Observation-Based Analyses of the Sensitivity of Ozone Formation in the Lake Michigan Region to NO_x and VOC Emissions

Jerrold Acdan¹, Michael Vermeuel², Timothy H. Bertram^{1,2} and R. Bradley Pierce^{1,3}

¹Department of Atmospheric and Oceanic Science, University of Wisconsin, Madison ²Department of Chemistry, University of Wisconsin, Madison ³Space Sciences and Engineering Center, University of Wisconsin, Madison

Executive Summary

Regulating the concentration of surface ozone (O₃) is necessary to maintain and improve public health and agriculture. At elevated concentrations, long-term exposure to O₃ is linked to increased mortality in humans from respiratory illnesses (Jerrett et al., 2009) and the slowing of stomatal responses in plants to harsh environmental conditions (Mills et al., 2009). Short-term exposure to O₃ results in the inflammation of bronchial airways and acute lung damage (Gauderman et al., 2000; McDonnell et al., 1991). To prevent these adverse effects, the U.S. Environmental Protection Agency (EPA) enforces National Ambient Air Quality Standards (NAAQS) for O₃ and particulate matter. Effective regulation of O₃ concentrations is challenging due to the complex nonlinear chemistry involved in ozone production. It is well established that the production rate of O₃ is a function of the concentration of nitrogen oxides (NO_x \equiv NO + NO₂) and volatile organic compounds (VOCs), where the sensitivity of the O₃ production rate (*P*_{O3}) depends on the relative concentrations of NO_x and VOC as shown by the O₃ isopleth. To enact effective O₃ control strategies it is critical to determine the chemical regime (NO_x *vs.* VOC limited) for the airshed

under consideration. The calculated response of odd oxygen $(O_x \equiv O_3 + NO_2)$ production (over a course of 5 hours) to changes in NO_x and VOC emissions for the Chicago plume advected over Lake Michigan is shown in Fig. 1, adapted from recent work by the Bertram research group. This highlights the non-linear sensitivity of O₃ production to changes in NO_x and VOC emissions. In the NO_x limited regime a reduction in NO_x emissions (E_{NOx}) leads to decrease in O₃ production, while in the VOC limited regime, а corresponding reduction in E_{NOx} can result in an increase in O_3



Figure 1: Modeled O_x production (calculated over 5 hours) as a function of NO_x and VOC emissions. NO_x and VOC emissions are shown relative to 1990 estimates. Adapted from *Vermeuel et al.* 2019.

production rates. This non-intuitive response is due to the delicate balance between HO_x and NO_x radical propogation *vs*. termination in the VOC limited (NO_x saturated) regime.

Multiple observation-based and chemical modeling approaches have been developed to determine the sensitivity of O₃ production to changes in NO_x and VOC emissions. Observation-based indicators include, but are not limited to: i) the response of $[O_3]$ to changes in $[NO_x]$ (Pusede & Cohen, 2012), ii) simultaneous measurements of the change in [VOC] or VOC reactivity and [NO_x] or [NO₂], including remote sensing measurements of tropospheric column ratios of HCHO/NO₂ (Duncan et al., 2010; S. Sillman, 1995b, 1995a; Sanford Sillman & He, 2002), and iii) direct measurements of the termination products of HO_x-NO_x cycling (e.g., H₂O₂ and HNO₃), the ratio of which reflects the oxidation environment where O₃ is produced (S. Sillman, 1995b; Vermeuel et al., 2019). In parallel, chemical models, driven by accurate NO_x and VOC emission fields can be used to assess the sensitivity of O_3 production in the model to changes in NO_x and VOC emission rates. Here, we describe the results of two parallel analyses focused on assessing the sensitivity of O_3 production relative to VOC and NO_x using observation-based approaches involving satellite measurements of nitrogen dioxide (NO₂) and formaldehyde (HCHO) (Task 3) and photochemical box modeling and detailed observation-based analysis of observations from the 2017 Lake Michigan Ozone Study (LMOS) which exploit the comprehensive coverage of chemical and meteorological measurements at the Zion and Sheboygan super sites (Task 4). Outcomes from each of these studies include:

Task 3: This study explored the use of satellite-based estimates of the ratio of formaldehyde to nitrogen dioxide (HCHO/NO₂) as an indicator of ozone-NOx-VOC sensitivity in the Lake Michigan region. The satellite based HCHO/NO₂ values were interpreted using two different sets of thresholds for ozone production sensitivity; model-based thresholds from Duncan et al. (2010) and observationally based thresholds from Jin et al. (2020). In general, we recommend the use of the Jin et al. (2020) thresholds for interpreting the satellite ratios and the Duncan et al. (2010) thresholds for interpreting the EPA PAMS surface ratios presented in this work.

