Final Report for: Monitoring network assessment for the City of Fort Collins

Assessment of the current ozone monitoring network based on the analysis of observations and model simulations

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Overview

In the summer of 2014 (July 15 – August 18), a large experiment was carried out focused on studying the air quality in the Colorado Front Range. Meteorological and chemical measurements on-board four aircraft (NCAR C-130, NASA P-3B, NASA B-200 and NASA-FALCON), as part of the NASA DISCOVER-AQ and NCAR/NSF and State of Colorado FRAPPÉ initiatives (in here referred to as FRAPPÉ/DAQ), were combined with numerous surface-based measurements of meteorological and chemical species at several sites in the Colorado Front Range. The flight patterns of all four aircraft and the full data set including data from surface sites are publicly available at http://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html. The NASA P-3 flew a repetitive pattern on every flight conducting spirals over six core sites, one of which being Fort Collins. The NCAR C-130 followed variable patterns dictated by conditions and individual objectives.

The goal of this project is to perform a comprehensive analysis of the data set collected during both the FRAPPÉ and the DISCOVER-AQ missions together with chemical transport modeling to characterize the current ozone monitoring network for the City of Fort Collins. It will be assessed whether the existing ozone monitoring sites (FC CSU, FC West) are optimally located or whether there might be other locations more suited to convey a representation of the spatial variability and that could provide better information on potential health impacts.

1. Summary from previous reports

In here we briefly summarize work that has been discussed in the previous Interim Reports from January 2017 and March 2017. For this work, we analyzed surface ozone and wind measurements from the two monitoring sites FC West, located west of the city and FC CSU, located in the center of Fort Collins as well as detailed chemical aircraft measurements and ground based NO_x and wind measurements at FC West from the FRAPPÉ/DAQ campaign.

1.1. Spatial and temporal variability in ozone and ozone precursors

Wind patterns in the NFRMA are dominated by typical summertime thermally driven mountain-valley flows that transport polluted air from the east/south-east to the two ground sites in Fort Collins bringing ozone and VOC enriched air to the monitoring sites. Generally, FC West experiences 5-10 ppbv higher ozone concentrations than FC CSU, and also during nighttime ozone concentrations at FC West are about 10 ppbv higher than at FC CSU. This is likely due to higher NO emissions close to FC CSU leading to a titration of ozone forming NO_2, a temporal ozone reservoir. (see Appendix A on the non-linearity in ozone production). As the air is transported west to the FC West site, this temporal ozone reservoir can reform ozone by photolysis of NO_2 followed by reaction with O_2. Additionally, there is more time available for air to chemically process while being transported from the east across the urban area of Fort Collins. During nighttime, cleaner air is flowing down the slopes from the north-west bringing air lower in ozone to the plains. The lower NO_x concentrations at FC West inhibit ozone titration, whereas at FC CSU local sources lead to higher NO_x levels and more ozone loss. Compared to NO_x observations in other cities in the Front Range, NO_x concentrations in the Fort Collins are on the low end of the range.

In summary, ozone at FC West shows characteristics of a site that is more strongly impacted by transported pollution (photochemically aged regional pollution mixed with pollution from the city of Fort Collins), whereas FC CSU shows the characteristics of a site that is impacted by nearby sources.

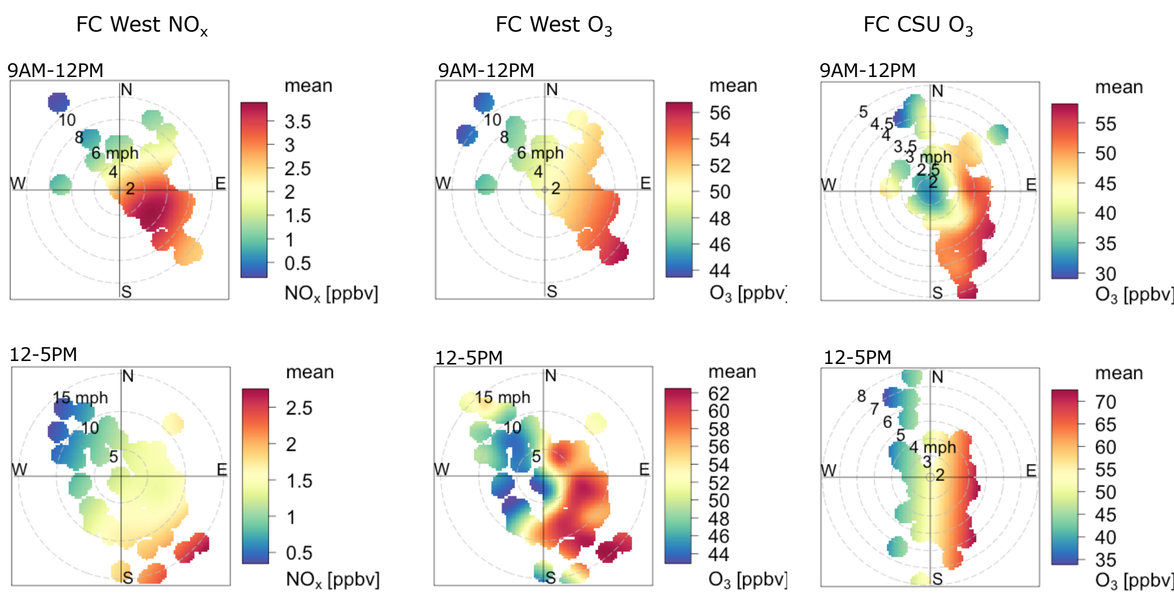


Figure 1: Polar plots of NO_x at FC West (left) and ozone at FC West and FC CSU for morning (9AM-12PM; top) and afternoon (12-5PM; bottom). Only days with available NASA GSFC wind and NO_x measurements are included.

1.2. VOC concentrations and Reactivity

VOC observations available from both aircraft (NCAR C-130 and NASA P-3) reveal species-specific spatial patterns over the Fort Collins area. Their potential to form ozone was analyzed using a chemical box model. This analysis suggests that air sampled in the north-east sector of the Fort Collins area had the highest VOC concentrations and the highest potential to form ozone. Ozone concentrations in Fort Collins are therefore not only influenced by local sources, but also both by emissions to the east and southeast with subsequent transport and photochemical processing of these air masses.

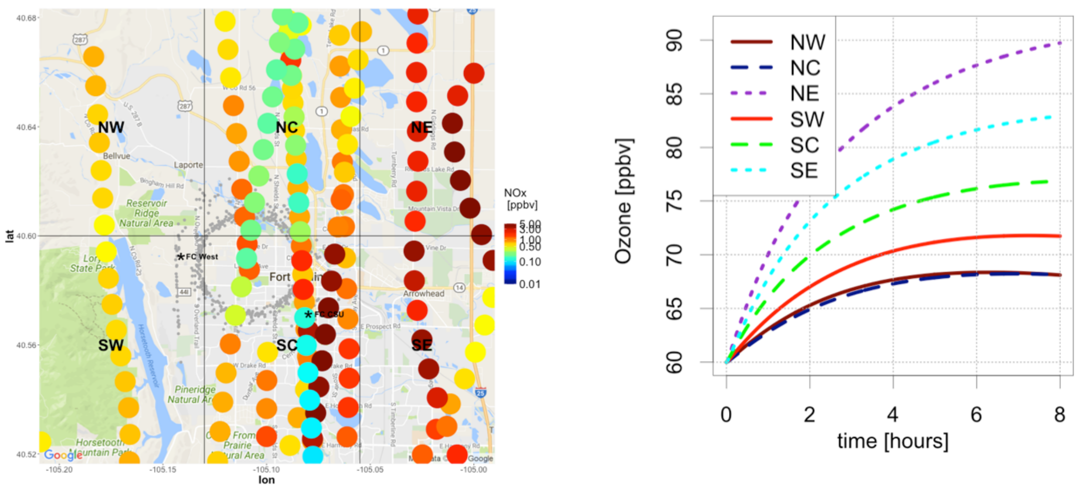
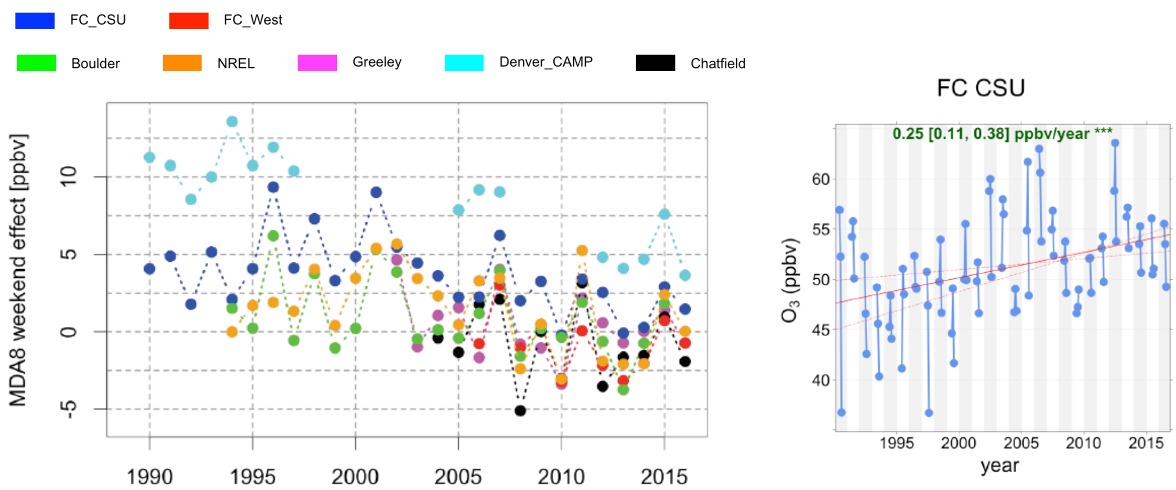


Figure 2: Left: Maps with NCAR C-130 NO_x data colored by measured mixing ratio, the Fort Collins surface sites are marked with black stars, grey markers indicate NASA P-3 spirals. The black lines divide the map centered in Fort Collins into six sectors: north-west (NW), north-center (NC), north-east (NE), south-west (SW), south-center (SC) and south-east (SE). Right: Ozone formation potential of the trace gas mix measured by the NCAR C-130 for the six different sectors. For this plot all ozone starting concentrations were set to 60 ppbv.

