Surface ozone in the Northern Front Range and the influence of oil and gas development on ozone production during FRAPPE/DISCOVER-AQ

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INTRODUCTION

The northern Front Range of Colorado presents a unique setting for ozone production, containing a mixture of larger municipalities, major oil and gas developments in the D-J basin, agriculture (crops and cattle), and complex local meteorology during the summertime. Since 2007, the Front Range has been classified by the U.S. EPA as a non-attainment area for ozone (O_3) due to its summertime exceedances of the National Ambient Air Quality Standard (NAAQS) for O_3. Oil and gas production is the primary source of VOC O_3 precursors in the region (Gilman et al., 2013; Eisele et al., 2009; Abeleira et al., 2017).

A previous study by McDuffie et al. (2016) used chemical box models to estimate that on average, oil and gas VOCs contribute ~3 ppb to daily maximum photochemical O_3. However, exceedances of EPA standards are determined by single days of extreme O_3, therefore it is important to understand the contributions of oil and gas emissions and other regional pollutant sources to O_3 production on individual high O_3 episode days.

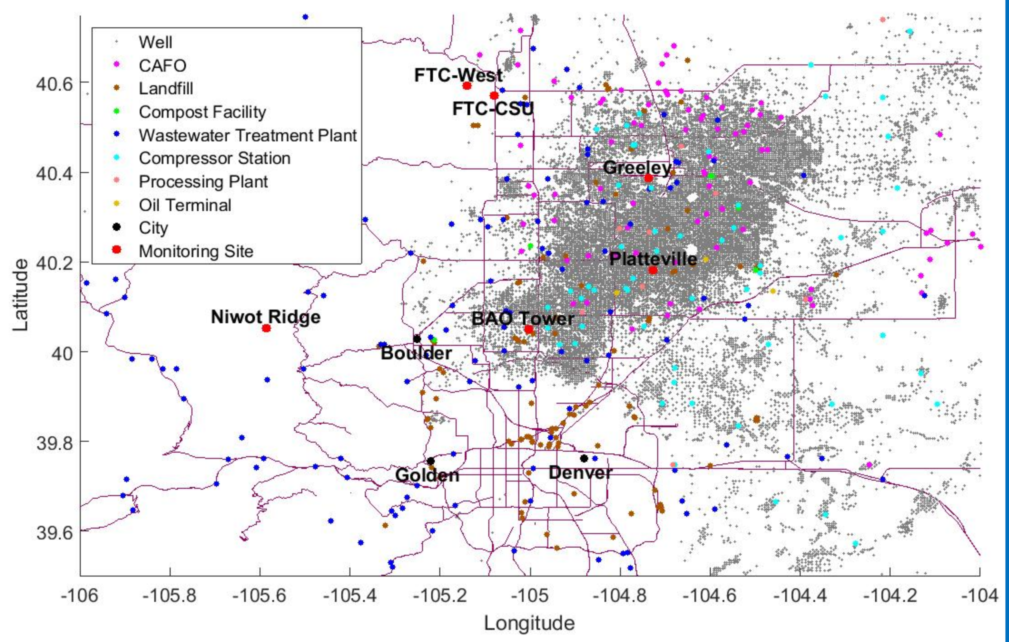

Figure 1. (Right) Map of Front Range with monitoring sites and potential emission sources.

CASE STUDIES: SURFACE O_3 OVERVIEW

Detailed analysis of O_3 and a variety of gaseous species was performed for 3 days during July and August, 2014. O_3 mixing ratios at surface monitoring sites throughout the northern Front Range are shown in Figures 8-10 to demonstrate overall O_3 levels in the region on the case study dates.

