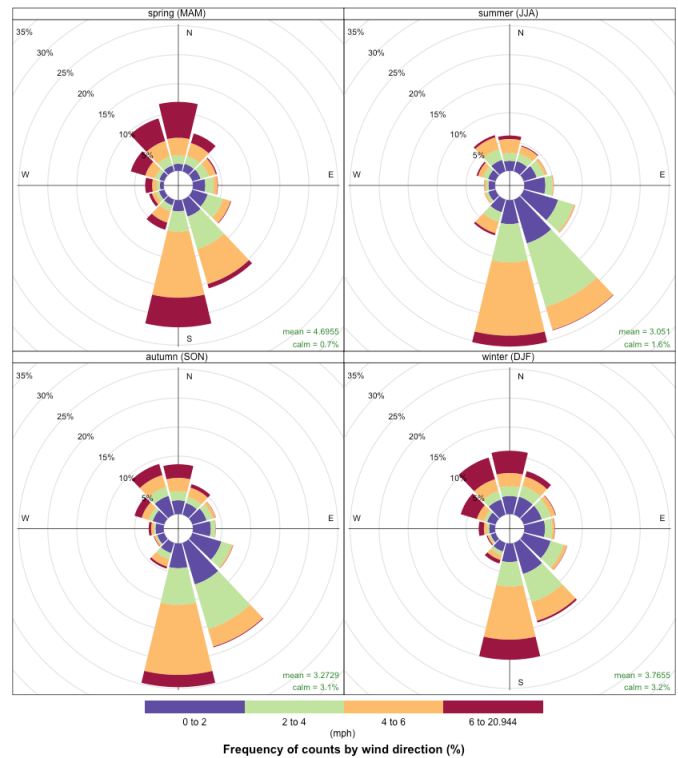


Figure 5A: Hourly averaged wind roses during daytime (9AM-5PM) for the different seasons averaged over the years 1990-2016. This should be compared to Figure 2 in Report #1. *[Note: the years 2013 & 2015 are excluded due to potential wind sensor issues as discussed]*

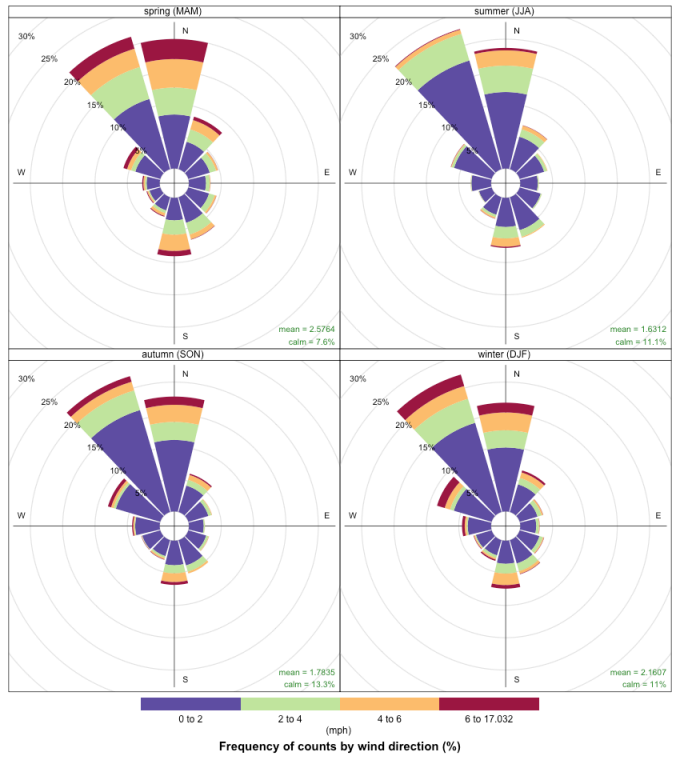


Figure 5B: Hourly averaged wind roses during *nighttime (8PM-7AM)* for the different seasons averaged over the years 1990-2016. This should be compared to Figure 2 in Report #1. [Note: the years 2013 & 2015 are excluded due to potential wind sensor issues as discussed]