1.3. Trends in Surface Ozone Concentrations

The analysis of long-term ozone concentration measurements revealed that since 2012 ozone MDA8 concentrations at FC CSU exceed the 75 ppbv NAAQS, on average, 0.5 times per month during summertime. At FC 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 of 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/DAQ) 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.



Annual trend in JJA MDA8 weekend effect *Annual trend in JJA MDA8*

Figure 3: Annual Trend in the JJA average weekend effect at various sites in the NFRMA (left) and trends in JJA average MDA8 at FC CSU (right).

2. Chemical Transport Modeling for Fort Collins

The included modeling results are tightly linked to the modeling conducted for the State of Colorado as part of Project RFP # FAAA 2016000120 (FRAPPÉ and DISCOVER-AQ Data Analysis). The final report for this project (referred to as CDPHE/State of Colorado report) will be available from CDPHE and will include a detailed description and analysis of the modeling work. For this reason, only a short background on the modeling background is given here and focus is placed on model results relevant for assessing the current network in Fort Collins.

2.1. Model Description

CMAQ modeling work is conducted using the latest CMAQ version v5.2 beta and has been performed by NCAR postdoc Sojin Lee. In accordance with the Colorado SIP modeling work, we defined a 2-domain setup including a 12 km x 12 km outer domain (d01) covering the Western U.S. and a 4 km x 4 km inner domain (d02) over Colorado. The model top is set at 50 hPa with 37 vertical levels. WRF v3.8.1 is run to create hourly meteorological fields for driving CMAQ. We applied the suggested nudging method from the Western State Air Quality Modeling Study (WSAQS) WRF simulation and also include FRAPPÉ observations of surface and C-130 wind observations in the nudging routine. The model simulations are started on 9 July 2014 and run through 20 August 2014; instantaneous output is saved every hour.

Anthropogenic emission inputs for CMAQ are based on several different data sets. We acknowledge Dennis McNally (Alpine Geophysics) for providing the 2017 onroad mobile inventory data and Dale Wells (CDPHE) for providing the 2014 oil and gas emission (O&G) input data. EPA emission totals were derived from the EPA 2011 v6.3 platform (ftp://ftp.epa.gov/EmisInventory/2011v6/v3platform/reports) and the EPA 2014 Emissions Inventory System (EIS) sector summary (https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data, download date: 05/04/2017). The EPA 2017 emission information is derived from the emission summary available from ftp://ftp.epa.gov/EmisInventory/2011v6/v3platform/reports/2017ek_county_monthly_report.xlsx (download date: 03/28/2017). The total NOx and ethane emissions derived from these original input data is shown in Figure 4 and the emission totals for NOx and VOCs are listed in Table 1. Note that ethane emissions in Weld County reach up to 2 moles/s, up to a factor of 1000 higher than for the Fort Collins area. Total anthropogenic emissions in Larimer County account for about 8% of all NFRMA NO_x and 5% of all NFRMA VOC emissions.

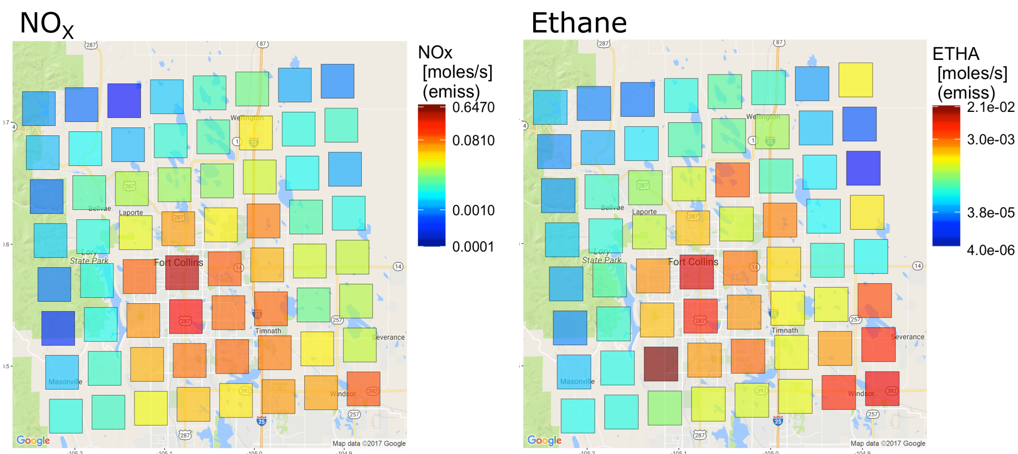


Figure 4: Emissions for NOx (left) and Ethane (right) for the Fort Collins area for the original input inventory.

Emission Sector	NOx (tons/year)	VOC(tons/year)
Offroad mobile	885	1,305
Onroad mobile	4,225	2,341
O&G	21	305
Industrial	922	3,022
CEM	1,420	38
Others	69	720
Anthro. Total	*7,542*	*7,731*

Table 1: NO_x and VOC emission totals for different emission sectors in Larimer County. For a list of emission totals for other counties we refer to the CDPHE/State of Colorado report.

Comparison with C-130 detailed chemical composition measurements indicate various shortcomings in this "a priori" (S0) inventory and for development of our base emissions (S05) the following updates on the NFRMA emissions were applied:

- a factor of 2 increase in ethyne from all mobile emissions (on and off road)
- a factor of 2 increase in on-road mobile emissions in all urban regions outside the Denver metro area
- a factor of 2 increase in NO_x and VOC emissions from O&G except for ethane

For a description of the methodology and evaluation of the base emission inventory we refer to the CDPHE/State of Colorado report. Our base simulations (S05) are conducted using this inventory.

2.2. Model Evaluation: Fort Collins Surface Measurements

Figure 5 shows both observed and modeled daytime and nighttime winds from FC CSU and FC West. For comparison with the measurements, the hourly model output for the grid box containing the measurement location is used. The model performs well at FC West, which is a more "free standing" location and reflects better the regional flows. At FC CSU, modeled maximum wind speeds are about 2 times higher than the observed winds and the model does not reflect the dominance of winds from the SSE. This is, because the model does not capture the surface conditions near FC CSU (buildings, roads) but rather reflects the more regional flows and therefore looks similar at both stations.

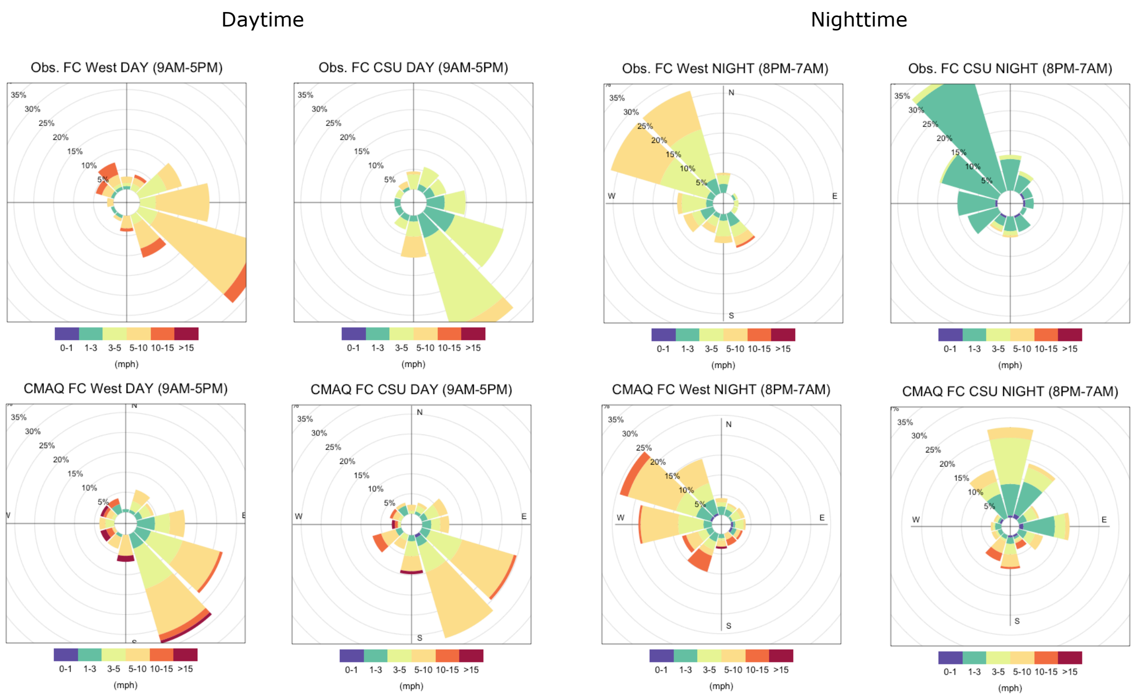


Figure 5: Wind roses during daytime and night time at FC West and FC CSU for observations (top row) and CMAQ model (bottom row). Only days when wind measurements at FC West are available have been used.

Figure 6 compares the diurnal cycles of observed and modeled ozone concentrations at FC West and FC CSU as well as surface NO_x at FC West and surface CO at FC CSU. The daytime concentrations at FC West are well captured by the model whereas they are overestimated at FC CSU. Nighttime ozone is biased high at both sites. CO at FC CSU is underestimated in the model at most times during the day except during the morning rush hour. The high measured CO concentrations suggest a local source as also discussed in Interim Report II. The local nature of the FC CSU location poses a challenge for the model. Given the 4 km spatial resolution we do not expect that the model captures the localized airflows and boundary layer height, and as a result local disturbances to ozone concentrations. At FC West, the model overestimates the NO_x measurements specifically during nighttime and early morning when the boundary layer is low.