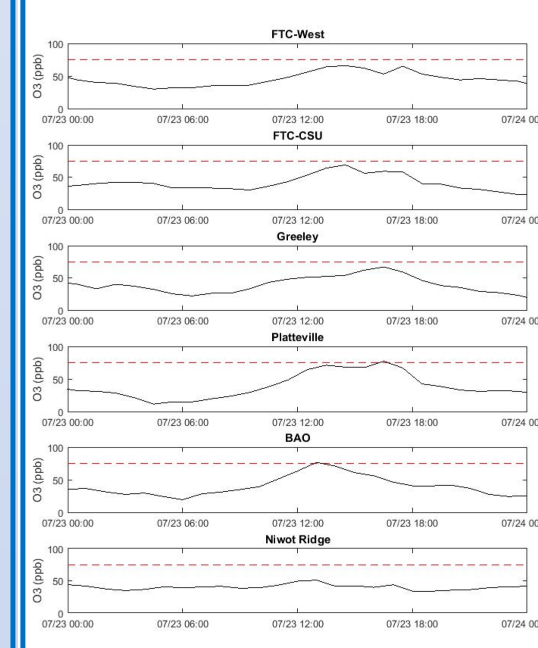

Figure 8. (Above) Hourly average O_3 measurements at six surface sites on July 23, 2014. Dashed red lines indicate 75 ppb concentration.

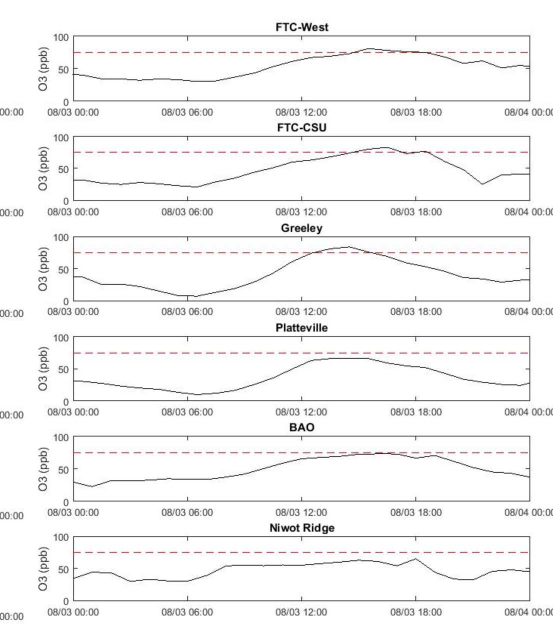

Figure 9. (Above) Hourly average O_3 measurements at six surface sites on August 3, 2014.

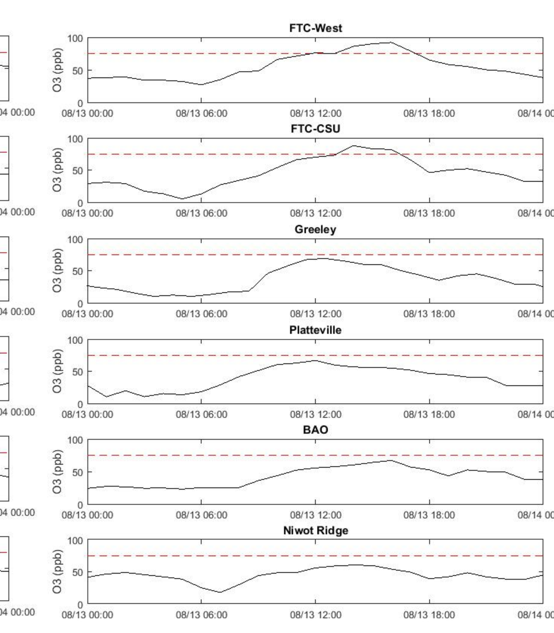

Figure 10. (Above) Hourly average O_3 measurements at six surface sites on August 13, 2014.

AUGUST 13, 2014: OIL AND GAS EMISSIONS AND LOCALIZED ELEVATED O_3

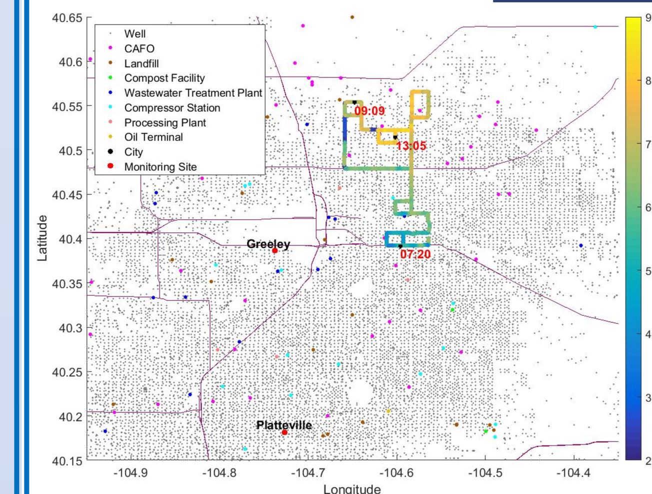

Figure 17. (Left) Map of mobile lab O_3 measurements on August 13, 2014.