During the 2018 and 2019 ozone seasons, monthly composite results show that in the Lake Michigan region, the Chicago Metropolitan Area (CMA) is VOC sensitive, its surroundings and north along the Wisconsin shoreline up to Milwaukee are in the transition zone, with the rest of the region falling within the NOx sensitive ozone production regime based on the Jin et al. (2020). During the ozone season and during Chicago ozone exceedance events, the Chicago CMA remains VOC sensitive, but the spatial extent of the transition zone that surrounds Chicago and extends north up to Milwaukee decreases during ozone exceedance events using the Jin et al. (2020) thresholds. Statistical tests show us that these higher ratios are due to higher HCHO levels rather than changes in NO₂. This is likely attributed to increased temperatures during the ozone exceedance events, which leads to increased biogenic VOC emissions and thus increased ozone production (Sillman & Samson, 1995). These seasonal, satellite-based results are generally consistent with detailed box model calculations of NOx-VOC sensitivities conducted under Task

4 of this project during specific ozone exceedance events that occurred during the 2017 LMOS field campaign.

Task 4: This study highlighted the use of chemical indicators in determining the O_3 -NO_x-VOC sensitivity at pollutant source regions along the Lake Michigan coastline and along the airmass trajectory as it advects over the lake from source to receptor region. We present a box model that can be used in a trajectory analysis when coupled to backward trajectory retrievals. This box model was used for five case study days during LMOS 2017: 06/02, 06/04, 06/11, 06/12, and 06/15. The model was validated by comparing model solutions to ground monitor measurements of O_3 and NO_x at the beginning and end of a parcel trajectory. The model shows reasonable agreement between the model and endpoint measurements of HNO₃ at a supersite in Zion, IL. The model consistently underpredicted H₂O₂ concentrations at the endpoint (Zion) compared with measurements, pointing to an incomplete understanding in the sourcing of VOCs at the Zion site and/or poorly constrained VOCs at the start of the trajectory.

A primary O₃-NO_x-VOC sensitivity analysis was performed by generating isopleths of ΔO_3 (where $\Delta O_3 = [O_{3,endpoint}-O_{3,source}]$) under varying emissions of anthropogenic NO_x and VOC. An instantaneous sensitivity analysis was performed by generating isopleths of P_{O3} under varying HCHO and NO₂. This allowed for the comparison of three indicators, $\frac{P(H_2O_2)+P(ROOH)}{P(HN_3)}$, HCHO/NO₂, and L_N/Q in determining the sensitivity regimes of each case study as well as defined new, case-specific transition region values for each indicator. All case studies aside from 06/02 transitioned from more VOC-sensitive at the source region to NO_x-sensitive at Zion, IL with peak net P_{O3} regularly between 11 and 15 CDT, indicative of photochemistry that occurs during the day. This analysis allows for the prescription in the source region of two VOC-sensitive days (06/02 and 06/04), one NO_x-sensitive day (06/11), and two days in the transition region (06/12 and 06/15). In order to more accurately model O₃ chemistry along this trajectory, additional measurements of the spatial and temporal variability in VOC concentrations is required. In addition, it is recommended that more CO monitors are utilized and implemented to determine the parcel dilution factor (τ_{mix}) that can strongly control O₃ production at periods in the trajectory when the parcel is advecting over Lake Michigan.

Observation-Based Analyses of the Sensitivity of Ozone Formation in the Lake Michigan Region to NOx and VOC Emissions

Task 3: TROPOMI HCHO/NO₂ Analysis Final Memo September 30, 2020

Jerrold Acdan & R. Bradley Pierce

1. Introduction

The use of the ratio of formaldehyde (HCHO) to nitrogen dioxide (NO₂) as an indicator for ozone production sensitivity is an active area of research. Satellite-based estimates of formaldehyde (HCHO) and nitrogen dioxide (NO₂) have been constructed using retrievals from the Ozone Monitoring Instrument (OMI) onboard the NASA Aura satellite, and ratios of these retrievals (HCHO/NO₂) have been used to assess ozone production regimes for various regions of the United States (Chang et al., 2016; Duncan et al., 2010; Jin et al., 2017; Jin et al., 2020). Duncan et al. (2010) used Community Multiscale Air Quality Modeling System (CMAQ)-based studies that apply radical vs NOx sinks (L_{HOx}/L_{NOx}) as an indicator of ozone production NOx-VOC sensitivity, and find that OMI HCHO/NO₂ ratios less than 1 indicate volatile organic compound (VOC) sensitivity, ratios between 1 and 2 indicate transition between VOC and NOx sensitivities (the transition zone), and ratios greater than 2 indicate NOx sensitive ozone production. A more recent study by Jin et al. (2020), which connects OMI-derived HCHO/NO2 ratios to high ozone event probabilities calculated from in situ ground monitor data, suggests that HCHO/NO₂ ratios less than 3.2 indicate VOC sensitive ozone production, ratios between 3.2 and 4.1 indicate the transition zone, and ratios greater than 4.1 indicate NOx sensitivity. The highlighted studies have different threshold values because the Duncan et al. (2010) study is based on CMAQ modeling while the Jin et al. (2020) study is based on in situ data. The current work uses both sets of thresholds to conduct analyses, and the differences between the interpretations of results depending on which thresholds are used is a focal point of discussion.