As mentioned above, for comparison to surface sites, we choose the grid box containing the location of this site. In the case of FC West, the location lies at the edge of the grid cell and the center of the selected model grid box is 2.1 km from the FC West location. To test the sensitivity of the results to the spatial resolution, we show in Figure 7 surface observed and modeled surface NO_x and ozone at FC West, but instead of selecting the model grid box containing the site, we are selecting a grid box just to the West of it. In this case, the center of the selected grid box is 3.4 km from the FC West location. As can be seen, the good agreement with ozone observations during daytime remains, but the high model bias during nighttime increases somewhat. Model NO_x is in much better agreement for this grid selection and overall biased slightly low. These results demonstrate the strong influence of the model spatial resolution, especially on emission species, but suggest that overall the modeled values can be considered representative for measured concentrations.

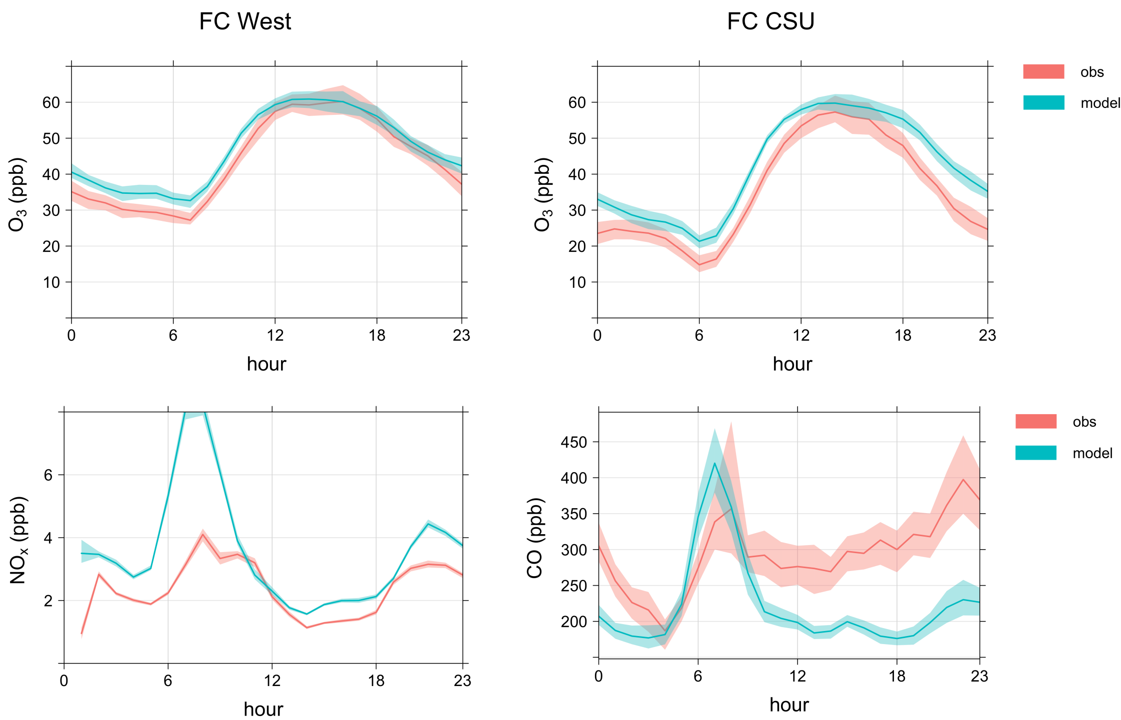


Figure 6: Observed and modeled average diurnal cycle in surface ozone concentrations for FC West and FC CSU (top) and surface NO_x at FC West and surface CO at FC CSU (bottom).

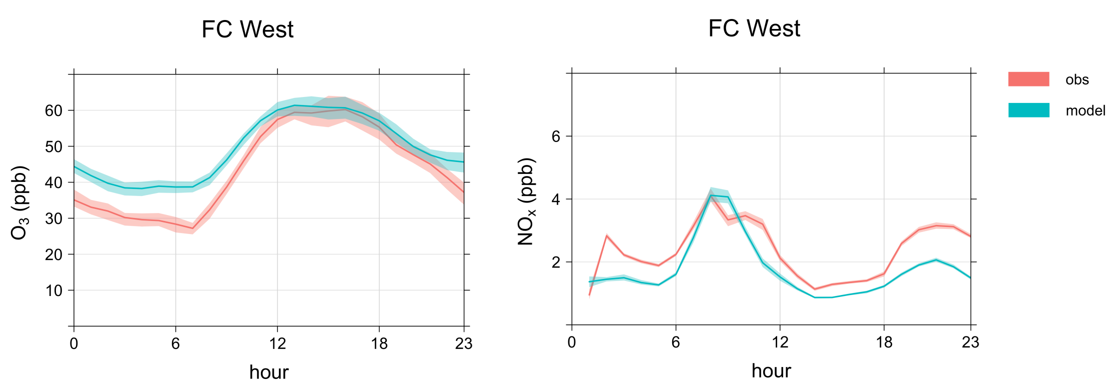


Figure 7: Observed and modeled average diurnal cycle in surface ozone and NO_X concentrations FC West. CMAQ model results are derived for a grid box just to the West of the one containing FC West.

2.3. Model Evaluation: C-130 Aircraft Measurements

For comparison of CMAQ model results to C-130 aircraft data, we interpolated the hourly model output to the location and time of the 1-minute observations. The campaigns were not focused exclusively on the Fort Collins area, but measurements are available from overflights on a number of days. This provides a limited data set for evaluation and characterization and the random sampling certainly poses larger challenges to the model. Data from 11 flights were used with the flights on July 27 and 28 having the most coverage.

In Figure 8 we show measured and modeled NO_x concentrations filtered by wind direction. The filtering is based on the measured wind direction only, but the graphs show that this also works well for the modeled data reflecting that the model generally agrees with the observed wind direction. Note that these data are selected from all flights and contain data from different days with quite different meteorological conditions. Hence the patterns shown are not only representing spatial variability but also the variability between different flight days and times. We only select data below 1 km a.g.l. to better relate the aircraft measurements to the surface conditions. Highest NO_x is measured over the city and to its East and South and when winds are from the East or South. No aircraft data were collected when westerlies prevailed. The data filtered for winds from the North nicely show the low NO_x levels North of the city and increasing as the aircraft flies over the city picking up local pollution. The model reasonably well reflects the patterns and overall measured concentrations with slightly lower concentrations when winds are from the South.

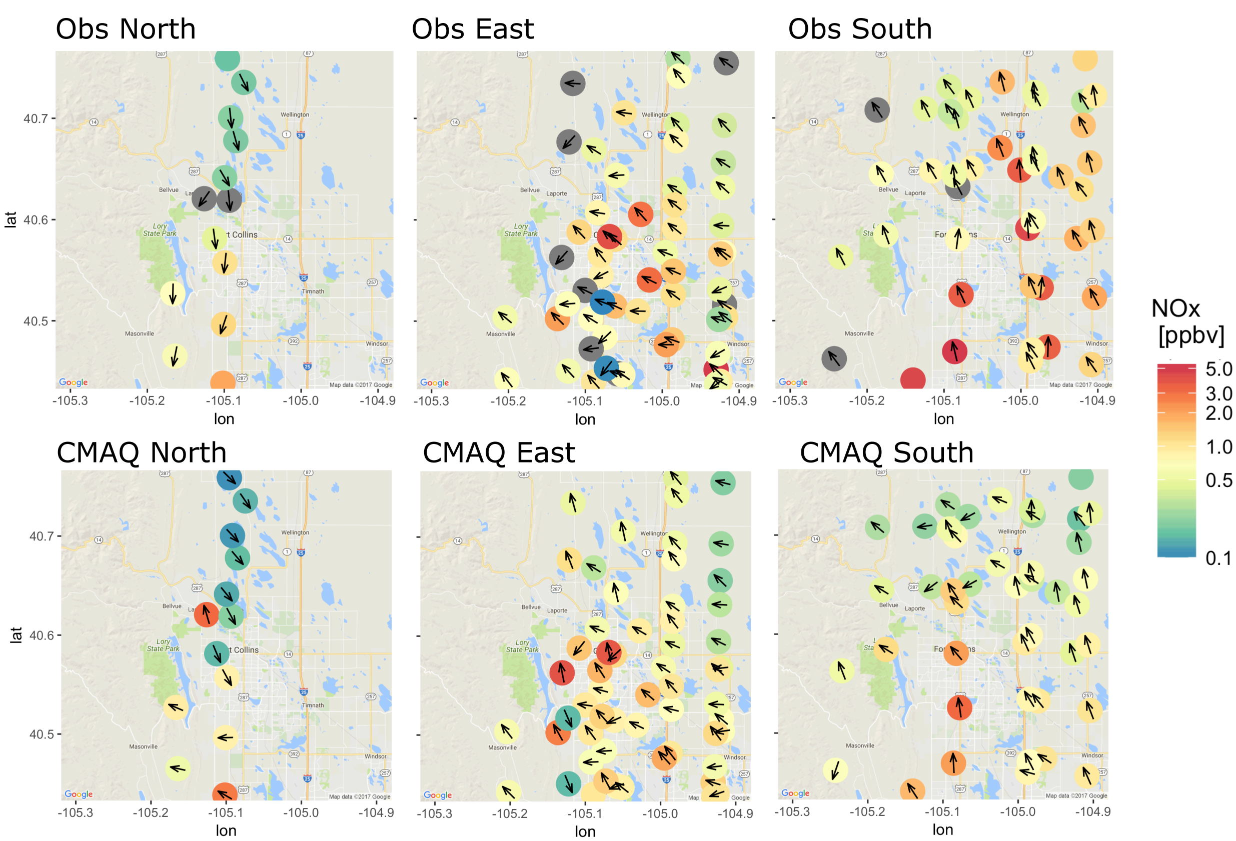


Figure 8: Observed (top) and modeled C-130 (bottom) NO_x concentrations filtered by aircraft wind direction. Only data below 1km a.g.l. are included.