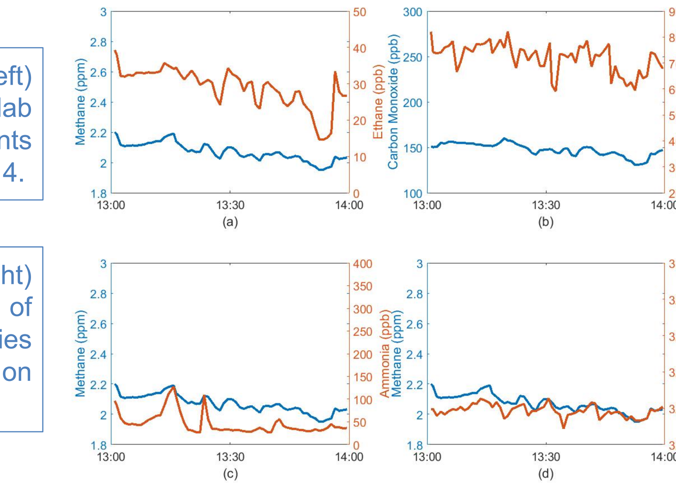

Figure 18. (Right) Time series of gaseous species from mobile lab on August 13, 2014.

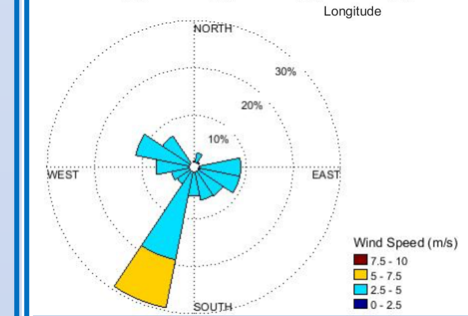

Figure 19. (Above) Wind rose from mobile laboratory drive during period of high O_3 from 13:00-14:00 on August 13, 2014.

The August 13 drive measured high O_3 levels in a remote area and were greater than the O_3 measured at the surface O_3 stations in Greeley and Platteville. The high O_3 was linked to elevated ethane and methane, strongly indicating a potential oil and gas source of precursors. Agricultural and urban emissions were not elevated during the drive, demonstrating the limited influence of those sectors on methane emissions and O_3 formation. The modestly elevated levels of carbon monoxide (~150 ppb) were strongly correlated with ethane and lacked correlation with acetylene, hence the attribution of high O_3 to oil and gas related rather than urban emissions sources.

O_3 GROWTH RATES

Figure 2 is used to estimate the underlying O_3 distribution on days when O_3 concentrations are minimally impacted by boundary layer photochemical production. The median daytime maximum at the Niwot Ridge high elevation site is a suitable estimate for the baseline northern Front Range O_3 concentration. The range of O_3 in the northern Front Range on days with limited photochemical production was determined to be 45-50 ppb. O_3 levels above this value are likely due to more significant photochemical production and can be enhanced by pollution sources such as oil and gas activities and urban emissions. Figure 3 shows days where morning O_3 growth continues into the afternoon and growth rates are about twice as high as in Figure 2.