This memo summarizes the methodology and results of the TROPOspheric Monitoring Instrument (TROPOMI) HCHO/NO₂ analysis (Task 3) conducted under contract to the Lake Michigan Air Directors Consortium (LADCO) by the University of Wisconsin-Madison Space Science and Engineering Center (SSEC). The TROPOMI instrument onboard the Sentinel-5 Precursor satellite has signal to noise ratios (SNRs) that are similar to OMI but provides much higher spatial resolution (De Smedt et al., 2018; Veefkind et al., 2012). Task 3 focuses on applying the aforementioned OMI thresholds to TROPOMI data in order to better determine the spatial variability in ozone-NOx-VOC sensitivity in the Lake Michigan region. The subtasks of Task 3 include: (1) downloading and archiving TROPOMI HCHO and NO₂ data; (2) constructing

composites of HCHO, NO₂, and HCHO/NO₂ columns binned onto a grid covering the LADCO domain for the ozone season and ozone exceedance days; and (3) comparing these TROPOMIbased ratios to available surface observations to assess the robustness of the results (Table 1). The LADCO domain covers the states of Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin. However, the TROPOMI composites created for this study cover a much larger area that extends north into southern Canada, east to the East Coast, south to the northern portions of the Gulf states, and west covering portions of central states such as Nebraska.

Task	Status
3.1: TROPOMI Data Acquisition and Archival	Completed – March 8, 2020
3.2a: TROPOMI Data Binning to 'LADCO Grids'	Completed – May 18, 2020
3.2b: Generation of Exceedance Day Composites	Completed – June 28, 2020
Deliverable: Draft Memo	Submitted – June 15, 2020
3.3: Comparison to Ground-Based Ratios	Completed – July 18, 2020
Deliverable: Final Memo	Submitted – September 30, 2020

Table 1. Summary of Task 3

2. Methodology

2.1 TROPOMI Data Binning to 'LADCO Grids'

TROPOMI Version 1 tropospheric NO₂ (KNMI, 2018, 2019) and HCHO (DLR, 2019a, 2019b) orbital (L2) data were downloaded from the NASA Goddard Earth Sciences Data and Information Services Center (GES DISC) (see Appendix A). TROPOMI L2 data were locally stored on a UW-Madison SSEC cluster file server. Gridded monthly TROPOMI L2 NO₂ and HCHO clear sky (good quality with cloudy radiance fraction < 30%) composites were constructed using quality controlled L2 retrievals based on the recommended qa_value > 0.75 from the TROPOMI NO₂ and HCHO README files (Eskes et al., 2019a, 2019b). In addition, we generated monthly composites of TROPOMI L2 NO₂ good quality cloudy retrievals and over scenes covered by snow/ice (0.5 < qa_value < 0.75) to allow for future estimates of lightning NOx signatures. Additional 'detection limit' filters of 1.5×10^{15} mol/cm² for NO₂ (Duncan et al., 2010) and 1.8×10^{15} mol/cm² for HCHO (Chance et al., 2002) were applied to the L2 orbital retrievals used in the monthly composites.

The gridded monthly composites for NO₂ and HCHO were constructed using Meteorology-Chemistry Interface Processor (MCIP) files from the LADCO modeling platform 12 km² Lambert Conformal grid. At the request of LADCO, we also constructed monthly composite NO₂ data on the LADCO modeling platform 4 km² Lambert Conformal grid to provide a high resolution NO₂ dataset for future emission inventory studies. Both 12 km² and 4 km² monthly composites were produced in netcdf format for the periods June to October, 2018, and May to October, 2019, and include the following 2-dimensional variables: Latitude, Longitude, Cloudy_Lightning_NO2, Cloudy_Lightning_NO2_Obs_Count, Clear_Sky_NO2, and Clear_Sky_NO2_Obs_Count. The 12 km² composites, which are the primary datasets used in the subsequent analyses of this report, also include the variables: Clear_Sky_HCHO, Clear_Sky_HCHO_Obs_Count, and HCHO_to_NO2_Ratio. Global attributes of the monthly composite netcdf files include the MCIP grid information (map projection, earth radius, etc.), which allows the netcdf files to be converted into geographic information system (GIS) files. The resulting 12 km² HCHO/NO₂ ratios were constructed using the monthly composite values of HCHO and NO₂ for each grid cell to reduce the impact of noise in the HCHO retrieval.

