Summertime Ozone Production and its Sensitivity to NOx and VOCs in the Salt Lake Valley

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Abstract

Ozone within the lower troposphere is a significant hazard to human health. Unfortunately, ozone is frequently formed during the summer season due to the combination of sunlight and anthropogenic/biogenic emissions. The two main precursors of ozone production are Volatile Organic Compounds (VOCs) and Nitric Oxides (NOx), which are common emissions from vehicles and industry sources. High maximum daily ozone levels (> 69 ppb) are often observed within the Salt Lake Valley during the summertime. These high ozone levels are not only an acute and chronic public health problem but also exceed the National Ambient Air Quality Standard for ozone. Previous research has shown that developing a VOC to NOx ratio can help characterize how ozone production functions within an airshed. Results from a VOC to NOx ratio analysis allow a characterization of an airshed as VOC-limited, NOx-limited, or transitional, where ozone production is limited by VOCs, NOx emissions, or both, respectively. Understanding if ozone formation is NOx or VOC-limited can help develop more targeted and effective controls. The objective of this investigation was to develop an in-depth observational analysis of the VOC to NOx ratio in the urban SL airshed, thus aiding the formulation of future control strategies to decrease ozone within the Salt Lake Valley. The ratio analysis focuses on hourly GC data and DNPH-cartridge data gathered every third day from the Hawthorne UDAQ site during Jun-Aug 2021. Additionally, a weekday vs. weekend analysis between ozone and NOx is developed from observations of MD8A ozone and NOx from the Erda and Hawthorne sites during the years 2017-2021. Observations of VOC species and NOx as well as cartridge samples are used in the calculation of a VOC to NOx ratio. A few different methods are utilized for tabulating total VOC emissions, including VOC concentration weighted by Maximum Incremental Reactivity (MIR) (i.e. reactivity respective to ozone production/per unit VOC). On average, results exhibit hourly and daily ratio values that fall within a transitional regime. Provided a transitional regime, controls (reductions) on both VOCs and NOx emissions are noted as a potential strategy to decrease ozone levels.

Background

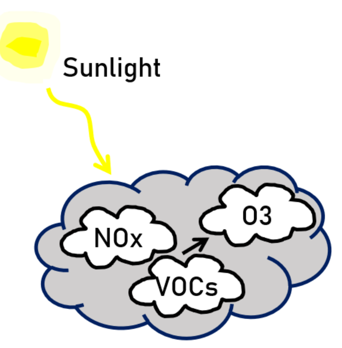
Problem at Hand

What can be done to address the O3 problem along the Wasatch?

Reduce VOCs? OR **Reduce NOx?**

O3 production varies depending on the particular mixture of ambient VOCs to NOx and solar radiation

NOx and VOCs are precursors to O3 formation. Finding the ratio of VOCs to NOx can help distinguish control measures to reduce O3.



What regime characterizes the Salt Lake airshed?

VOC limited	NOx limited
O3 ↓ with ↓ VOC	O3 ↓ with ↓ NOx
O3 ↑ with ↓ NOx	O3 ***insensitive*** to changes in VOCs

Objectives

1. Report a VOC to NOx ratio representative of the Salt Lake Valley airshed, using available GC datasets (Hawthorne UDAQ site)
2. Determine the regime (*transitional*, *VOC*, or *NOx limited*) that characterizes the urban SL airshed.
3. Conduct Weekday vs. Weekend NOx and MD8A ozone analysis to add evidence to ratio analysis.
4. Interpret the ratio/regime and relate it to potential O3 reduction control strategies.

Analysis

Methods and Approach

Develop a VOC:NOx ratio for the Salt Lake Valley

Data for Analysis: PAMs GC dataset from Hawthorne, UT Jun-Aug 2021. Hourly samples of NOx, O3, 57 VOC species, and Total non-methane organic carbon (TNMOC) and carbonyl samples 8hr avg/every three days.

Weekday vs. Weekend NOx and O3 analysis

Generally lower NOx concentrations on the weekends compared to weekdays. If O3 increases on the WE with decreased NOx levels, VOC limited regime possible.

No one standard method to calculate VOC:NOx

Varying the components that comprise total VOCs can change the VOC:NOx ratio significantly. Weigh VOC concentrations by Maximum Incremental Reactivity (MIR), where MIR relates O3 production/per unit VOC.