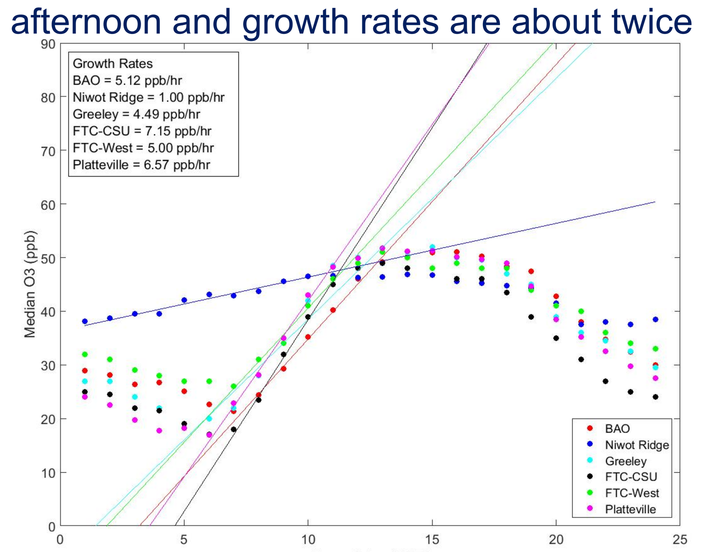

Figure 2. (Above) Median O_3 growth rates at six surface sites on low peak O_3 days (<60 ppb) including Jun, Jul, and Aug of 2013, 2014, and 2015.

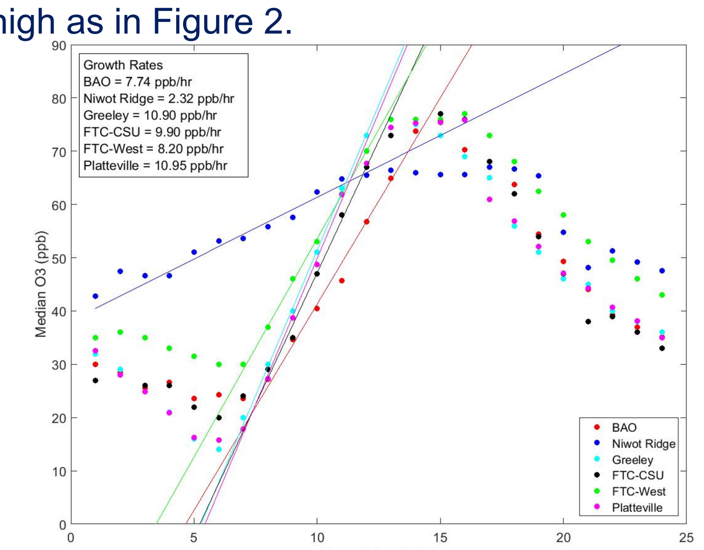

Figure 3. (Above) Median O_3 growth rates at six surface sites on high peak O_3 days (≥75 ppb) including Jun, Jul, and Aug of 2013, 2014, and 2015.

JULY 23, 2014: O&G EMISSIONS, MODERATE O_3 LEVELS

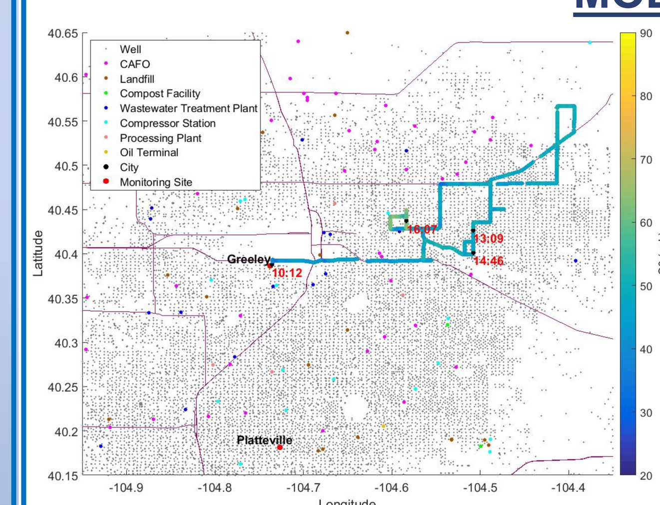

Figure 11. (Left) Map of mobile lab O_3 measurements on July 23, 2014.