2.2 Generation of Exceedance Day Composites

The second major activity under Task 3 was computing composites for ozone exceedance days. After discussion with LADCO and the Wisconsin Department of Natural Resources (WDNR), we decided to construct TROPOMI HCHO/NO₂ ratios based on ozone exceedance days for both individual and combined non-attainment areas (NAAs). Donna Kenski (LADCO) provided ozone exceedance data for NAAs within and neighboring the LADCO domain (Chicago, Cincinnati, Cleveland, Columbus, Detroit, Louisville, Sheboygan, St. Louis, and Western Michigan). We defined an 'ozone exceedance day' as having at least one monitor within an NAA measuring maximum daily 8-hour average (MDA8) ozone > 70 ppbv. Most of the ozone exceedance days for each NAA. The composites were created following the same methodology explained in *Section 2.1* using TROPOMI data only for the identified ozone exceedance days for each individual NAAs or combined (regional) NAAs (i.e. the individual NAAs within the combined region must have ozone exceedance events that occurred on the same days).

2.3 Ground-Based Ratios

Donna Kenski (LADCO) also provided Environmental Protection Agency (EPA) Photochemical Assessment Monitoring Stations (PAMS) data for use in the calculation of ground-based HCHO/NO₂ ratios. In order to compare the ground-based ratios to the satellite-based data, the EPA PAMS data were filtered to sites within the LADCO domain with concurrent HCHO and NO₂ measurements. This filtering process resulted in four sites of analysis: Site 3103 in Cook County, Illinois; Site 78 in Marion County, Indiana; Site 15 in Wayne County, Michigan; and Site 85 in St. Louis City County, Missouri.

After identifying the analysis sites, we converted the PAMS HCHO data to the same units as the NO₂ data, averaged the hourly NO₂ data to get a daily value (as the HCHO measurements at three of the four analysis sites were daily samples; note that the Indiana site required additional HCHO data processing as the samples were taken every eight hours), and calculated daily HCHO/NO₂ ratios. These daily ratios were then composited to get monthly ratio values in order to compare them to the previously generated monthly composites of TROPOMI data. The nearest TROPOMI

monthly composite grid boxes were identified and used to extract the satellite-based ratios for comparison.

To explore the impact of daily averaging on the ground-based EPA PAMS HCHO/NO₂ ratios, we also analyzed data collected during the 2017 Lake Michigan Ozone Study field campaign (Abdioskouei et al., 2019) at the Spaceport Sheboygan EPA ground site. Because the data at this site were collected in one-minute intervals, we were able to assess the impact of sampling intervals and daily averaging on the calculation of ground-based HCHO/NO₂ ratios, thus providing additional context to our comparisons between the EPA PAMS and TROPOMI HCHO/NO₂ data.

3. Results & Discussion

3.1.1 Monthly Mean Composites – Full 12 km² Grid

Figures 1 and 2 show the results of the 12 km^2 monthly NO₂ and HCHO composites for July 2018 and July 2019, respectively. Peak July clear sky tropospheric NO₂ columns occur over New York City (NYC) and reach 12×10^{15} mol/cm² in 2018 and 7.1×10^{15} mol/cm² in 2019. The July 2019 NO2 composite shows a region of elevated NO2 over Eastern Ohio, Western Pennsylvania, and Northern West Virginia that is not present in 2018. Peak July clear sky tropospheric HCHO columns (20x10¹⁵ mol/cm²) occur over Oklahoma, Arkansas, and Missouri in 2018 and along the eastern seaboard during 2019. The number of NO₂ and HCHO observations per grid box varies considerably across the analysis domain. This is due to a combination of the distribution of cloudiness as well as the detection limit threshold that was applied in the filtering of the L2 retrievals. The highest density of NO₂ observations within each bin occurs in urban areas, and there are a fairly low number of NO₂ retrievals above the detection limit over rural areas. Grid boxes with a low number of binned NO2 retrievals have 'noisy' composite values and thus questionable HCHO/NO₂ values (e.g. in Ontario, Canada, north of the Minnesota border). However, this is not a major concern for this study because the subsequent analyses focus on regions with a relatively high number of binned NO₂ retrievals. The density of HCHO observations is generally higher than that of NO₂ in both rural and urban areas. This is reasonable since HCHO is a secondary product of both biogenic and anthropogenic VOCs and also has primary anthropogenic emissions.



Figure 1. July 2018 12 km² composite clear sky NO₂ (x10¹⁵ mol/cm², upper left), HCHO (x10¹⁵ mol/cm², upper right), number of NO₂ retrievals (lower left), and number of HCHO retrievals (lower right)

July 2019 Clear Sky HCHO Clear Sky NO₂ 0 15 2 [HCHO] x10¹⁵ molec/cm² 10 20 25 [NO2] x1015 molec/cm2 Number of Clear Sky NO₂ Observations Number of Clear Sky HCHO Observations 100 40 60 Number of Observations 80 100 40 60 Number of Observations 80 20 20

Figure 2. July 2019 12 km² composite clear sky NO₂ (x10¹⁵ mol/cm², upper left), HCHO (x10¹⁵ mol/cm², upper right), number of NO₂ retrievals (lower left), and number of HCHO retrievals (lower right)