VOC Concentration Calculation

1. Hourly TNMOC (excl. ethane)
2. Hourly identified VOCs (excl. ethane) weighted by MIR
3. Daily avg identified VOCs (excl. ethane) and carbonyls weighted by MIR

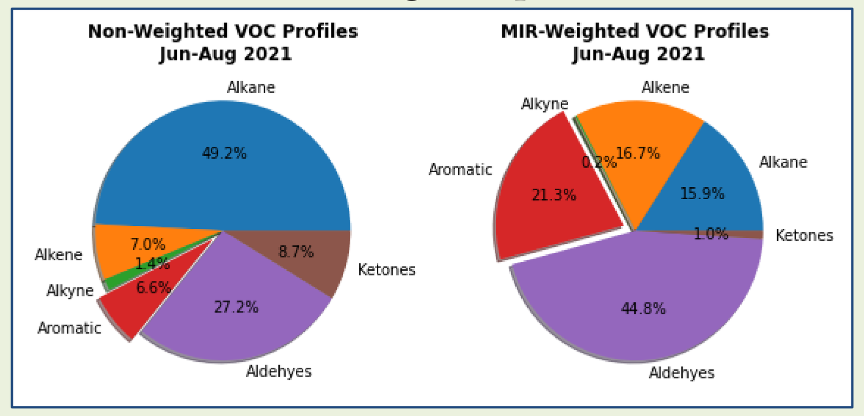
$$VOC\_mir = MIR \times VOC[ppbv] \times VOC\_mol/O3\_mol$$

(Zou, Y et al., 2015)

Thresholds:

VOC:NOx < 5 → *VOC limited*
VOC:NOx > 15 → *NOx limited*
VOC:NOx 5-15 → *transitional*

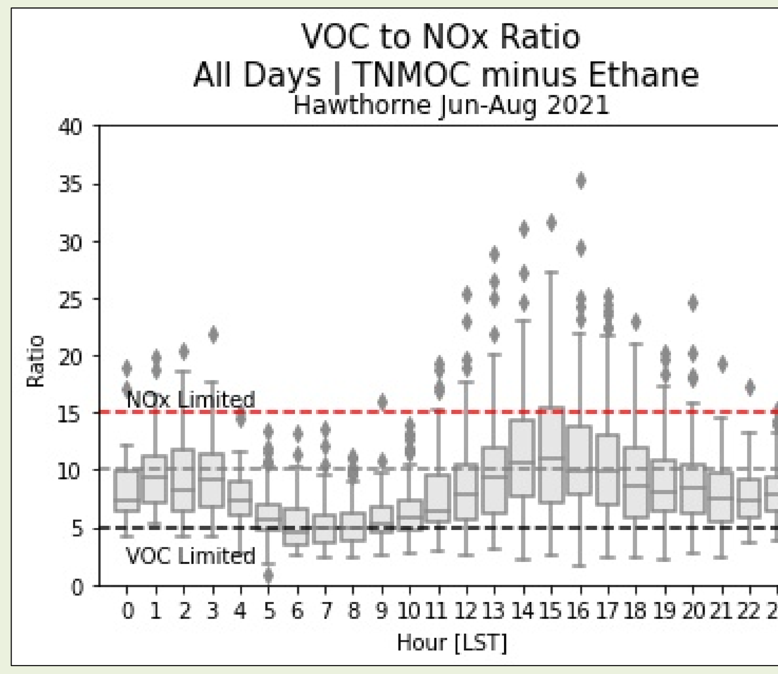
MIR -Weighted VOC profiles vs. Unweighted profiles