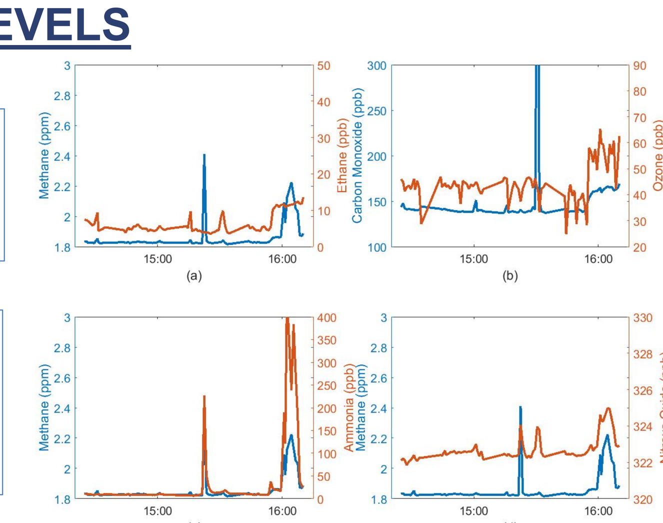

Figure 12. (Right) Time series of gaseous species from mobile lab on July 23, 2014.

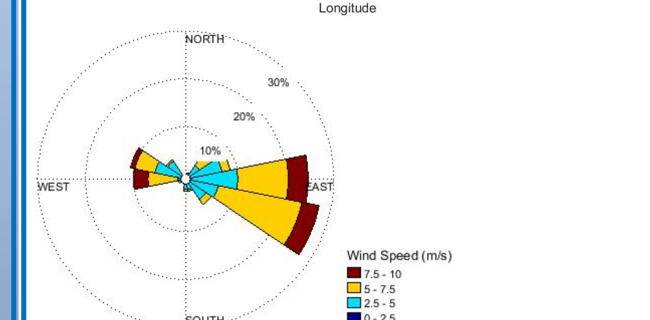

Figure 13. (Above) Wind rose from mobile laboratory drive during period of baseline O_3 and O_3 increase from 14:00-16:10 on July 23, 2014.

The majority of the July 23 drive demonstrates low, background-level emissions for the area with moderate mixing ratios relative to other drives. At the conclusion of the drive, shifting winds throughout the area corresponded to increases in both ethane and O_3. Enhanced oil and gas markers mixing ratios were measured in flasks collected at Platteville and high O_3 was recorded at the Platteville surface monitoring site (peak of ~75 ppb), indicating potential contributions of oil and gas emissions to the higher O_3 measured at that site.

DISCUSSION

Three case studies during FRAPPE/DISCOVER-AQ form the basis for attributing oil and gas related emissions to significant O_3 enhancements. The average concentrations of ethane, carbon monoxide, and O_3 that were measured by the mobile lab on the three case study drives are shown in Figure 20. The highest average O_3 was recorded during the August 13 drive, a day that also showed elevated ethane and only moderate concentrations of carbon monoxide. August 13 demonstrates that in the northern Front Range, high O_3 can be produced on a day when the dominant emission signature is oil and gas (indicated by ethane) with low urban emissions (indicated by carbon monoxide).

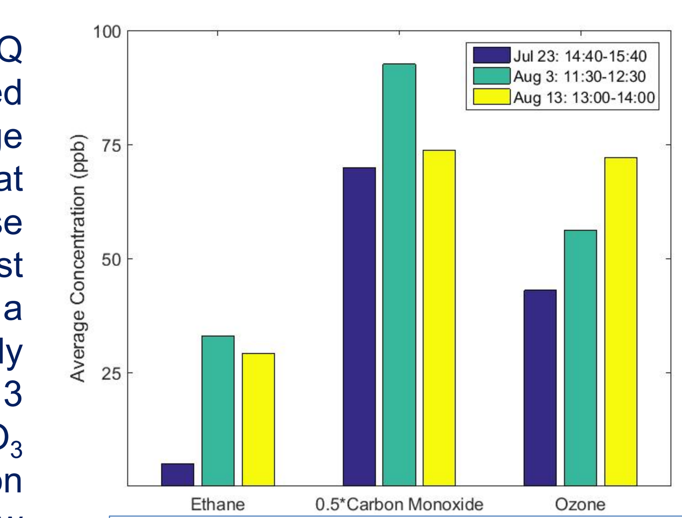

Figure 20. (Above) Average ethane, carbon monoxide, and O_3 measured during the case study drives.