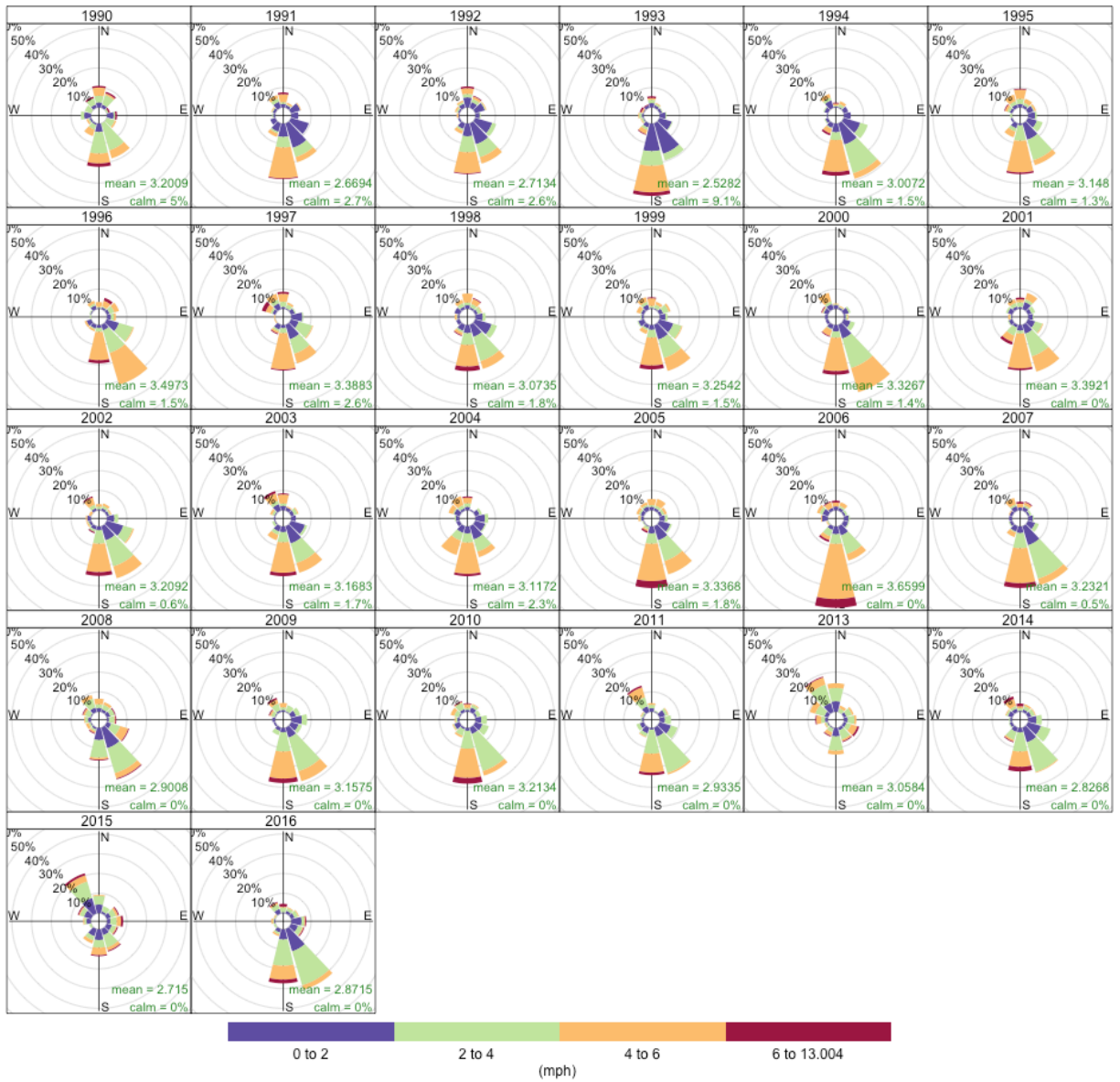


Figure 6: Hourly averaged wind roses for July & August of each year (9AM-5PM). This should be compared to Figure 2 in Report #1

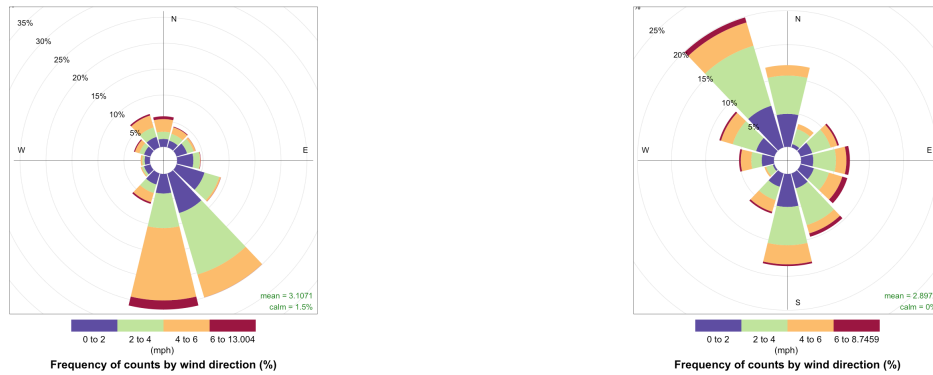


Figure 7: Hourly averaged wind roses during July & August (daytime) for all years but 2013 & 2015 (left) and only 2013 & 2015 (right).

5. Seasonal and annual ozone polar plots (FC CSU)

The long-term record of ozone and wind data at FC CSU also allows to look at polar plots similar to Figure 4A and Figure 4B from Report #1. Figure 8 shows polar plots for ozone concentrations in the morning (9AM-12PM) separated by season. During summertime, high ozone concentrations are on average from the SE in the morning. This is similar to what we observed during FRAPPÉ (Figure 4A Report #1). During spring, high ozone also is seen from the SE sector with additional high values from the W. Fall and winter show overall low ozone due to titration with a dominance of large scale background ozone on the order of 40 ppbv arriving from the W.

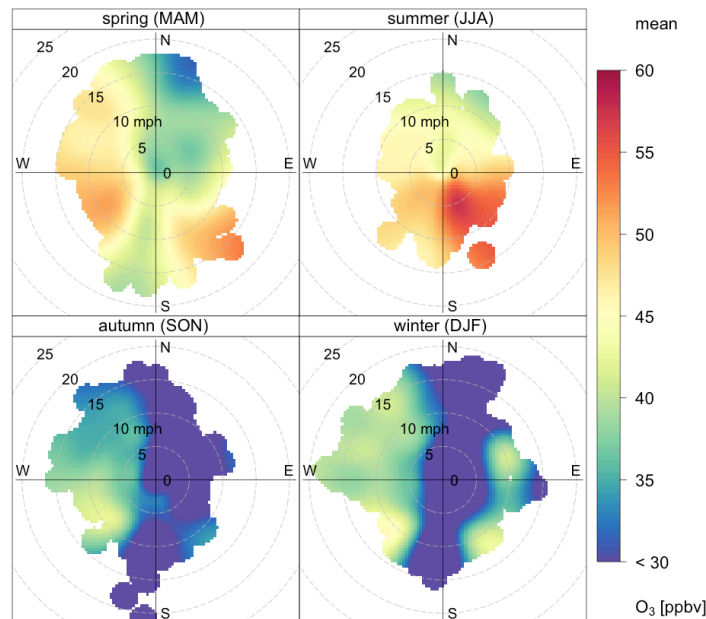


Figure 8: Seasonal ozone polar plots for the morning hours (9AM-12PM) using hourly averaged ozone concentrations and wind data. This should be compared to Figure 4A in Report #1. Note: the years 2013 & 2015 are excluded due to potential wind sensor issues.