Figure 8 shows a similar analysis but for ethane concentrations, which is a tracer for O&G emissions. Also in this case, we find the highest values when winds are from the East and the South-East. In contrast to NO_x, there is no increase in ethane data for northerly winds when air masses pass over the city. The model reflects the dependence of concentrations on wind direction, but overall underestimates the measured concentrations. This is in contrast to our findings for the entire NFRMA, where overall the model is estimated to be slightly biased high in ethane. We explain this in that we compare here to a very limited set of measurements. There are no significant sources of ethane in the Fort Collins area and the elevated levels are solely due to transport. The model will dilute plumes and slight errors in model transport or emission location will not average out in this comparison.

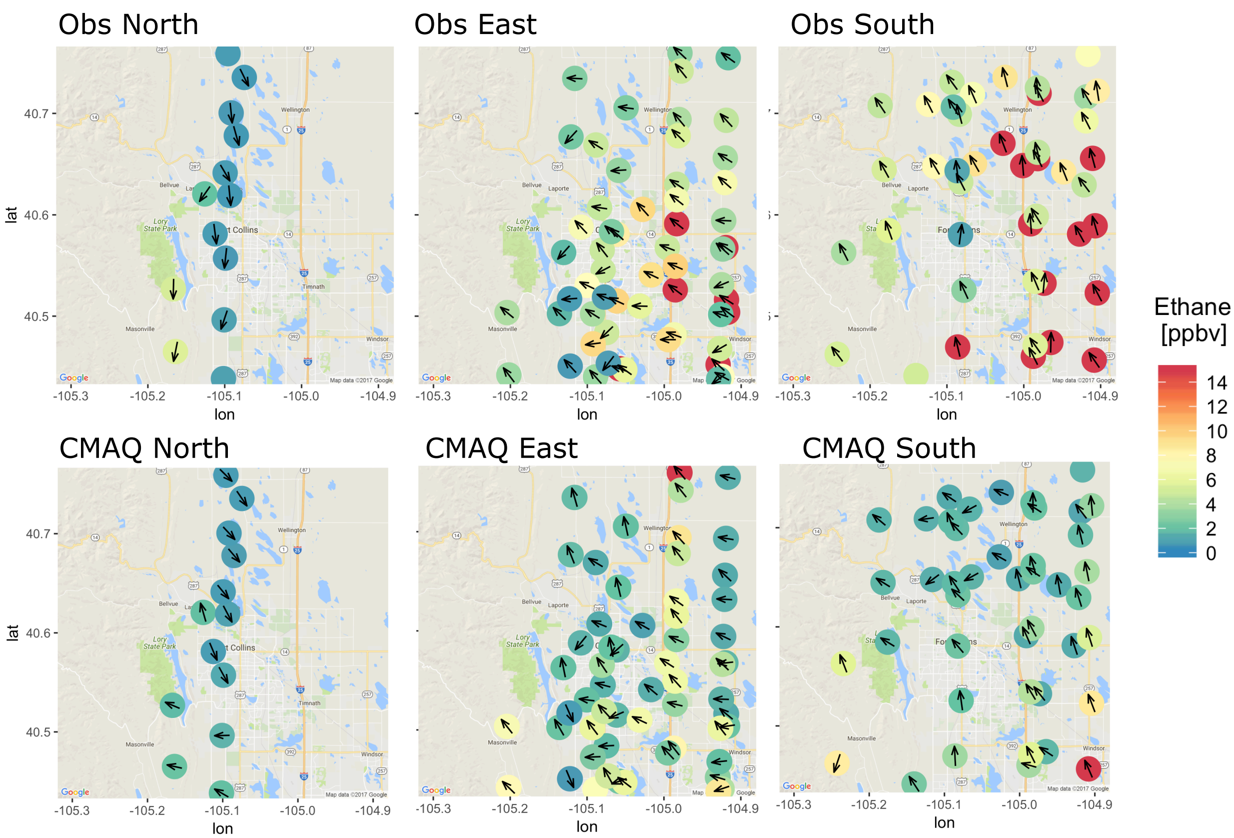


Figure 9: As Figure 8 but for ethane.

The comparison for ozone is shown in Figure 10, but instead of filtering by wind direction we filter the data for local afternoon to account to some degree for the ozone diurnal cycle. However, given the large dependence of ozone on meteorological conditions and the associated large day-to-day variability, we caution that the spatial ozone distribution from the aircraft sampling in no way can be considered as representative for the regional ozone picture. In here, it is mostly considered for assessing the model performance. The model overall is low in ozone but represents the spatial/temporal variability quite well. There are a number of reasons that might explain the low bias. Together with the low bias for ethane and the fact that the majority of these data points has winds with an easterly component, it might suggest that the model underrepresents the transport from the O&G region and/or the ozone production in the Weld county area. The model also is biased low on the days when a Denver cyclone was sampled (27th and 28th of July) and while the model on these days represents the cyclonic flows, it does not place the cyclone in the correct location thus representing different mixing of emission sources. In addition, uncertainties in the altitude placement due to incorrect representation of the boundary layer height or vertical mixing, model resolution and timing contribute to the differences. As discussed below, an underestimate of the modeled background ozone could also contribute to a low ozone bias.

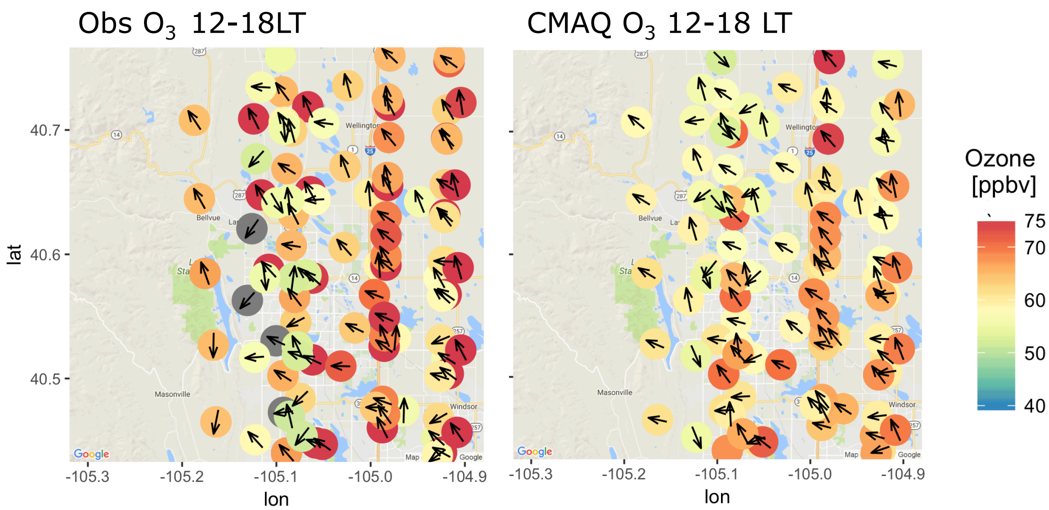


Figure 10: Measured (left) and modeled (right) C-130 ozone for data collected between 12-18 LT and below 1 km a.g.l.

2.4. Model Evaluation: P-3 Aircraft Measurements

The NASA P-3 aircraft flew a repetitive pattern during the campaign. The flight pattern included spiraling over six ground sites, one of them Fort Collins. The location of the spirals is indicated in Figure 2. For most flights, there are up to 4 spirals available, in total for Fort Collins this amounts to 25 spirals with valid ozone data during 10-17 LT. In Figure 11 we compare the model to the average concentrations measured from these spirals for NO_x, ethane and ozone as well as benzene, toluene and CO. In addition to the observations and the base emission scenario S0.5, we further include results from:

- S0: a simulation including the original (a priori) inventory
- S1: a simulation in which all O&G VOC emissions in S0 were multiplied by a factor of 4 and in addition to onroad mobile sources also offroad sources outside of Denver were multiplied by a factor of 2.
- S2: a simulation similar to S1 but where also NO_x from O&G sources was multiplied by a factor of 4.

All simulations include the same meteorology.

Similar to the C-130 comparison we find a low mean bias in NO_x and ethane at the lowermost altitudes. Similarly, there is a low bias in benzene, which is emitted from both O&G and urban sources. Model simulations with increased O&G and mobile emissions show a reduced bias, but are overall still too low. Note that the S0.5 emission scenario was chosen as a base case because it agreed best with measurements over all the individual source regions. This could indicate, similarly to the comparison with C-130 data, that the model transport from the O&G area might be underestimated or that the modeled boundary layer is too high (as will be discussed in Section 2.5), diluting concentrations more than observed. Toluene, mostly from urban sources, compares rather well but there is a slight high bias for the higher emission scenarios, whereas CO agrees somewhat better for S1 and S2 versus S0 and S0.5. These results demonstrate that there are a number of factors that impact the comparison.