Figure 3 shows the 12 km² composite TROPOMI HCHO/NO₂ ratios for July 2018 and 2019. The minimum value of 1.5 occurs over NYC in 2018 while the minimum value of 2.2 occurs over Chicago in 2019. According to the Duncan et al. (2010) thresholds, this TROPOMI-based HCHO/NO₂ analysis suggests that no urban centers within the domain are VOC sensitive (HCHO/NO₂ < 1) and that major urban centers (Chicago and NYC) fall into the transition between NOx and VOC sensitivities during July 2018 and 2019. However, the Jin et al. (2020) thresholds suggest that Chicago and NYC fall in the VOC sensitive ozone production regime (HCHO/NO₂ < 3.1) during July 2018 and 2019. When using the Jin et al. (2020) thresholds to interpret the composites, more of the domain is classified as VOC sensitive or in the transition zone as compared to using the Duncan et al. (2010) thresholds, which classifies much of the domain as NOx sensitive. The differences between 2018 and 2019 HCHO/NO2 ratios can be largely attributed to increased HCHO over the Eastern Seaboard in 2019. Results of all the monthly composites are included in Supplement 1 entitled "S1 LADCO Project - Monthly Binning Results -Chronological.pdf". These show that the July 2019 minimum HCHO/NO₂ ratio of 2.2 was the largest minimum during the analysis period. The lowest minimum ratios occur in NYC in October, reaching 0.7 and 0.9 in 2018 and 2019, respectively.



Figure 3. 12 km² composite clear sky HCHO/NO₂ ratios for July 2018 (left) and July 2019 (right)

We have also created 2018-2019 "ozone season" composites by computing the weighted mean (based on the number of observations per month per grid box) of HCHO and NO₂ and then computing the HCHO/NO₂ ratio for June-October 2018 and May-October 2019. *Figure 4* shows the resulting HCHO/NO₂ ratios for the 2018 and 2019 ozone seasons combined. The minimum

ratio occurs over NYC (1.64) with Chicago also slightly less than 2 (1.92), placing the urban centers in the transition regime between NOx and VOC sensitivities according to Duncan et al. (2010) but in the VOC sensitive regime according to Jin et al. (2020). Detroit, Toronto, and Montreal show values between 2 and 3, making these urban centers in the Duncan et al. (2010) NOx sensitive regime and the Jin et al. (2020) VOC sensitive regime. Ozone season compositing shows a number of urban areas in the SE US with lower (~4.5) ratios than the SE rural areas but still well within the NOx sensitive regime for both the Duncan et al. (2010) and Jin et al. (2020) thresholds. There is an interesting feature along the North Dakota/Minnesota border that shows ratios of ~3.5. These lower ratio values are associated with higher tropospheric NO₂ columns in June and October 2018, and May, June, and October 2019 (see Supplement 1).



Figure 4. 12 km² composite clear sky HCHO/NO₂ ratios for the 2018 and 2019 ozone seasons combined

3.1.2 Monthly Mean Composites – Lake Michigan Region

Figure 5 displays the results from *Figures 1, 2,* and *3* when zoomed into the Lake Michigan region, which we defined as between latitudes 41°N and 45.3°N and longitudes 88.6°W and 85.49°W. Table 2 lists the summary statistics of HCHO, NO₂, and HCHO/NO₂ values for this domain. The highest values of HCHO can be seen along the eastern coast of Lake Michigan, resulting in the highest HCHO/NO₂ ratios within the domain. The highest values of NO₂ are found in the Chicago Metropolitan Area (CMA), resulting in the lowest HCHO/NO₂ ratios in the region. In July 2018, the CMA had a minimum ratio value of 1.79, placing it in the Duncan et al. (2010) transition zone but the Jin et al. (2020) VOC sensitive regime. In July 2019, the minimum ratio value within the CMA increased to 2.21 due to a decrease in NO₂, indicating NOx sensitive ozone production

according to Duncan et al. (2010) but still within the Jin et al. (2020) VOC sensitive regime. Outside of the CMA, HCHO/NO₂ ratios are greater than 2, making ozone production in the rest of the domain NOx sensitive for both July 2018 and 2019 according to Duncan et al. (2010). Using the Jin et al. (2020) thresholds, we see a larger area classified as being in the transition zone surrounding the CMA in July 2018 and 2019, but just as using the Duncan et al. (2010) thresholds, most of the Lake Michigan domain is classified as NOx sensitive. The changes seen between the TROPOMI observations in July 2018 and 2019 can be due to many reasons, such as differences in emissions (e.g. reductions in NO₂) and meteorological conditions (e.g. higher temperatures and varying transport patterns).