Figure 9 shows polar plots for ozone concentrations in the afternoon (12PM-5PM) separated by season. Summertime afternoon high ozone concentrations are, on average, during winds from the SE and low wind speeds. This is similar to what we observed during FRAPPÉ (Figure 4B Report #1) but there is also a potential for high ozone transported to the FC CSU site by winds from the West. Such winds occur rarely (Figure 7 left) except for the years 2013 & 2015, which are omitted from this analysis. There are a number of possible explanations for high ozone arriving from the W-NW. Regional and long-range transport is one possible cause. Another explanation might be occasional early onsets of downsloping winds, which have the potential of circulating pollution back into the city. Downslope winds typically develop towards the evening and the recirculation potential is increased then as can be seen from polar plots for 4-8pm. During all other seasons, highest afternoon ozone concentrations arrive from the SE or W.

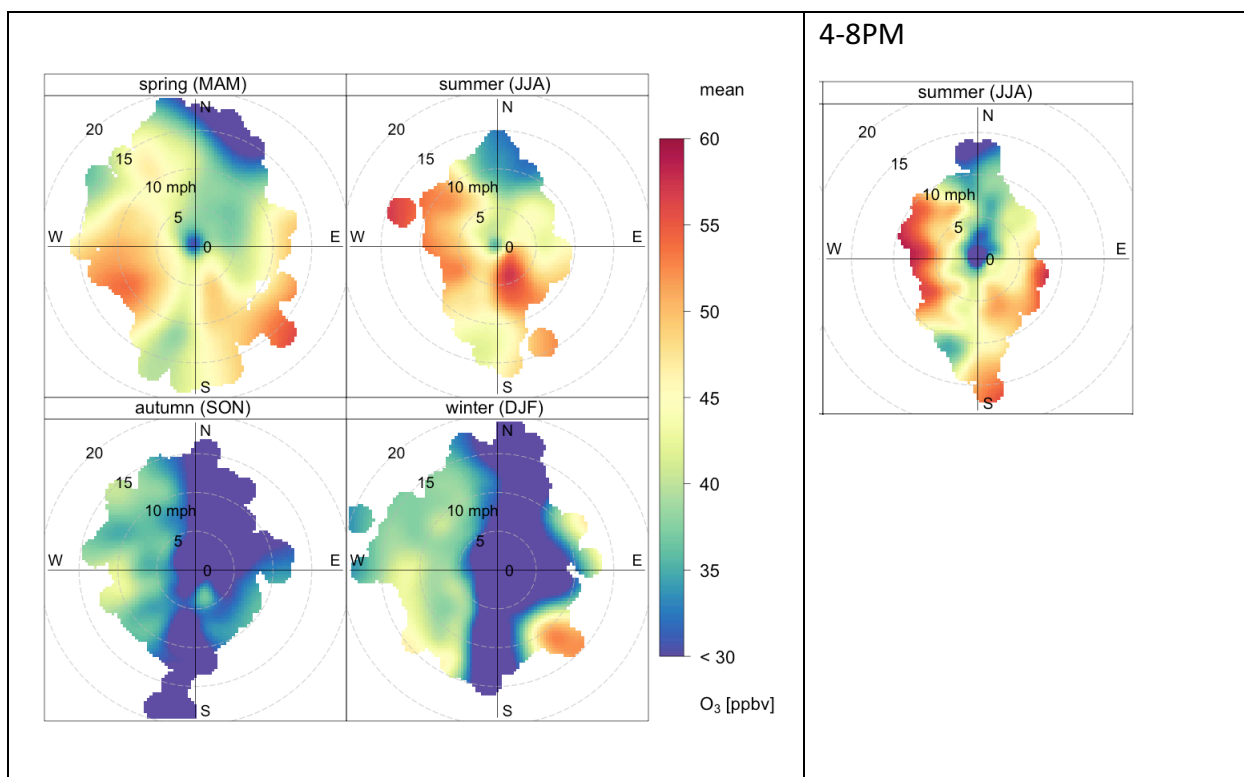


Figure 9: Seasonal ozone polar plots for the afternoon hours (12PM-5PM) using hourly ozone and wind averages and for summer 4-8PM. This should be compared to Figure 4B in Report #1. [Note: the years 2013 & 2015 are excluded due to potential wind sensor issues]

As summertime wind directions were very different for the years 2013 & 2015 we analyze morning and afternoon polar plots for the two different sets of years separately (Figure 10 & 11) albeit not placing high trust into the wind data from the years 2013 & 2015. While typical years have strongest ozone transport from the SE in the morning and afternoon with some

influence from the NW in the afternoon, the years 2013 & 2015 show no pattern under which wind direction or speed the FC CSU surface sites experiences the highest ozone concentrations.

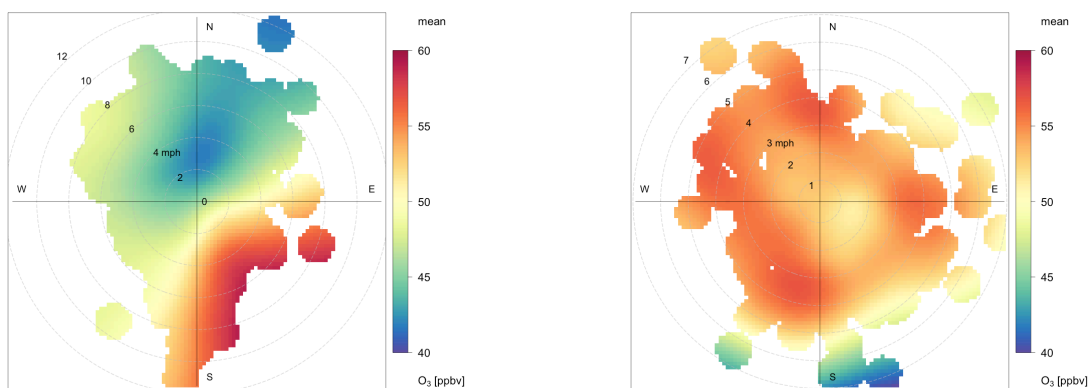


Figure 10: July & August morning (9AM-12PM) ozone polar plots for all years but 2013 & 2015 (left) and only 2013 & 2015 (right) using hourly averaged ozone and wind data.