Ozone is underestimated in all emission scenarios. The low bias in ozone is not only seen at the lowermost altitudes, but reaches throughout the vertical coverage of the aircraft data suggesting an overall underestimate in background ozone. This has been discovered also in WRF-Chem simulations our group and other members of the FRAPPÉ Science Team conducted (Yo Yan Cui, "Using potential vorticity to specify the effect of stratosphere-troposphere exchange on the vertical distribution of ozone during the FRAPPE 2014 field campaign", presented at the May 2017 FRAPPÉ/DISCOVER-AQ Science Team Meeting) and it has been found that part of the low model bias is caused by the models not capturing enhanced background ozone, specifically during the last week of July. This indicates that the low model bias in ozone in comparison to the C-130 and P-3 aircraft data can in parts be explained by large scale features and is not necessarily due to regional and local effects.

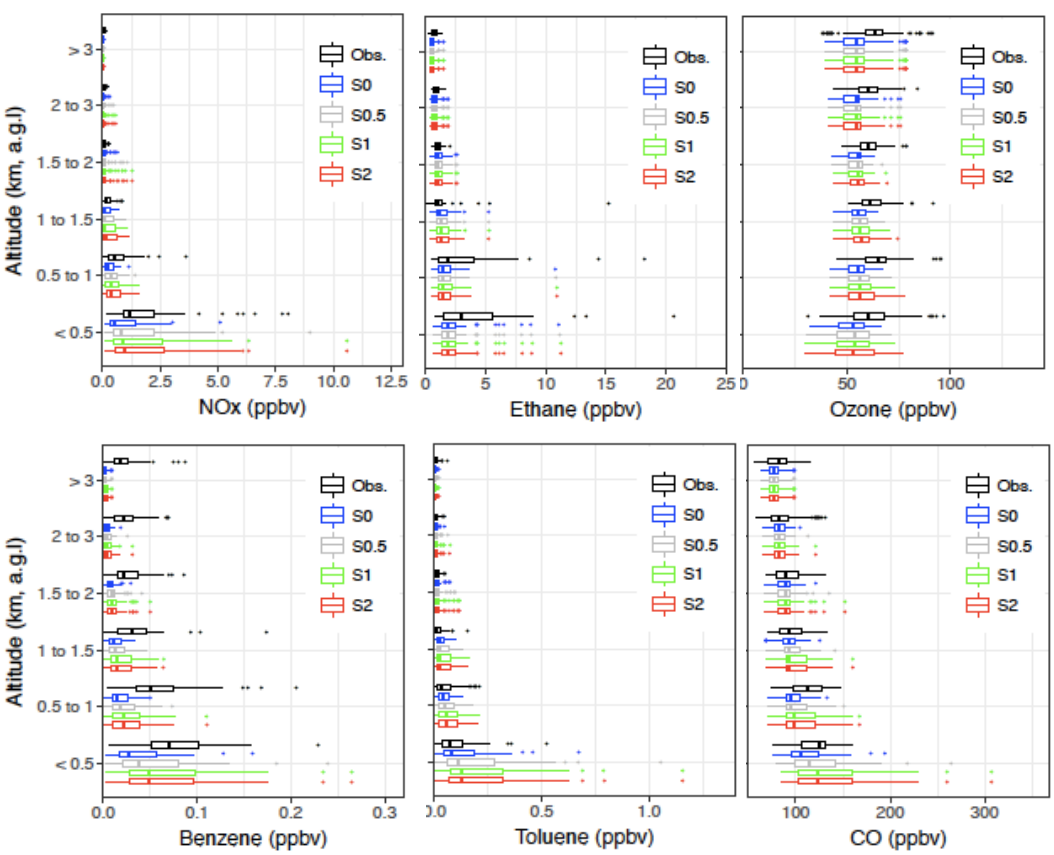


Figure 11: Bar-Whisker plots for vertical profiles of various trace gases as measured and modeled for the spirals over Fort Collins. See text for explanation of the different model simulations.

2.5. Sensitivity of Surface Ozone in Fort Collins to different emission sectors

From the model evaluations discussed above as well as in the CDPHE/State of Colorado report we can have confidence in the model overall reflecting well the NFRMA conditions albeit not necessarily capturing day-to-day changes. In this Section, we discuss the sensitivity of surface ozone in terms of MDA8 to different emission sectors in the NFRMA. The different scenarios rely on a zero-out approach, which means that for each model scenario the emissions from the respective sector have been set to zero. It has to be cautioned that these results provide an estimate of the sensitivity but, due to the non-linearity in ozone production, the results will not scale linearly with a reduction in the same emission sector. The scenarios under consideration include the following:

- S_OG: S0.5 but without NFRMA emissions from the O&G sector (area & point)
- S_Mobile: S0.5 but without NFRMA emissions from mobile sector (onroad & offroad)
- S_Ind: S0.5 but without industrial emissions (area & point)
- S_CEM: S0.5 but without Continuous Emission Monitoring System emissions
- S_Bckg: S0.5 but without anthropogenic emissions in the NFRMA

For a more detailed discussion on the scenarios we refer to the CDPHE/State of Colorado report.

In Figure 12 we show the average MDA8 for the campaign period for the base simulation (S0.5) as well as the different scenarios. In the base simulation graph we also denote the average observed MDA8 from the surface sites. On average, the highest surface ozone is found in the SW part of the domain, and the lowest concentrations in the NE Sector. This is in contrast to the ozone distribution seen from the C-130 measurements, but this can be explained by the limited sampling of the aircraft in time and space. Specifically, for a photochemically produced species like ozone with large day-to-day variability and a pronounced diurnal cycle we cannot expect that the aircraft samples are representative of the surface MDA8 distribution. Surface ozone is also more strongly impacted by deposition, the influence of which mitigates with increased altitude.

The model agreement with surface observations mirrors the results derived from analysis of the average diurnal cycle. The model is biased high compared to MDA8 observations at FC CSU, with observed MDA8 in the order of 55 ppb compared to 59 ppb for the respective model grid cell. The 59 ppb average MDA8 observed at FC West is well represented by the model (60 ppb).

Turning off all NFRMA anthropogenic emissions in the model reduces the average MDA8 to values around 48-50 ppb (S_Bckg). The scenarios with turned off industrial emissions (S_Ind) and CEM (S_CEM) emissions lowers the base MDA8 only slightly whereas turning off O&G (S_OG) or mobile emissions (S_Mobile) show the largest reductions in MDA8.

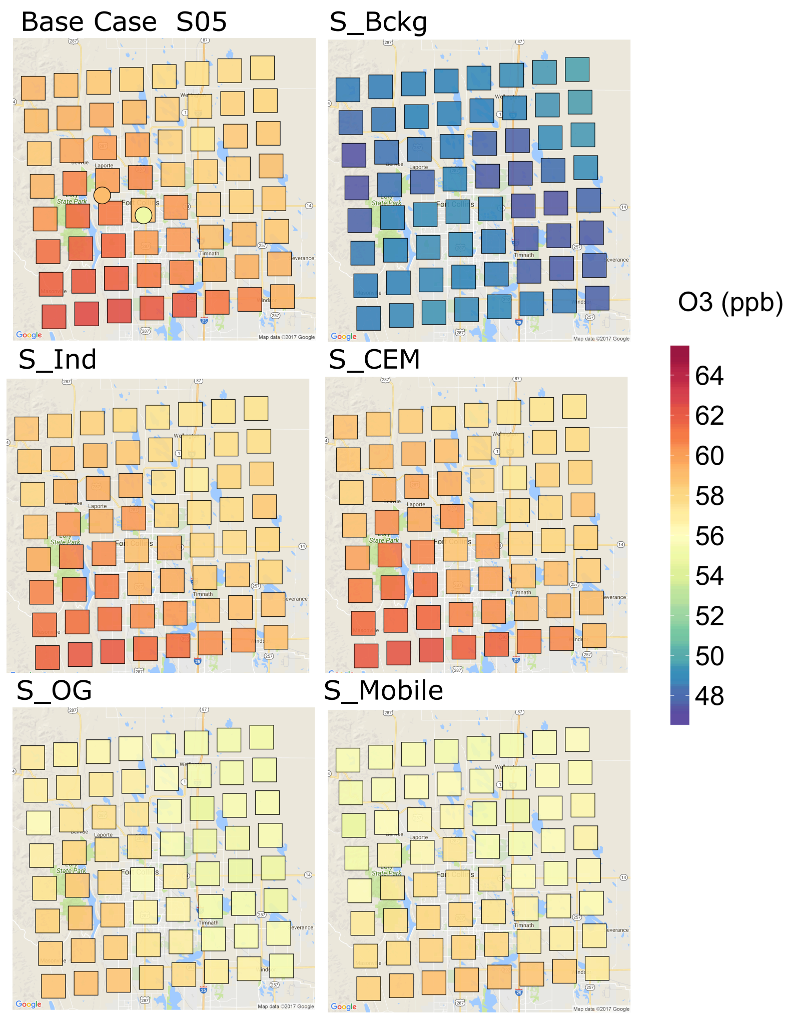


Figure 12: Average MDA8 for 17 July - 18 August 2014 for the Base simulation and the different zero-out emission scenarios. The average MDA8 derived from measurements at FC West and FC CSU is indicated by the filled circles in the plot for the base simulation.

In Figure 13 we show the change in the average MDA8 between base simulation and the different scenarios. The negative change shown here can also be interpreted as the estimated positive contribution of the considered emission sector to the total MDA8. As mentioned above, the smallest changes are seen for S_CEM and S_Ind with average MDA8 reductions of less than 1ppb across the considered domain. On individual days, the reduction can reach up to 2 ppb. For S_OG we find a reduction in average MDA8 ranging from 2 to 4 ppb reaching up to 10 ppb on individual high ozone days. A similar sensitivity is found for S_Mobile with average changes of 1 to 4 ppb and maximum changes up to 11 ppb. Note the much smaller impact around downtown Ft. Collins due to reduced ozone titration with local NO when mobile emissions are turned off. S_Bckg (not shown here), on average, is 8 to 14 ppb below the average total MDA8, but can be up to 33 ppb lower on certain days.