July 2018	Minimum	Mean	Maximum		
HCHO (mol/cm ²)	8.56x10 ¹⁵	12.10x10 ¹⁵	15.60x10 ¹⁵		
NO ₂ (mol/cm ²)	1.76x10 ¹⁵	2.31x10 ¹⁵	6.44x10 ¹⁵		
Ratio	1.79	5.40	7.28		
July 2019	Minimum	Mean	Maximum		
HCHO (mol/cm ²)	9.56x10 ¹⁵	12.70x10 ¹⁵	15.20x10 ¹⁵		
NO ₂ (mol/cm ²)	1.71x10 ¹⁵	2.37x10 ¹⁵	5.89x10 ¹⁵		
Ratio	2.21	5.50	7.79		
Difference (2019 - 2018)	Minimum	Mean	Maximum		
HCHO (mol/cm ²)	-4.28x10 ¹⁵	0.57x10 ¹⁵	4.32x10 ¹⁵		
NO ₂ (mol/cm ²)	-2.00x10 ¹⁵	0.06x10 ¹⁵	1.04x10 ¹⁵		
Ratio	-1.80	0.10	2.05		

Table 2. Summary statistics of HCHO, NO₂, and HCHO/NO₂ from Figure 5



Figure 5. Lake Michigan region 12 km² composite clear sky HCHO (top row), NO₂ (middle row), and HCHO/NO₂ ratios (bottom row) for July 2018 (left column), July 2019 (middle column), and the difference between the years (2019 – 2018; right column)

3.2 Ozone Exceedance Composites

Ozone exceedance composites were created by gridding TROPOMI HCHO and NO₂ data collected during ozone exceedance events that occurred in individual or regional LADCO NAAs. Appendix B provides a list of the ozone exceedance days for each individual non-attainment area. *Figure 6* focuses on the Lake Michigan region (as defined in the previous section) and shows a comparison between HCHO, NO₂, and HCHO/NO₂ ratios for the ozone season composite and for ozone exceedance days within the Chicago NAA. The Chicago NAA had the largest number of ozone exceedance events (33) of all the NAAs within the LADCO domain during 2018 and 2019 and consequently has the most robust statistics. For brevity, we only discuss our analysis of the Chicago NAA in the rest of this section. All results for Task 3.2b can be found in Supplement 2 entitled "S2 LADCO Project – Ozone Exceedance Days Composites.pdf", which shows figures for each of the LADCO NAAs as well as days with regional exceedances.



Figure 6. 12 km² composite clear sky HCHO (top row), NO₂ (middle row), and HCHO/NO₂ ratios (bottom row) for the combined 2018 and 2019 ozone seasons (left column), ozone exceedance events in the Chicago NAA (middle column), and the difference (exceedance composite – ozone season; right column)

The minimum HCHO/NO₂ ratio during 2018 and 2019 over Chicago is 12% lower (1.73) during ozone exceedance days than the minimum for the average ozone season (1.92). However, the largest differences are associated with larger HCHO/NO₂ ratios in non-urban areas during ozone exceedance events. This is associated with larger background HCHO abundances and is likely due to increased temperatures during ozone exceedance events, which lead to increased biogenic VOC emissions and thus increased ozone production (Sillman & Samson, 1995). To investigate this further, we created histograms and cumulative distribution functions (*Figure 7*) of HCHO, NO₂, and HCHO/NO₂ values for the ozone season and during Chicago ozone exceedance events within the Chicago subdomain shown in *Figure 6*. To determine whether the differences between the ozone season and ozone exceedance distributions were statistically significant, we performed two-sample Kolmogorov-Smirnov (K-S) tests. The two-sample K-S test assesses whether the two sample distributions come from the same distribution (Heckert, 2016). At a confidence level of 95%, we reject the null hypothesis that the sample distributions come from the same distribution when the p-value is less than 0.05. The results of the two-sample K-S tests are shown in Table 3.

Two-Sample K-S Test	p-value	K-S statistic	Result
нсно	8.0x10 ⁻¹⁸⁴	0.680	Significant
NO ₂	0.196	0.053	Not Significant
Ratio	2.6x10 ⁻⁴⁹	0.363	Significant

Table 3. Summary of two-sample K-S tests performed on the distributions in Figure 7

As seen in the histograms in *Figure 7*, there are shifts toward higher HCHO and HCHO/NO₂ values during ozone exceedance days within the Chicago NAA. The results of the two-sample K-S tests show that these shifts are statistically significant. Because the result of the two-sample K-S test for NO₂ has a p-value greater than 0.05 (Table 3), NO₂ is not statistically different during ozone exceedance events versus the typical ozone season. As a result, we can conclude that higher HCHO/NO₂ ratio values during ozone exceedance events are due to higher HCHO values. This finding supports the hypothesis that increased biogenic VOC emissions lead to higher HCHO/NO₂ ratios outside of urban areas during ozone exceedance events. This behavior was similarly found for each of the LADCO NAAs considered in this study.