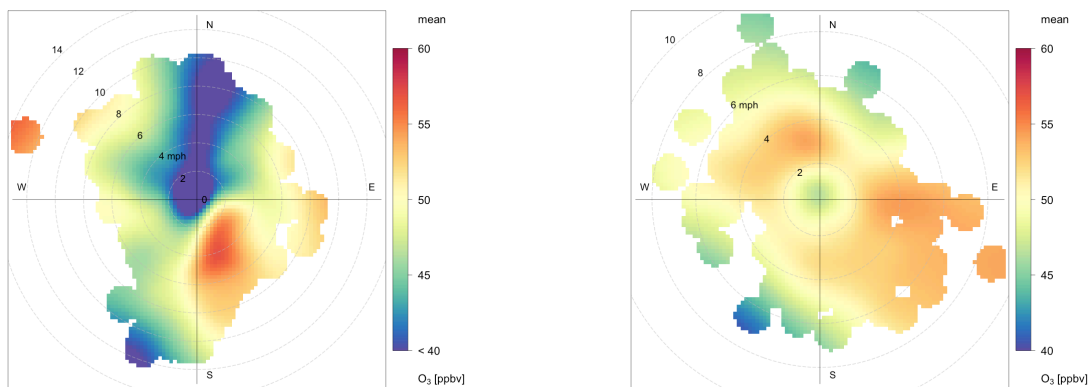


Figure 11: July & August afternoon (12PM-5PM) ozone polar plots for all years but 2013 & 2015 (left) and only 2013 & 2015 (right) using hourly averaged ozone and wind data.

5. Carbon monoxide “weekend effect”

As previously shown in Report #1 (Figure 4A and 4B) highest CO concentrations during FRAPPÉ/DISCOVER-AQ at FC CSU originated from the SE during the morning (9AM-12PM) and even higher CO was seen from the NW in the afternoon (12PM-5PM) at low wind speeds. As mentioned before, winds from the NW are infrequent in the afternoon during summertime though. The coincidence of highest CO and lowest windspeeds indicates nearby sources and we investigate in the following a potential weekend effect of this source looking at long term measurements of CO at FC CSU. As above, we excluded wind data from 2013 & 2015 and therefore investigate the weekend effect in CO for the summers 2012, 2014 & 2016. Figure 12A

and 12B show weekday and weekend polar plots of CO during the morning (9AM-12PM) and afternoon (12PM-5PM) respectively. During both morning and afternoon higher CO concentrations reach the FC CSU site during weekdays compared to weekends, which is in line with reduced transportation and transportation being a major source for CO. Nearby parking lots might actually be responsible for some of the clearly higher CO readings. CO concentrations have strongly decreased since the start of the record in 1990, especially during winter months (Figure 13). This decrease has flattened out in 2010. Since then CO concentrations are constant, with a tendency to increase in spring.

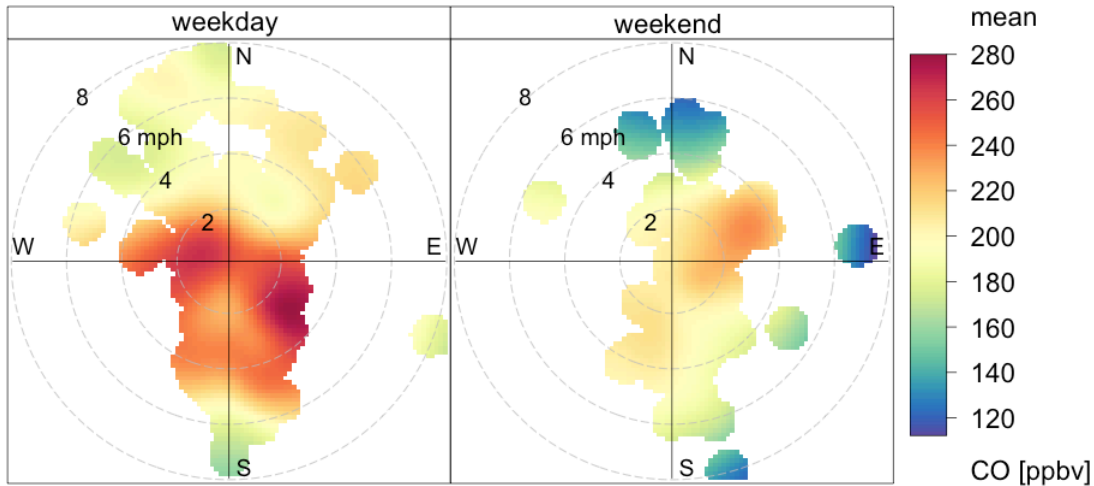


Figure 12 A: July & August morning (9AM-12PM) CO polar plots for 2012, 2014 & 2016 for weekdays (left) and weekends (right) using hourly averaged CO and wind data.