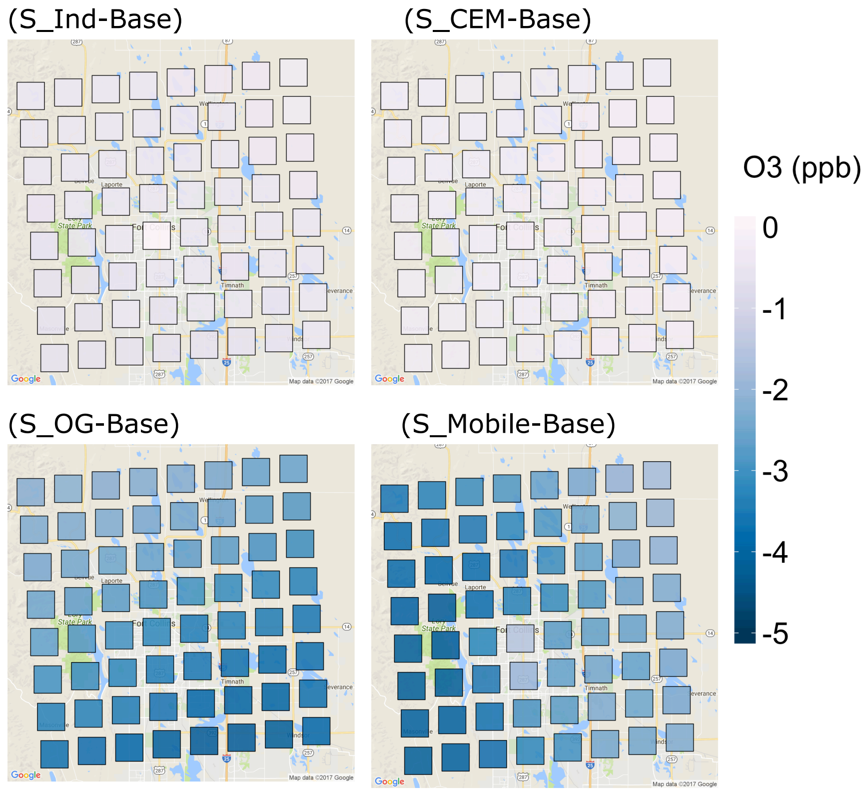


Figure 13: Reduction in average MDA8 for 17 July - 18 August for the different zero-out scenarios.

The days when maximum MDA8 ozone reductions in S_OG and S_Mobile are simulated are 22 July 2014 (DOY 203) and 31 July (DOY 212), respectively. These two days are show in Figure 14; in addition to the difference we also include the average total MDA8 for these days. Note that the model wind vectors are graphed for the time when the observed surface ozone at FC West reaches its maximum.

On 22 July 2014, the largest impact from O&G sources is reached in the SW corner of the selected region (-10 ppb) and the Western part of the domain experiences also the highest total MDA8. Winds are from the SE and the modeled winds agree fairly well with wind observations at FC CSU. The total MDA8 is underestimated in the model compared to the surface observations at FC West and FC CSU. 22 July 2014 was one of the highest ozone days experienced throughout the campaign. Sunshine and weak upslope conditions contributed to efficient ozone production as well as a slow growing boundary layer (PBL) that only reached about 1.5 km a.g.l. later in the day (Appendix B). The model represents well the average winds and the widespread high ozone and also simulates a delay in the PBL growth as shown in Appendix B, but grows the PBL faster and higher compared to the observations. This translates into a stronger dilution in the model and a less efficient ozone production. Zeroing out mobile emissions on this day amounted to a reduction of 8.5 ppb and the MDA8 was estimated to be 21 ppb above background ozone on this day.

On 31 July 2014, winds had a more southerly direction and the largest impact from removal of mobile emissions is reached in the NW part of the domain (–11 ppb) suggesting a major contribution from transport of mobile sources from the South as well as from Fort Collins itself.

The MDA8 also is highest in the Western part of the area, with highest values in the NW corner. The model overestimates the observed ozone on this day as is the case for the entire Front Range (Appendix B). From Appendix B, we can also see that the model simulates a fairly well established upslope flow, whereas the wind measurements across the NFRMA are highly variable. The measured PBL shape is disturbed with a rather sharp short peak at 2 km a.g.l. compared to the model PBL which represents a smooth development throughout the day reaching a height of more than 2.5 km a.g.l. The flight forecast summary for this day (available from the FRAPPÉ NCAR/EOL Field Catalog at http://catalog.eol.ucar.edu/frappe/report/66/499/92583/35406269) stated *"We are going through a pattern where forecasting will be tricky…. Models seem to underestimate the amount of clouds and convection…."* reflecting that the model on this day simulated a rather typical fair weather day whereas in reality clouds and thunderstorms interrupted the wind flows and ozone production.

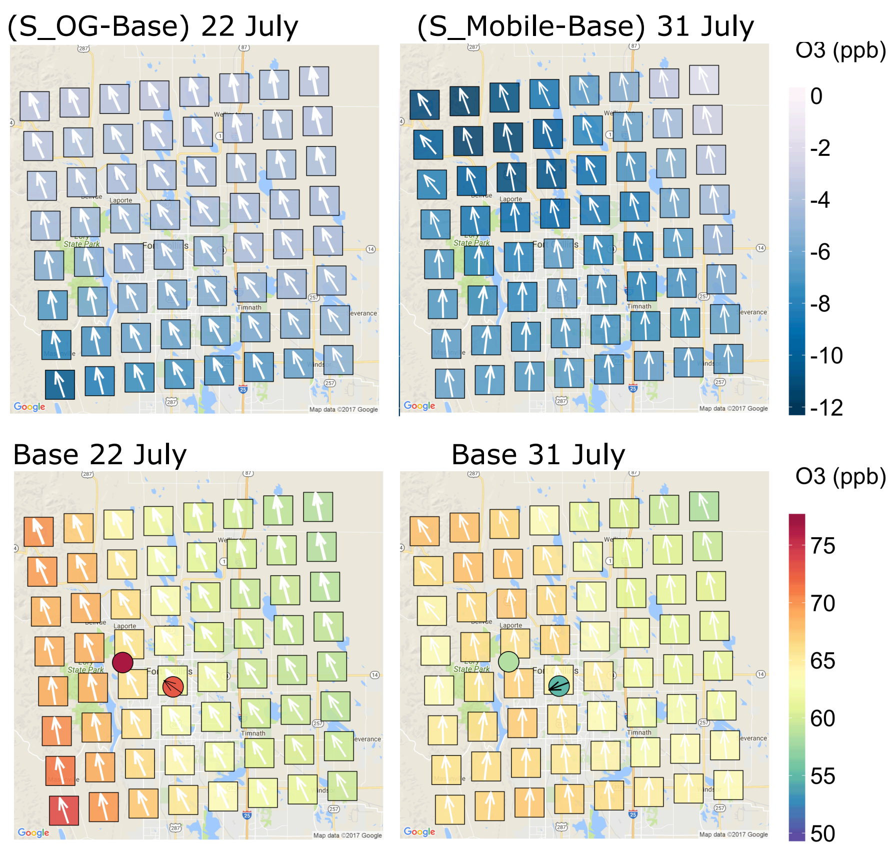


Figure 14: Top: Reduction in average MDA8 for S_OG on 22 July 2014 (left) and S_Mobile on 31 July 2014 (right). Bottom: Average MDA8 for 22 July 2014 (left) and 31 July 2014 (right). Measured wind vectors at FC CSU (black arrow) are show for the time when FC CSU observed MDA8 reaches its maximum, for the model they are shown when FC West observed MDA8 reaches its maximum. On both days, the maximum at the ground sites is reached ~15 LT.

In Figure 15 we show the average MDA8 for simulations with the original emission input data (S0), the base emission our zero-out scenarios are based on as well as the two other emission constraints scenarios S1 and S2 that were tested. Average MDA8 for the selected domain

ranges from 56-60 ppb for S0, 57-63 ppb for S05, 58-64 ppb for S1 and 60-66 ppb for S2. The increase in onroad emissions and O&G VOC and NO_x emissions in S05 over S0 increases MDA8 on average by up to ~3 ppb. S1 results in only in small changes (up to ~1 ppb) over S05 even though O&G VOCs were doubled over S05 and also the offroad sector was increased. However, S1 does not include the NO_x increase in O&G emissions. The high sensitivity of surface ozone to NO_x can be seen when comparing S1 with S2, which only differ in that the latter also includes an increase in O&G NOx emissions. In this case, the average MDA8 increases by ~2-3 ppb.
The differences can vary significantly for different days. Maximum changes at individual grids for S2 over S1 can reach -4 ppb to +10 ppb and for S1 over S05 can reach -1 ppb to +6 ppb. Maximum S05 changes over S0 are in the order of -1 ppb to +6 ppb.