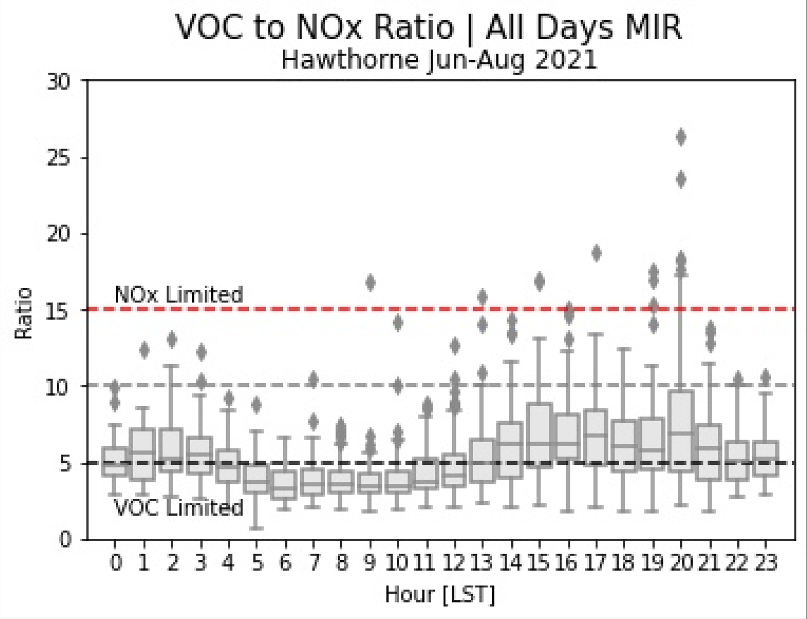
Above: Profiles of VOC groups unweighted (left) and MIR-weighted (right). Unweighted profiles reveal Alkanes (49.2%) largely dominate with largest contribution by concentration, where as MIR-weighted shows Aldehydes (44.8%) & Aromatics (21.3%) contribute most by concentration weighted by MIR

Results

1. TNMOC VOC:NOx

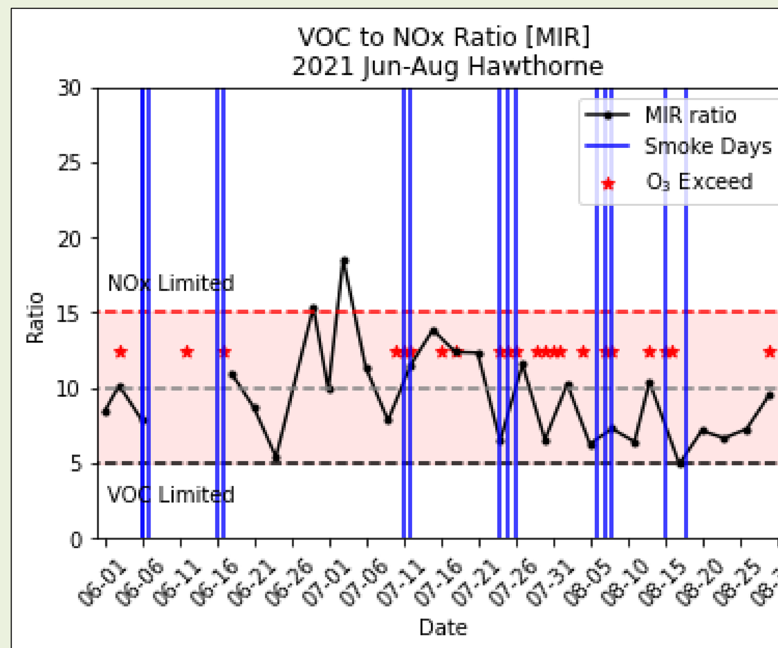


2. MIR-Weighted VOC:NOx



Above: Hourly VOC:NOx boxplot analysis calculated using **(1)** TNOMOC (**top**) and **(2)** MIR-weighted GC VOC concentrations (**bottom**). The *NOx limited* >15 (red dotted line) and *VOC limited* <5 (black dotted line) thresholds are overlaid, with the *transitional regime* residing between these two thresholds. Ratio values in all plots are typically within *transitional* regime outside of the morning commute period (0600-1000) when values dip into the *VOC limited* regime.

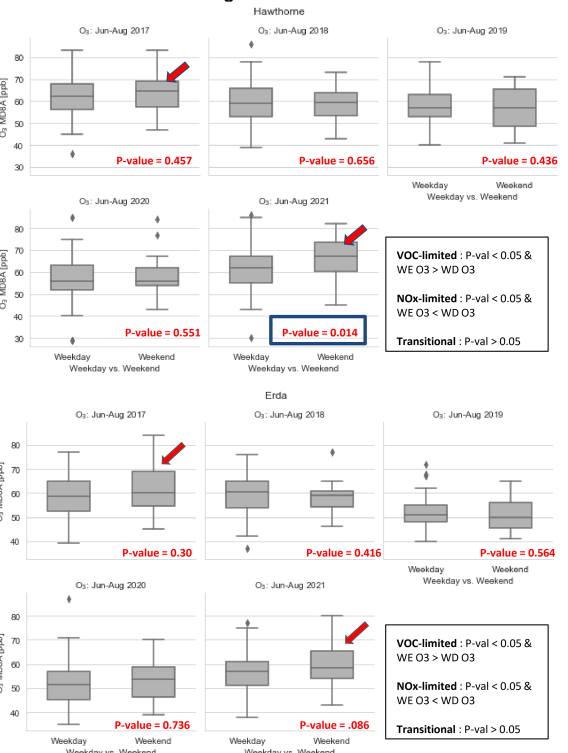
3. MIR-Weight VOC:Nox Incl. Daily Carbonyls