Values during Ozone Season	Values during Chicago Ozone Exceedance Days	VOC Sensitive Ratio < 1.0 (Duncan et al., 2010)	NO _x Sensitive Ratio > 2.0 (Duncan et al., 2010)	VOC Sensitive Ratio < 3.2 (Jin et al., 2020)	NO _x Sensitive Ratio > 4.1 (Jin et al., 2020)

Figure 7. Histograms and cumulative distribution functions (CDFs) of HCHO (top row), NO₂ (middle row), and HCHO/NO₂ ratio (bottom row) values for the combined 2018 and 2019 ozone seasons composite (blue) and for the ozone exceedance days within the Chicago NAA (green)

If we interpret the results using the Duncan et al. (2010) thresholds, it is important to note that while HCHO/NO₂ ratios are shifted to higher values during ozone exceedance events, the actual values themselves suggest that the Lake Michigan region is dominated by NO_x sensitive ozone production (HCHO/NO₂ > 2) both during ozone exceedance events and during the typical ozone season. None of the values are below one, and a very small number of pixels (which are located within the Chicago Metropolitan Area) fall within the transition zone between NOx and VOC sensitive ozone production ($1 \le HCHO/NO_2 \le 2$). However, interpreting the HCHO/NO₂ ratio values using the Jin et al. (2020) thresholds tells a different story. During the typical ozone season, the CMA displays VOC sensitivity. Surrounding the CMA and north along the Wisconsin coast up to Milwaukee, the ratios suggest that ozone production falls in the transition zone. During Chicago ozone exceedance days, the CMA remains largely VOC sensitive and its surroundings still in the transition zone, but the overall spatial extent of the transition zone decreases. North of the CMA, the western portion of the lake and Wisconsin coast up to Milwaukee switch to being mostly NOx sensitive during Chicago ozone exceedance days. Figure 8 visually demonstrates how the Duncan et al. (2010) and Jin et al. (2020) thresholds lead to differing interpretations of ozone-NOx-VOC production in the Lake Michigan region. Similar figures for Sheboygan, Wisconsin, ozone exceedance days as well as Chicago-Sheboygan regional ozone exceedance days can be found in Supplement 2b entitled "S2b LADCO Project - Lake Michigan Ozone Production Regimes.pdf".



Figure 8. Classification of ozone production regimes within the Lake Michigan region during the 2018-2019 ozone seasons combined (left) and during Chicago ozone exceedance days (right)

We can compare these findings to Task 4 of the larger LADCO Project, which was conducted by Michael Vermeuel and Tim Bertram at the University of Wisconsin. Following a methodology based on earlier work (Vermeuel et al. 2019), Task 4 also investigated the sensitivity of ozone production in the same Lake Michigan domain using master mechanism box model chemistry predictions along trajectories constrained by high resolution wind and temperature analyses and in situ data. The study identified five days during the LMOS 2017 field campaign (June 2, 4, 11, 12 and 15, 2017) that experienced episodically high ozone levels and assessed the chemistry of air plumes as they traveled from their source regions through the southern Lake Michigan region. Their findings show that although the plumes on each day originated in different ozone production regimes (June 2 and 4 VOC sensitive; June 11 NOx sensitive; and June 12 and 15 transition zone), all of them trended toward less VOC sensitivity/more NOx sensitivity as they moved north from their origin sites to the Zion, Illinois, receptor site. Comparison of our results using the Duncan et al. (2010) thresholds suggests the entire Lake Michigan domain is NOx sensitive (except for ~ 3 grid boxes within the CMA that are in the transition zone). This is very different from the Task 4 results, which show the pollution plumes exhibit the full range of ozone production sensitivities at various points along their trajectories. While this difference could be due to a number of reasons (such as the fact that the Task 4 findings are based on 5 individual ozone exceedance events while our Chicago exceedance composite is made up of 33 ozone exceedance events), perhaps the most likely reason is the use of the Duncan et al (2010) definition in interpreting the satellite HCHO/NO₂ ratios. Comparison of the Task 4 results with our results using the Jin et al. (2020) HCHO/NO2 ratios, there is much better agreement. Both find a general south-north gradient in ozone production regimes that transitions toward less VOC sensitivity/more NOx sensitivity starting from the south in the CMA and going north along the western Wisconsin shoreline. This comparison to the Task 4 results suggest that using the Jin et al. (2020) thresholds may provide more insight when interpreting satellite HCHO/NO2 ratios than the Duncan et al. (2010) thresholds.

3.3 Ground-Based Ratios & Comparisons to Satellite-Based Ratios

For brevity, we focus our analysis on EPA PAMS Site 3103 in Cook County, Illinois, in this section. *Figure 9* shows time series plots of ground data collected at EPA PAMS Site 3103 in Cook County, Illinois, during the 2018 ozone season. As seen in the second plot, the daily and monthly mean HCHO/NO₂ ratio values are all below one. This stands in contrast to the monthly mean satellite HCHO/NO₂ ratio values seen in the bottom two plots, which are greater than one. Note that the bottom two plots contain the same data points but have different ozone production sensitivity thresholds displayed. The monthly mean ground ratio values ranged from a minimum of 0.068 in October to a maximum of 0.397 in July. In comparison, the monthly mean satellite ratio values ranged from a minimum of 1.419 in September to a maximum of 3.038 in June. There appears to be little to weak correlation (R = 0.497) between the ground and satellite ratio values have differing implications for ozone production when considering the Duncan et al. (2010) thresholds.