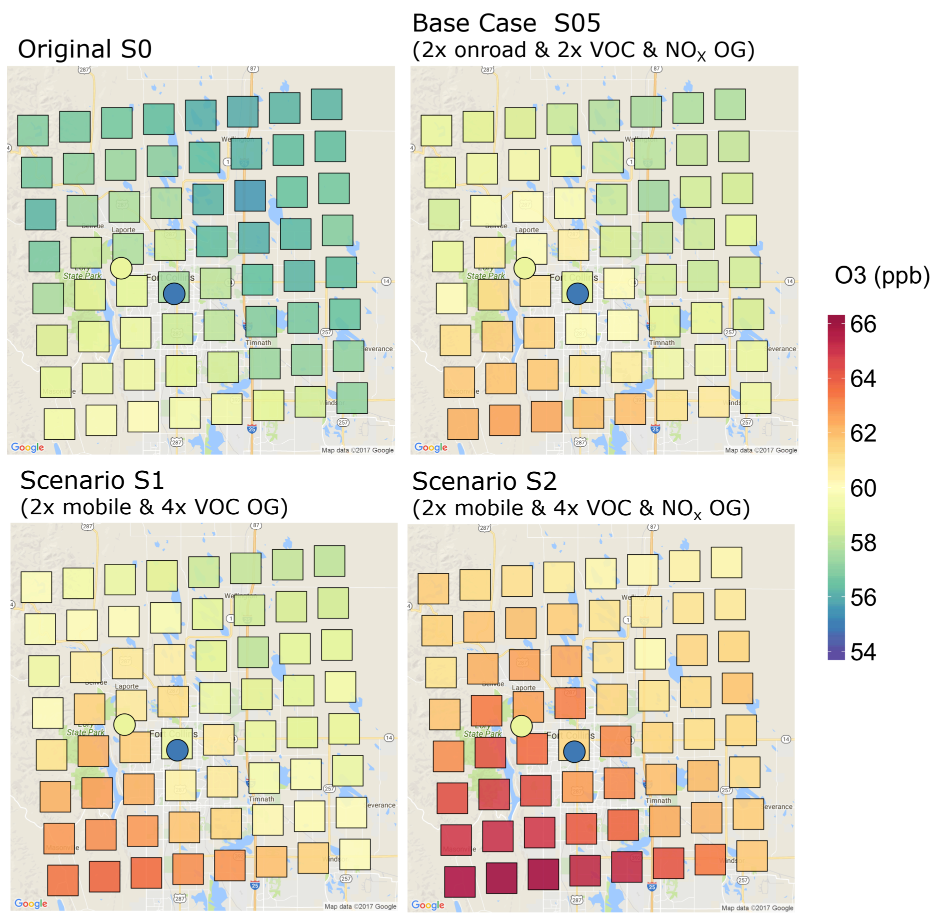


Figure 15: Average MDA8 for 17 July-18 August 2014 for the simulations with the original emission inputs (S0), the Base simulation S05 and the two other emission constraints that were tested (S1 and S2). The average MDA8 derived from measurements at FC West and FC CSU is indicated in the plot for the base simulation.

3. Tracer Modeling for Fort Collins

In the final Section, we want to briefly discuss results for specifically Fort Collins as derived from the WRF Tracer forecast that was run during the campaign and was used for flight planning. A 2-domain setup was used with a 15 km x 15 km outer domain covering the Western U.S. and an inner 3 km x 3 km domain covering Colorado and parts of neighboring States. Only results of the inner domain are considered here. We added a set of chemically inert tracers to WRF to track the transport of different source sectors. The tracers discussed here include an oil and gas tracer (TR^{OG}) representative of ethane emissions from oil and natural gas activities in Colorado and an "urban" tracer ($TR^{AreaMobile}$) representative of Colorado NO_x area and mobile emissions. Note since the tracers represent different trace gases, they cannot be compared quantitatively. Each tracer was given a 2-day lifetime. A paper on these simulations is under review for J. Geophys. Res. and includes a much more detailed description of transport patterns in the NFRMA. While the tracers are not directly related to the ozone concentrations, they provide insight into the influence of different sources.

Figure 15 presents the average diurnal cycle in surface ozone and model tracer concentrations for FC CSU and FC West. The model tracer concentrations have been averaged over the height of the PBL to reduce impacts of diurnal variations in the PBL. At both sites, TR^{OG} peaks during the day when upslope winds carry O&G emissions to the area. $TR^{AreaMobile}$ shows a peak during the morning rush hour reflecting impact from local sources; the evening rush hour is less pronounced. TR^{OG} is slightly higher at FC CSU compared to FC West likely because air masses from the O&G sources arrive first at FC CSU and become diluted further and chemically processed while being transported to FC West. The large standard deviation reflects the high variability in both ozone and tracers.

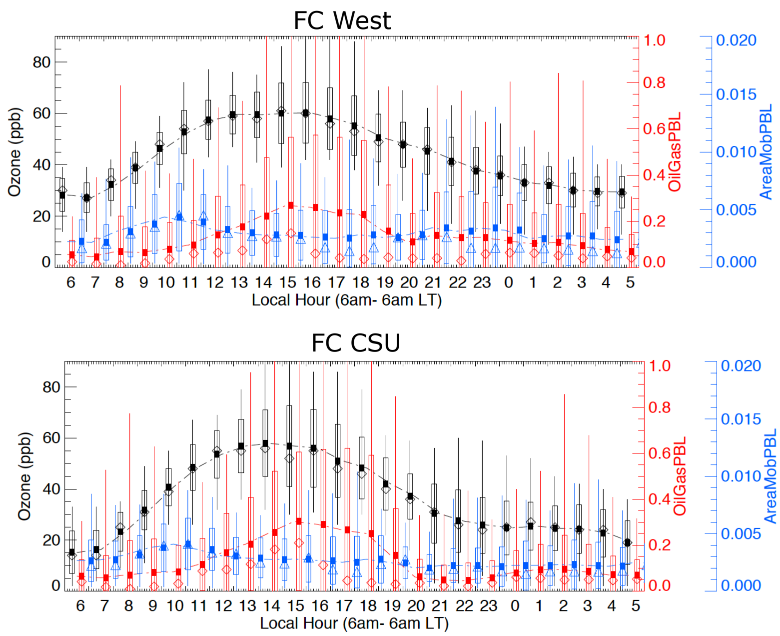


Figure 15: Average diurnal observed surface ozone (black) and PBL average concentrations for TR^{OG} (red) and $TR^{AreaMobile}$ (blue) for selected surface sites in the Front Range for 6am – 6am LT. Shown are mean, median, standard deviation, minimum and maximum.

Figure 16 compares tracer statistics for the two Fort Collins sites to other sites in the Front Range and the nearby Foothills. Between all NFRMA sites, Fort Collins lies rather in the lower range for TR^{OG} as well as $TR^{AreaMobile}$ concentration statistics. Interestingly, sites in Longmont or Boulder experience a higher influence from O&G sources compared to Fort Collins, but they show a similar characteristic in $TR^{AreaMobile}$. The Denver metro area sites experience a lower overall influence from O&G, but show some of the highest mobile tracer.

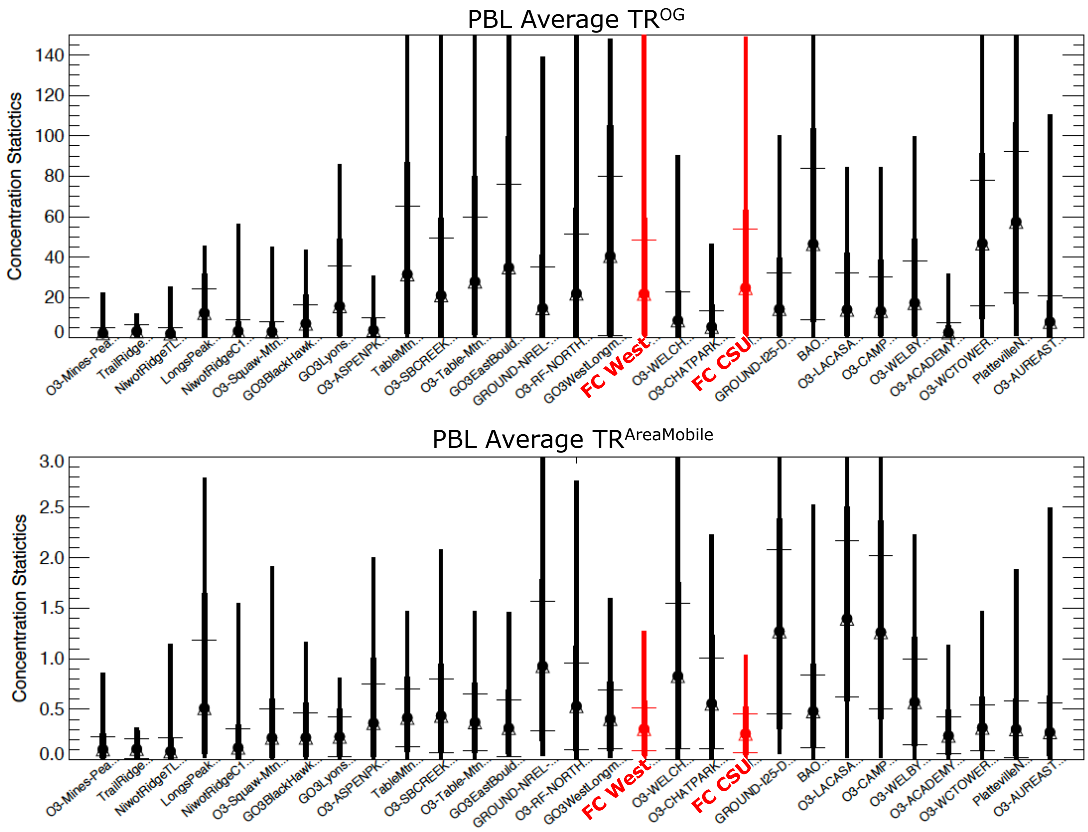


Figure 16: Tracer Statistics for surface sites employed during FRAPPÉ/DAQ for TR^{OG} (top) and $TR^{AreaMobile}$ (bottom). Sites are arranged from West to East and averaged over 10-17 LT (though an average over all times would not look vastly different). Sites in Fort Collins are colored in red. Shown are mean (dot), median (triangle), standard deviation (horizontal bars), 10^{th} and 90^{th} percentiles (thick line), minima and maxima (thin lines). The scales do not consider the whole range for 90^{th} percentiles and maxima, but are reduced in order to better show the mean, median and standard deviation.

4. Final Conclusions and Recommendations

- **The FC West site is representative of the "integrated" picture of FC ozone concentrations**

Analysis of wind patterns, the ozone diurnal cycle and the ozone weekend effect demonstrate that FC West is mostly representative of downwind pollution with air mostly from the city of Fort Collins arriving on high ozone days.