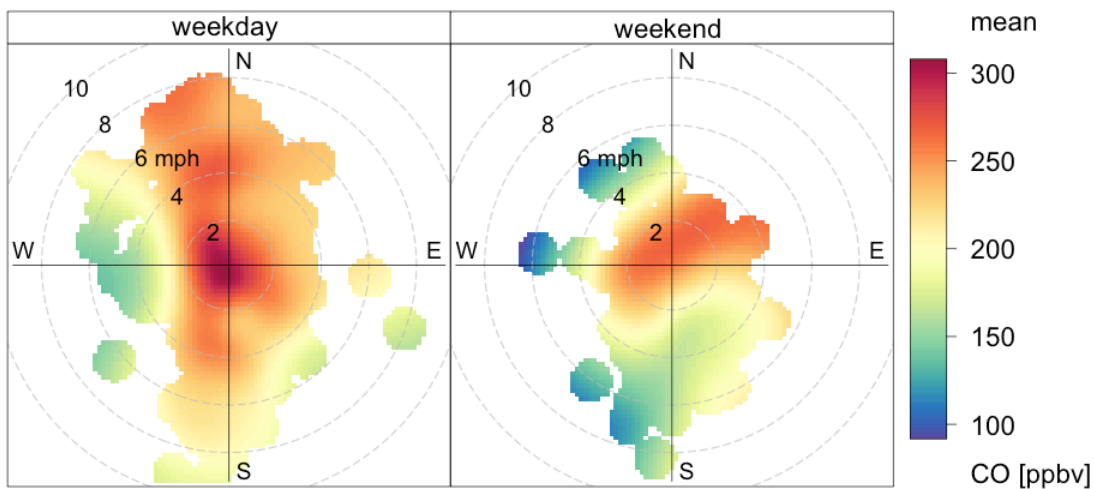


Figure 12 B: July & August afternoon (12PM-5PM) CO polar plots for 2012, 2014 & 2016 for weekdays (left) and weekends (right) using hourly averaged CO and wind data.

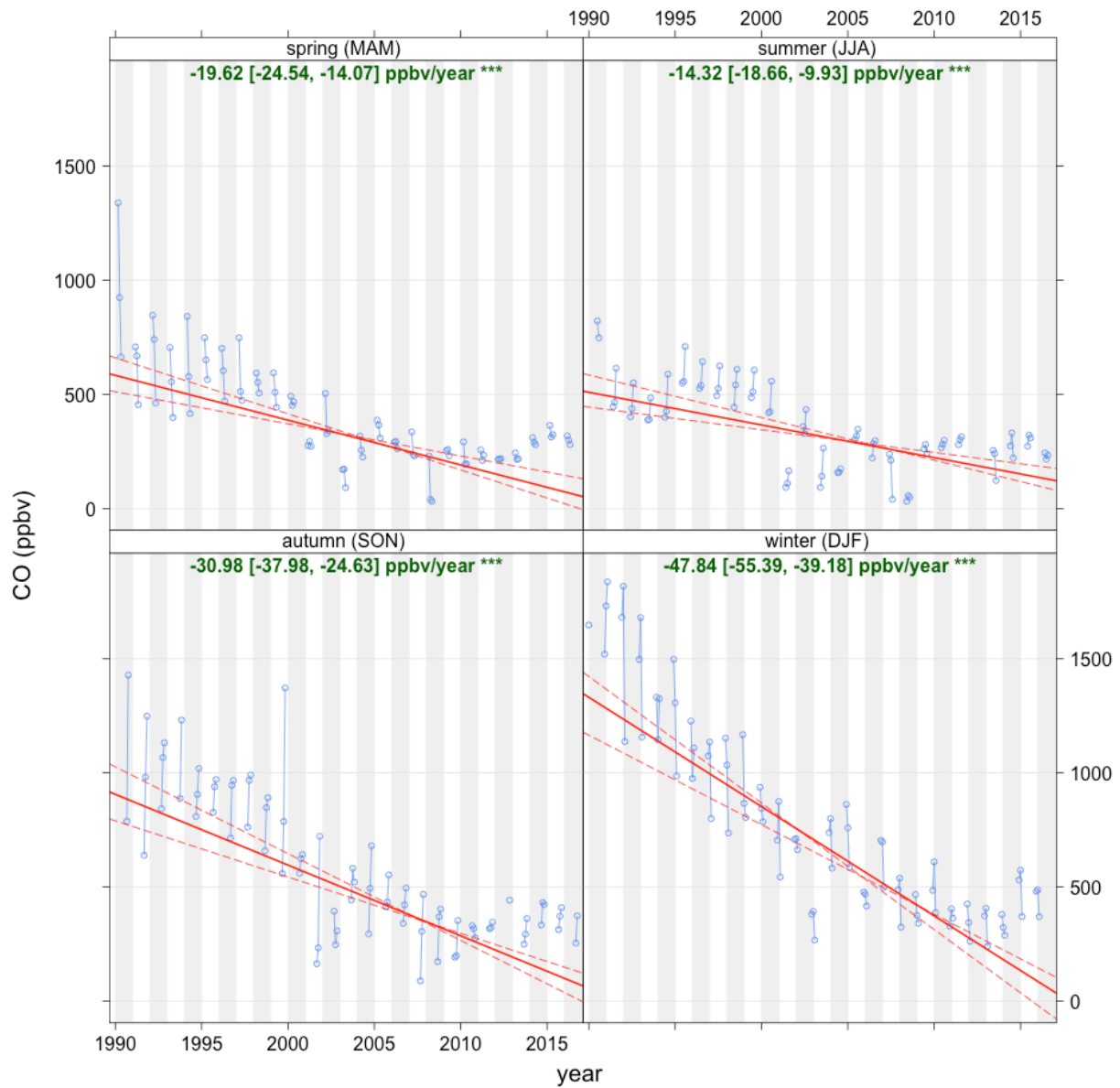


Figure 13: Seasonal long-term trends for CO concentrations at FC CSU

6. Long-term ozone trends in the overall Colorado Front Range and in Fort Collins (by season)

Summertime long-term ozone trends for six surface sites in the Colorado Front Range for MDA8 are shown in Figure 14. Differently to section 2, we analyze here the total available data set for each site as well as for the time period from 2006-2016. The latter is the time period with data availability for FC West, whereas time records of ozone at all other surface sites are longer than that. Table 3 summarizes the trends over the total available time period and for all seasons individually. Table 4 summarizes the total and seasonal trends of 2006-2016. The long-term

trends are either de-seasonalized or calculated for a single season. We do not correct for interannual variability due to meteorology.