These findings demonstrate that oil and gas activities were the primary source of O_3 production of ~30 ppb above median summertime levels (45-50 ppb) on August 13. The results provide a strong case for further examination of the potential impact of oil and gas emissions and related activities on O_3 production in the northern Front Range. Since exceedances of EPA standards are based on single days and not overall enhancement averaged over multiple days, the high O_3 mixing ratios measured on days when oil and gas activity is the primary contributor to elevated O_3 levels make it imperative to better quantify O_3 production from oil and gas operations to support strategies for staying within the NAAQS for O_3 in the region.

SURFACE WINDS AND O_3

Figures 4-7 show polar histograms with O_3 mole fractions based on wind direction at four surface monitoring stations in the northern Front Range from 5:00-10:00 (a) and 10:00-15:00 (b) for July 15 to August 10, 2014. O_3 concentrations (in ppb) are indicated by color and the percentages represent the frequency of wind coming from a particular direction. Several of the afternoon plots show potential for transport of oil and gas emissions related O_3 precursors and urban emissions to the monitoring sites during the time of photochemical O_3 production.

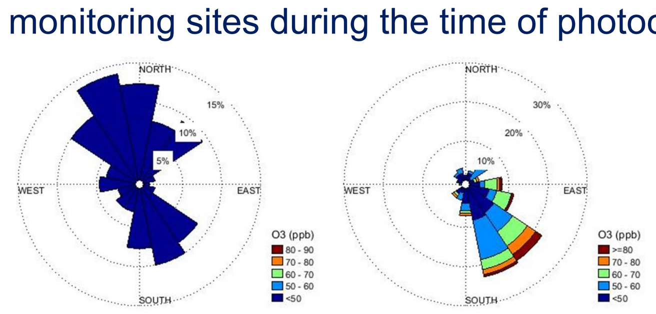

Figure 4. FTC-CSU polar O_3 histograms.

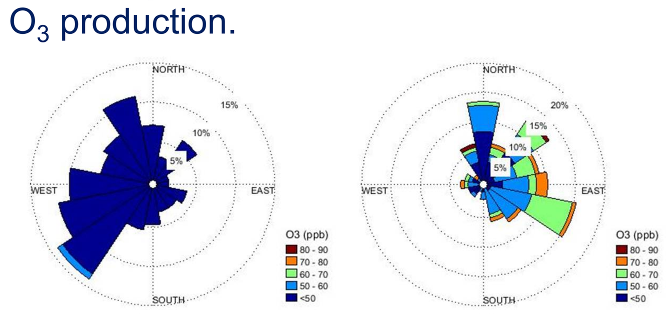

Figure 5. BAO Tower polar O_3 histograms.

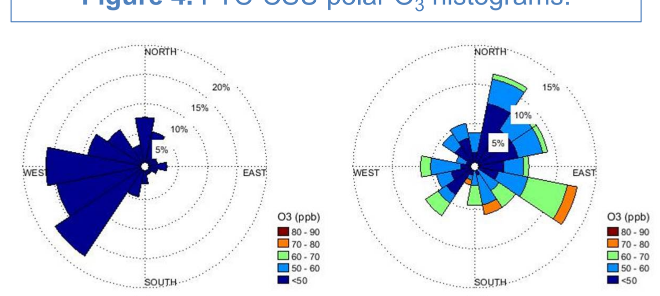

Figure 6. Platteville polar O_3 histograms.

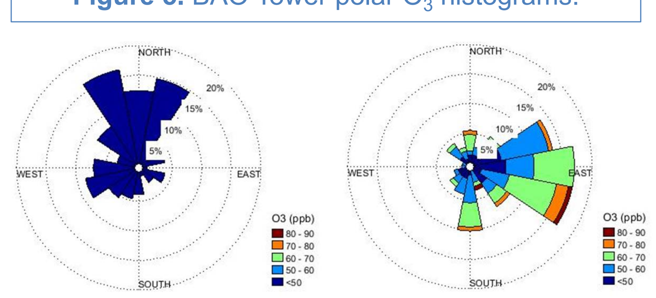

Figure 7. Greeley polar O_3 histograms.