- **FC CSU shows impact from nearby local sources and urban airflow**

Regional flows in the northern NFRMA are from the NW at nighttime and the SE-E during daytime. While winds at FC CSU during nighttime generally follow the regional patterns, during daytime they show a dominance of winds from the SSE-E suggesting a funneling of airflow due to urban structures. This is corroborated by the low wind speeds at this site. Available carbon monoxide measurements indicate anthropogenic influenced air arriving at the site from the SE sector at fairly low wind speed likely from a close-by source.

- **Mobile - and Oil and gas sources are the main contributors to Fort Collins ozone**

Zero-out emission scenarios with a chemical transport model for the FRAPPÉ time period suggest that the major contributions to surface ozone in Fort Collins are from mobile and O&G sources. On average the contribution to MDA8 in the Fort Collins area range from 2 to 4 ppb for O&G sources and 1 to 4 ppb for mobile with contributions on individual, high ozone days of up to 11 and 10 ppb from mobile and O&G, respectively. Background ozone in Fort Collins, on average, is about 48-50 ppb.

- **Addition of Wind Sensor at FC West**

Ozone concentrations at a location are determined by local production as well as transport of ozone. Hence, knowledge of the wind speed and direction is important for assessment of the origin of pollution. Operational monitoring at FC West only includes monitoring of ozone and wind measurements are only available during FRAPPÉ/DAQ. These measurements are very valuable and demonstrate that high ozone coincides with higher wind speeds from the SE, which is also the dominant daytime wind direction; Wind direction information is also essential to capture return flow of pollution during nighttime downslope winds.

- **Installation of a NO_x sensor in the city**

Long-term analysis of FC CSU surface ozone measurements indicates an ongoing shift towards a more NO_x limited ozone production regime. Tracking the changes in NO_x levels in the city is recommended as a further lowering of NO_x could lead to an increase in the local ozone production. NO_x measurements at the FC CSU site would also allow an estimate of ozone production during transport by comparing of the sum of ozone and NO_2 to ozone at FC West.

- **Establishment of a measurement site South/South-East of the cit**y

Highest ozone in the city Fort Collins occurs on days with winds from the SSE-SE. These winds bring pollution from other parts of the NFRMA with a dominant contribution from mobile and O&G sources to the city, where it mixes with local pollution to create high ozone. Expected future changes in development and urban growth in the NFRMA will have a significant impact on the air quality in Fort Collins and for this reason we recommend a measurement site equipped with ozone, wind, NO_x and (at least episodic) VOC measurements to be established to the SE of the city. On high ozone days, such a site would provide information on incoming pollution and in conjunction with measurements at FC West would provide a range of the overall ozone levels in the Fort Collins area and allow better assessment of the contribution of local production.

- **Long-term measurements**

A full set of meteorological and chemical measurements including capturing the vertical distribution as available from FRAPPPÉ is crucial for model evaluation and models are crucial in understanding current conditions and sensitivities and expected changes. While the FRAPPÉ data are a highly valuable dataset, they are limited in time and space which limits a comprehensive characterization or the detection of trends. In light of the rapid growth of the NFRMA and the changing emissions from a growing, but possibly better regulated oil and gas sector, we recommend the establishment of a few key sites with continuous ozone, NO_x, VOC and meteorological data and we also recommend conducting an aircraft and ground-based field campaign on a regular basis, e.g. every 5-7 years.

Acronyms:

NAAQS	National Ambient Air Quality Standard
MDA8	Maximum daily average 8-hour ozone
ppbv	parts per billion by 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
NO	Nitrogen Oxide
NO_2	Nitrogen Dioxide
NO_x	Nitrogen Oxides ($NO + NO_2$)
OH	Hydroxy Radical
ppbv	parts per billion by volume
pptv	parts per trillion by volume
VOC	Volatile Organic Compounds

Appendix A: Ozone production – EKMA Diagram

EKMA (Empirical Kinetics Modeling Approach) ozone isopleths can be used for developing air quality control strategies and illustrate the dependence of ozone production to NO_x and VOC concentrations. The exact values will depend on the VOC reactivity and environmental conditions, but the figure below gives a good example of the underlying ozone chemistry. In this example, for NO_x concentrations below 50 ppb further reductions in NO_x would not be effective in reducing the ozone concentration. However, at this level of NO_x the ozone concentrations are very sensitive to the VOC concentration. Hence a reduction or an increase in VOCs would lead to a decrease or increase in ozone, respectively. This example also shows that for higher NO_x concentrations, reductions in either the initial NO_x or VOC concentration may lead to less ozone.

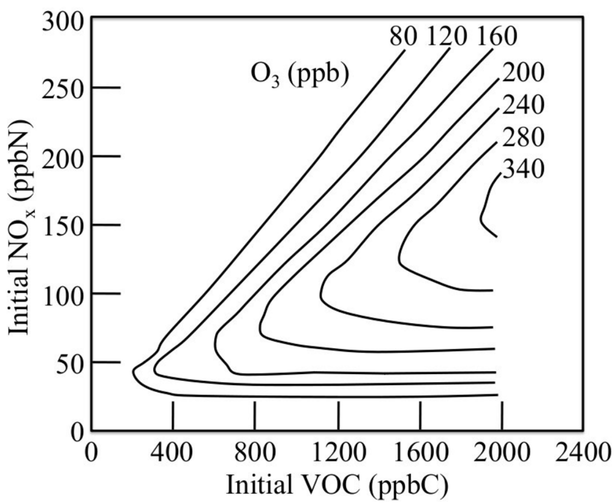


*Figure A-1: Relationship between NO_x, VOCs and ozone, expressed in the form of an EKMA diagram (from Stockwell et al., Atmosphere **2012**, 3(1), 1-32; doi:10.3390/atmos3010001)*

Appendix B

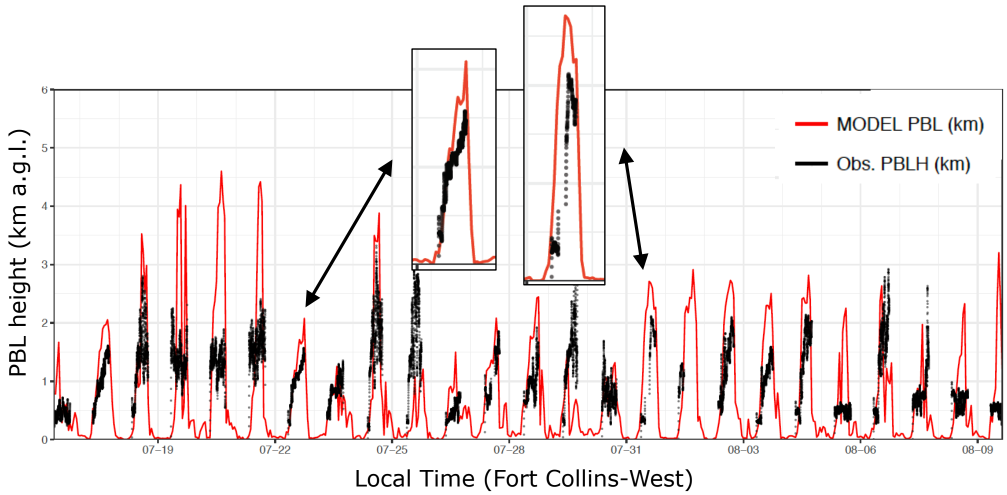


Figure B-1: Measured and modeled PBL height at FC West for 16 July-9 August 2014. The data for 22 July 2014 and 31 July 2014 are shown in the zoom-out.

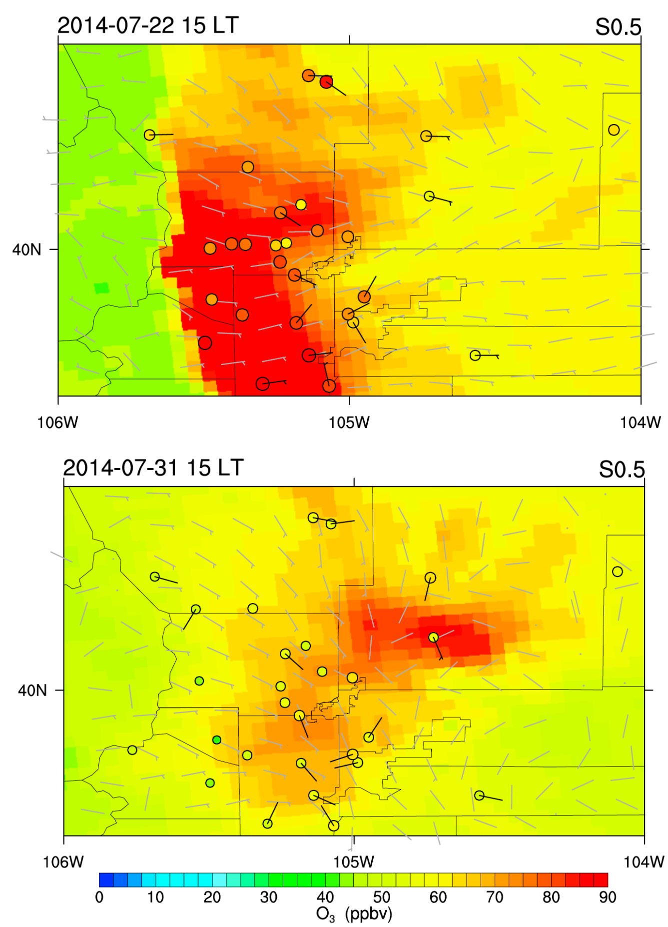


Figure B-2: NFRMA modeled and measured surface ozone and 10m winds for 22 July 2014 15 LT (top) and 31 July 2014 15 LT (bottom)