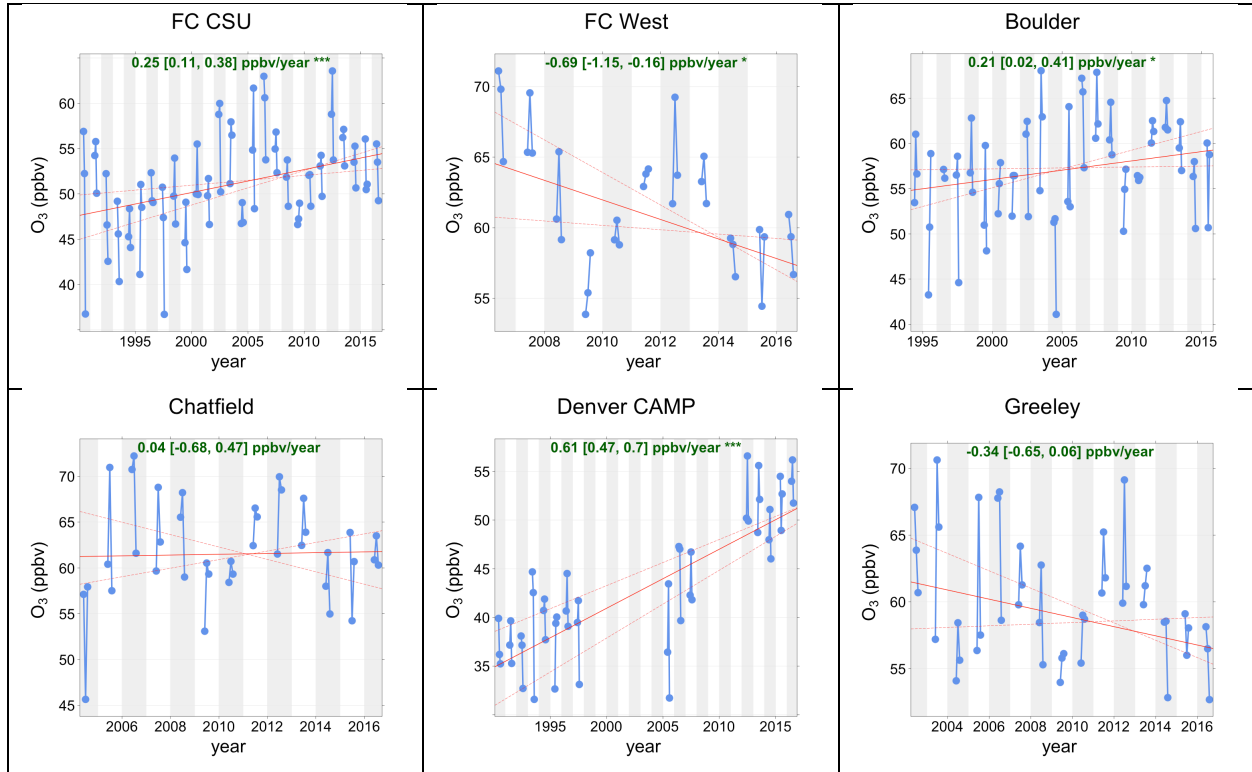


Figure 14: Mean summertime (JJA) MDA8 ozone concentration trends at six different sites in the Colorado Front Range.

Analyzing all available years for each site, Figure 14 shows that in summer there is a statistical significant positive trend of MDA8 at FC CSU, Denver (CAMP) and Boulder, whereas there is no significant trend at Chatfield and Greeley and a statistical significant negative trend at FC West. FC West observes a significant negative trend of -0.69 MDA8 ppbv/year in summertime. FC CSU, Boulder and Denver (CAMP) show significant increases in MDA8 during summertime.

To make the different sites more comparable we look at trends over the last 10 years at all sites, as FC West has observations available only in the last 10 years (Table 4). From all analyzed sites, only Golden, Denver (CAMP) and FC West show a significant trend in the MDA8 over the last 10 years, with increases of 0.23 and 1.59 ppbv/year and a decrease of -0.24 ppbv/year, respectively. The trends in the last 10 years are statistically significant for all seasons at Denver (CAMP). In Golden statistical significance is only found in winter and at FC CSU only in summer. None of the other sites show a significant trend in the last 10 years.

The lack of statistical significant trends at some sites does not necessarily imply that ozone levels have not changed over the past 10 years but likely reflects that the impact of inter-annual variability in meteorology is strong and might mask potential ozone trends. This is in agreement

with a recent CDPHE report on ‘Trends in weather corrected ozone and nitrogen dioxide’ (https://raqc.egnyte.com/dl/H0xiX8ACR4/TSD_TrendsInWeatherCorrectedOzone.pdf), where trends e.g. in Chatfield were found to decrease after correcting for inter-annual weather differences. The decreasing trend we find at FC West is also in line with a decreasing weather corrected trend shown in this report.

trends [ppbv/year]	all years	spring (MAM)	summer (JJA)	fall (SON)	winter (DJF)	data availability
FC CSU (MDA8)	0.24 (*)	0.20 (*)	0.25 (***)	0.23 (+)	0.26 (***)	1990-2016
FC West (MDA8)	-0.24 (*)	-0.26 (_)	-0.69 (*)	-0.04 (_)	0.06 (_)	2006-2016
Boulder (MDA8)	0.31 (***)	0.42 (***)	0.21 (*)	0.35 (*)	0.48 (***)	1994-2015
Chatfield (MDA8)	0.10 (_)	-0.06 (_)	0.04 (_)	0.24 (_)	0.30 (_)	2004-2016
Golden (MDA8)	0.26 (***)	0.27 (*)	0.07 (_)	0.36 (**)	0.34 (***)	1994-2016
Greeley (MDA8)	0.05 (_)	0.05 (_)	-0.34 (_)	0.10 (_)	0.46 (*)	2002-2016
Denver (CAMP) (MDA8)	0.38 (***)	0.52 (***)	0.61 (***)	0.45 (***)	0.51 (***)	1990-1997, 2005-2007, 2012-2016