AUGUST 3, 2014: MIXED EMISSIONS, HIGH O_3 DAY

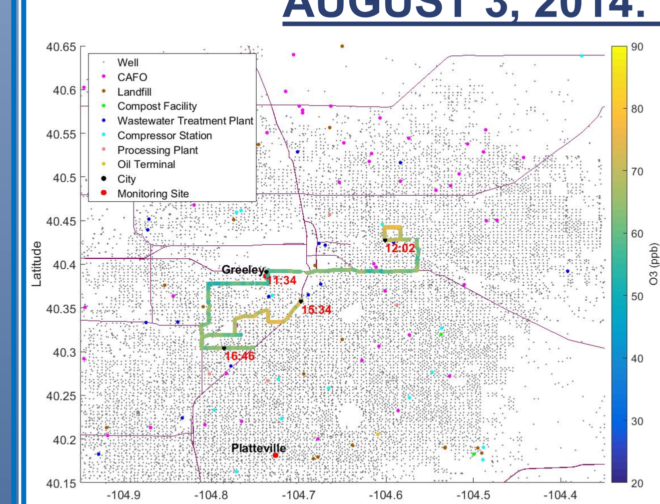

Figure 14. (Left) Map of mobile lab O_3 measurements on July 23, 2014.

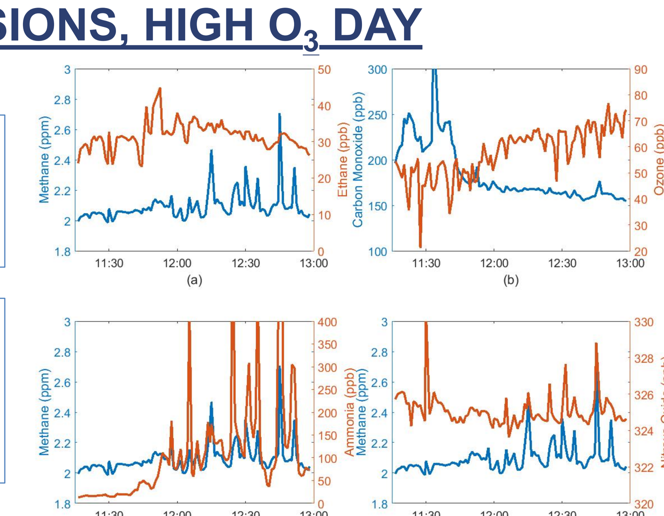

Figure 15. (Right) Time series of gaseous species from mobile lab on July 23, 2014.

O_3 was high at monitoring sites throughout the region on August 3 and the mobile lab measured high O_3 (~30 ppb above median summertime low production levels) along with a mixture of oil and gas, agricultural, and urban emissions. Urban signatures were decreasing throughout the drive and oil and gas related emissions were likely a major source of O_3 precursors, but it is difficult to separate and quantify the direct influence of oil and gas on O_3 production due to the mixture of emission sources.

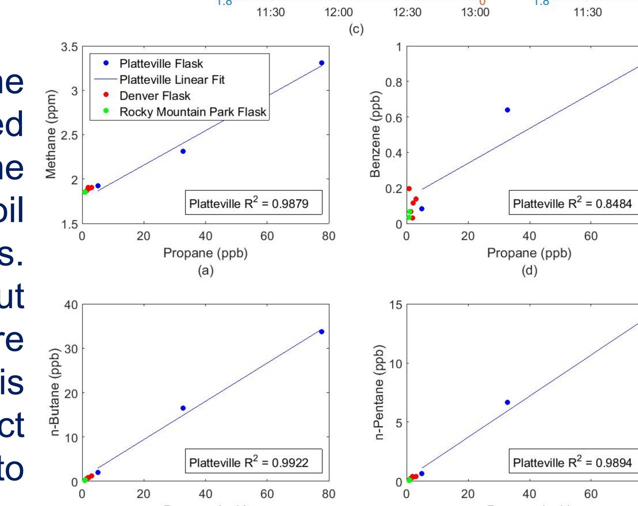

Figure 16. (Left) Mixing ratios measured in flasks collected on August 3, 2014 showing chemical signature of oil and gas emissions.

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