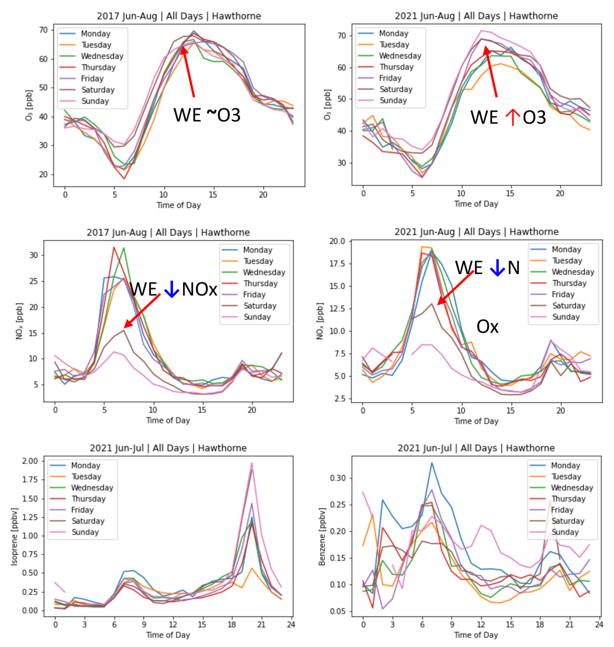
Above: (3) Daily average MIR-weighted GC VOCs and cartridge carbonyl observations. Overlaid on the daily ratio plot are exceedance (MD8A > 69 ppb) and wildfire smoke days. This was done to see if any relationship exists between ozone exceedance, wildfire smoke, and VOC:NOx.

Results

Weekday vs. Weekend Analysis



Right: WD vs. WE MD8A O3 box plot analysis for Hawthorne (urban site) (**top**) and Erda (rural site) (**bottom**) Jun-Aug 2017-2021. Higher average MD8A O3 on WE compared to WD for 2021 is statistically significant, which points to a *VOC-limited* regime. During the years 2017-2020 the difference in WD and WE average O3 is not significant, alluding to a *transitional* regime.



Left: 2017 and 2021 top to bottom (1) Hourly average O3 by day of the week, (2) NOx, and (3) anthropogenic VOC tracers. Ozone peaks on the WE for 2021 with lower NOx than WDs (*VOC-limited* regime). Similar hourly O3 concentration on the WE compared to WD for 2017, and lower NOx on the WE.

Conclusions and Next Steps

The VOC:NOx ratio and WD vs. WE analysis reveals a ***transitional*** regime characterizes the urban SL airshed, with the assumption that Hawthorne represents a sample of an urban airshed. Given a ***transitional*** environment, the most appropriate and effective control strategies will likely include some form of reductions on both VOCs and NOx (Li et al., 2013)(Main et al., 1999). This study only incorporates analysis from one site in the SL Valley. Next steps will include analysis from other sites (upon data availability) to investigate variability in the VOC:NOx ratio. Additionally, the VOC:NOx analysis will be compared with ongoing atmospheric chemical modeling work at UDAQ.

References & Acknowledgements

[1] Li, Y., Lau, A. K., Fung, J. C., Zheng, J., & Liu, S. (2013). Importance of NOx control for peak ozone reduction in the Pearl River Delta region. Journal of Geophysical Research: Atmospheres, 118(16), 9428-9443.
[2] Main, H. H., Alcorn, S. H., & Roberts, P. T. (1999). CHARACTERISTICS OF VOLATILE ORGANIC COMPOUNDS IN THE MID-ATLANTIC REGION.
[3] Zou, Y., Deng, X. J., Zhu, D., Gong, D. C., Wang, H., Li, F., Tan, H. B., Deng, T., Mai, B. R., Liu, X. T., and Wang, B. G.: Characteristics of 1 year of observational data of VOCs, NOx and O3 at a suburban site in Guangzhou, China, Atmos. Chem. Phys., 15, 6625–6636, https://doi.org/10.5194/acp-15-6625-2015, 2015.

Thanks to UDAQ, particularly the Technical Analysis and Modeling section for their ongoing help with this project.

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