Table 3: Average ozone trends of MDA8 ozone for all available years at each site and for each season. Symbols in parenthesis indicate the statistical significance of the trend with the following p-values: $p < 0.001 = ***$, $p < 0.01 = **$, $p < 0.05 = *$, $p < 0.1 = +$, $p > 0.1 = _$

trends [ppbv/year]	2006-2016	spring (MAM)	summer (JJA)	fall (SON)	winter (DJF)	data availability
FC CSU (MDA8)	0.01 (_)	-0.35 (_)	-0.10 (_)	0.37 (_)	0.17 (_)	2006-2016
FC West (MDA8)	-0.24 (*)	-0.26 (_)	-0.69 (*)	-0.04 (_)	0.06 (_)	2006-2016
Boulder (MDA8)	-0.19 (_)	0.05 (_)	-0.66 (_)	0.02 (_)	-0.27 (_)	2006-2015
Chatfield (MDA8)	-0.01 (_)	-0.05 (_)	-0.40 (_)	0.27 (_)	0.19 (_)	2006-2016
Golden (MDA8)	0.23 (*)	0.31 (_)	-0.16 (_)	0.44 (_)	0.36 (*)	2006-2016
Greeley (MDA8)	-0.08 (_)	-0.15 (_)	-0.45 (+)	0.24 (_)	0.33 (_)	2006-2016
Denver (CAMP) (MDA8)	1.59 (***)	0.81 (*)	0.81 (**)	1.13 (*)	0.90 (**)	2006-2006, 2012-2016

Table 4: Average ozone trends of MDA8 ozone for 2006-2016 at each site and for each season. The trend over the last 10 years was chosen as that is the time period that FC West has data availability. Symbols in parenthesis indicate the statistical significance of the trend with the following p-values: $p < 0.001 = ***$, $p < 0.01 = **$, $p < 0.05 = *$, $p < 0.1 = +$, $p > 0.1 = _$

At FC CSU, which has long-term wind measurements, the trend can be analyzed in more detail by wind direction (Figure 15 A & B). For all wind directions we find a significant increase of ozone over time. The positive ozone trend is strongest for winds from the N, NE and E and smallest for winds from the S. As noted in the Figure labels, this trend analysis is influenced by the dominance of Southerly wind directions during daytime.

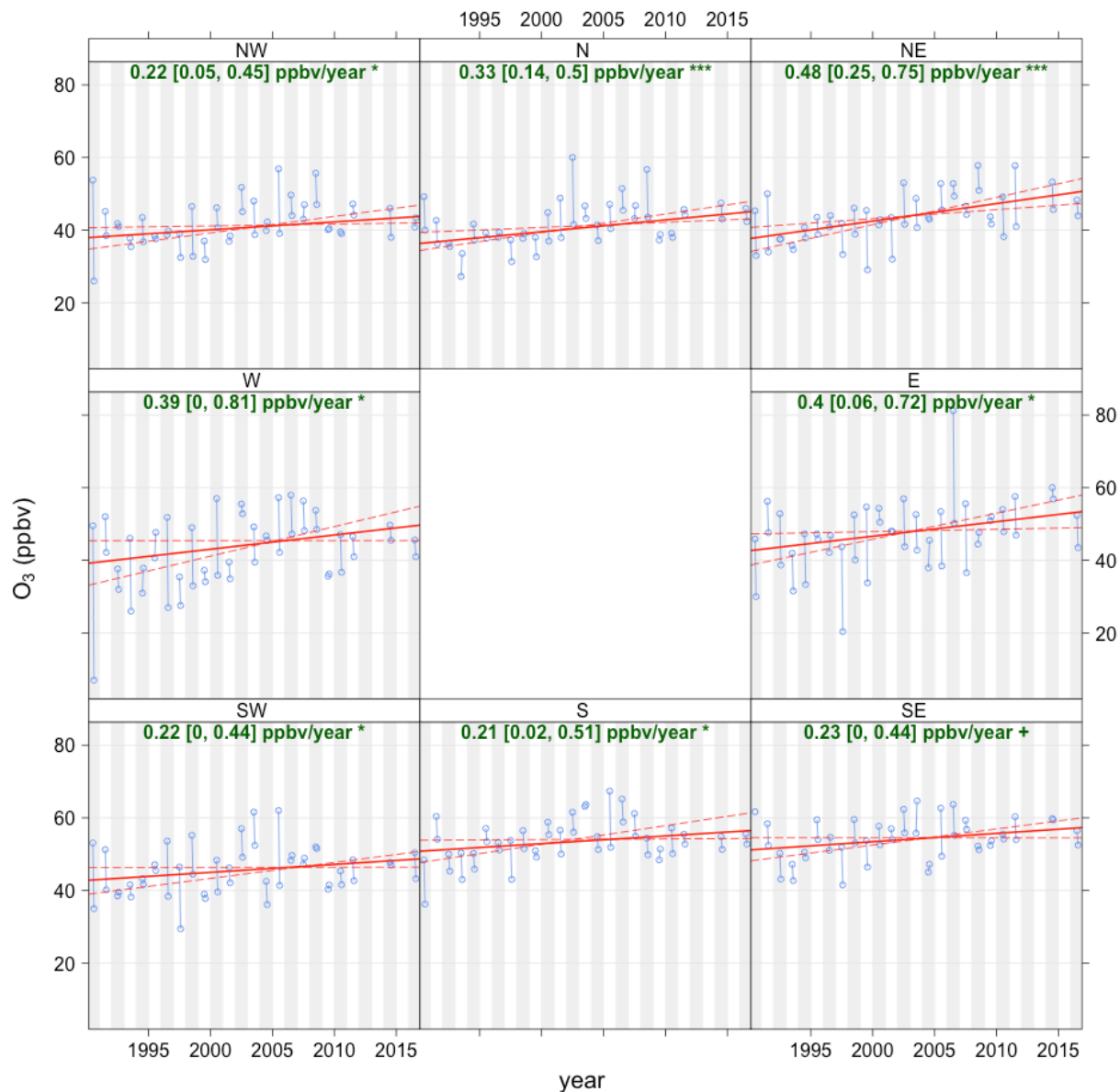


Figure 15A: Hourly daytime summertime (July & August 9AM-17PM) ozone concentration trends at FC CSU divided up in wind sectors (years 2013 & 2015 are removed due to potentially issues with wind sensors). Data coverage during daytime is best in SE and S with 22% and 36% of the total available data, as this is the dominant wind direction. All other wind sectors are rare wind directions during daytime and occur only 3-7% of all times each.

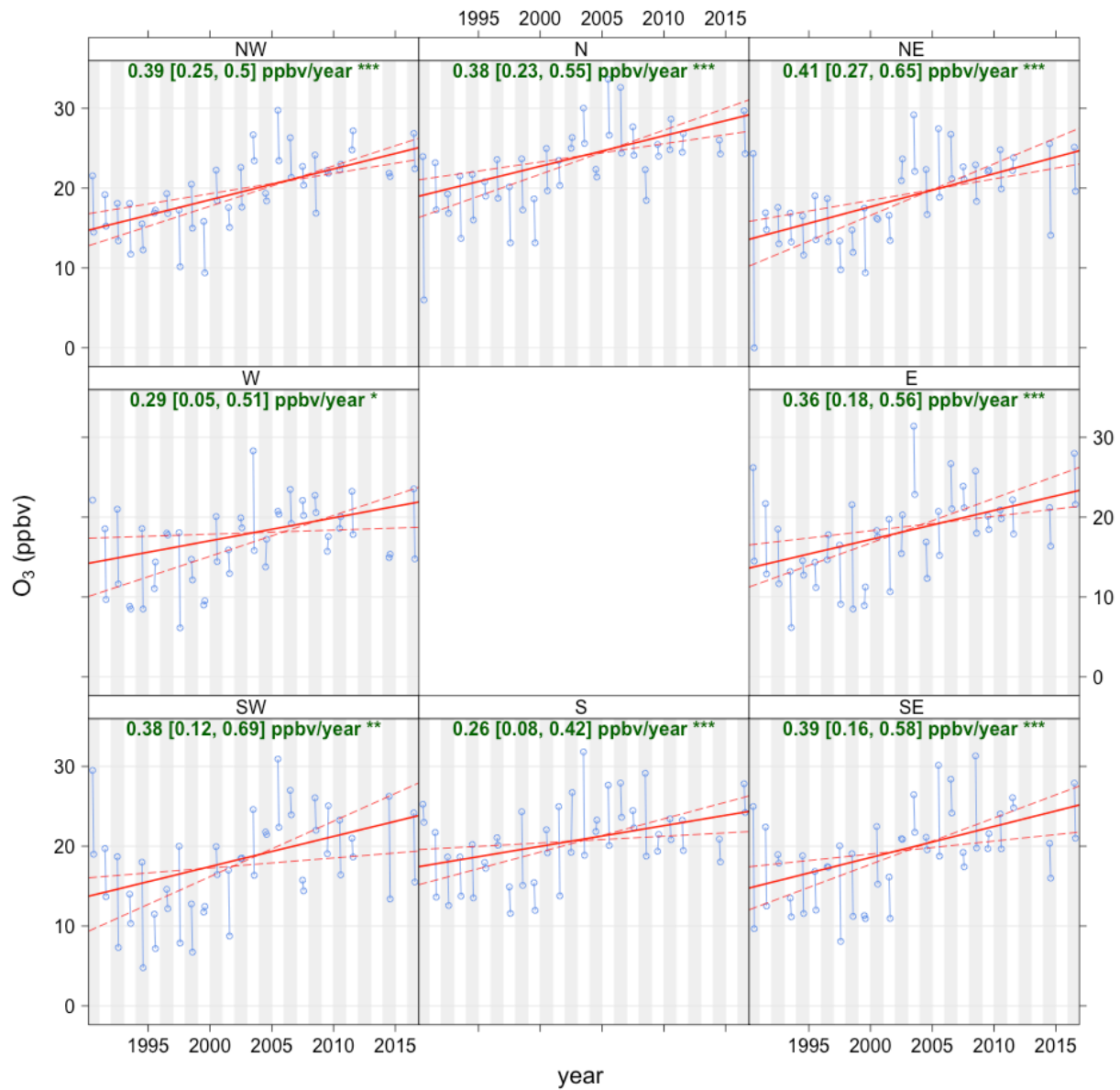


Figure 15B: Hourly nighttime summertime (July & August 8PM-7AM) ozone concentration trends at FC CSU divided up in wind sectors (years 2013 & 2015 are removed due to potentially issues with wind sensors). Data coverage during nighttime is best in NW and N with 24% and 33% of the total available data, as this is the dominant wind direction. All other wind sectors are rare wind directions during nighttime and occur only 5-9% of all times each.

Future work:

Our analysis to date has focused on the FRAPPE/DISCOVER-AQ intensive measurement period (Report #1) and the long-term analysis of surface measurements (Report #2). In the next steps, we will analyze the performance of a chemical transport model compared to the observations and put the current findings into perspective to existing emission inventories. Output from the

chemical transport model will after evaluation be used to assess the representativeness of the current monitoring sites.

Acronyms:

NAAQS	National Ambient Air Quality Standard
MDA8	Maximum daily average 8-hour ozone
ppbv	parts per billion volume
JJA	Average over June-July-August
SON	Average over September-October-November
DJF	Average over December-January-February
MAM	Average over March-April-May

Attachment 1:

The “ozone weekend effect” is defined as the phenomenon of ozone concentrations tending to be higher on weekends than on weekdays. The general weekend effect indicates a VOC-limited regime with an excess of NO₂ keeping the ozone formation low on weekdays via the titration reaction. On weekends, when emissions are reduced, the NO_x falls and the ozone concentration rises.