According to the monthly mean ground ratio values, ozone production at this site is VOC sensitive throughout the ozone season while the satellite ratios suggest that ozone production is NO_x sensitive from June to August but in the transition zone in September and October. However, using the Jin et al. (2020) thresholds, interpretations of the ground-based and satellite-based ratios are congruent with one another. Both the ground and satellite data suggest this site is VOC sensitive throughout the ozone season (HCHO/NO₂ < 3.2). Similar results were found for the 2019 data at this site as well as for all the other sites of analysis. Full results for Task 3.3 can be found in the Supplement 3 entitled "S3 LADCO Project – Ground Data Analyses.pdf".



• NO ₂	• нсно	Daily Ground Ratio	• Monthly Mean Ground Ratio	• Monthly Mean Satellite Ratio
VOC S	Gensitive	NO _x Sensitive	VOC Sensitive	NO _x Sensitive
Ratio	o < 1.0	Ratio > 2.0	Ratio < 3.2	Ratio > 4.1
(Duncan o	et al., 2010)	(Duncan et al., 2010)	(Jin et al., 2020)	(Jin et al., 2020)

Figure 9. Time series plots of HCHO and NO₂ (top), daily and monthly mean ground HCHO/NO₂ ratios (second), and monthly mean ground and satellite HCHO/NO₂ ratios (bottom two) for EPA PAMS Site 3103 in Cook County, Illinois

To investigate the impact of daily averaging on the large differences between the calculated monthly mean ground and satellite HCHO/NO2 ratios, we use data collected during the Lake Michigan Ozone Study (LMOS) 2017 field campaign at the Spaceport Sheboygan EPA ground site in Wisconsin. Because the data at this site were collected at a high temporal resolution of one minute, we were able to assess the impact of daily averaging on the PAMs HCHO/NO₂ ratios as seen in *Figure 10*. As the averaging interval increases, the calculated HCHO/NO₂ ratio decreases. Daily averaging of HCHO and NO_2 data may be especially misleading because both species have diurnal variations in their atmospheric abundances. Other studies have shown HCHO levels to peak around noon local time, gradually decrease in the afternoon, and drop off at night (Franco et al., 2016; Li, Wang, Zhou, & Zhou, 2014). Interestingly, the average HCHO diurnal cycle at Spaceport Sheboygan during LMOS 2017 (Figure 11a) has a different pattern than that found in the previously cited studies. The average NO2 diurnal cycle at Spaceport Sheboygan during LMOS 2017 (Figure 11b) follows a similar pattern as that for the Chicago Metropolitan Area found by Wang et al. (2020). Taking the average of all the data in Figure 11 yields a daily HCHO/NO₂ ratio of 0.69, but the HCHO/NO₂ ratio of the 1:00 pm datapoints (more closely resembling what TROPOMI would instantaneously observe during the Sentinel-5P satellite overpass time) is 1.24. This illustrates how the daily averaging of EPA PAMS data can lead to lower HCHO/NO₂ values than that measured by TROPOMI.



VOC Sensitive < 1.0	NO _x Sensitive > 2.0	—1 minute—	—5 minute—	—Hourly—	—Daily—
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Figure 10. Time series plot of HCHO/NO₂ ratio values calculated in differing averaging intervals at the Spaceport Sheboygan EPA ground site



Figure 11. Average diurnal cycles of (A) HCHO and (B) NO₂ at the Spaceport Sheboygan EPA ground site during LMOS 2017

Additionally, because the data were collected for 27 days between May 26 and June 21, 2017, we took the mean of all the calculated HCHO/NO₂ ratios for each time-averaging interval to get 'monthly' values. As seen in Table 4, the calculated monthly mean ratio value decreases as the original averaging block interval increases. The '1-minute' monthly mean ratio of 1.124 is about 44% larger than the 'daily' monthly mean ratio of 0.783. Depending on which number we look at, we arrive at different implications for ozone production at this site using the Duncan et al. (2010) thresholds as the '1-minute' monthly ratio suggests a transition between VOC and NO_x sensitivity while the 'daily' monthly ratio suggests VOC sensitivity. This reveals a limitation of the EPA PAMS data discussed earlier because the HCHO data for all the sites of analysis were either 8-hour or 24-hour samples and the NO₂ data were 1-hour samples. As a result of the lower temporal resolution of the HCHO measurements, monthly mean HCHO/NO₂ ratios calculated from EPA PAMS data are dampened to lower values than what would be calculated from instantaneous

higher temporal resolution measurements of HCHO and NO₂. This dampening of the ratio values could lead to incorrect conclusions on ozone production in the region.

Using the Jin et al. (2020) thresholds to investigate the effects of daily averaging ground monitor data does not yield the same insight. Both the '1-minute' and 'daily' monthly mean ratios (1.124 vs 0.783) would still be classified as VOC sensitive. This brings up an important point of discussion regarding the two threshold studies. The Jin et al. (2020) thresholds were calculated by connecting in situ ground data to OMI data specifically for the application of using HCHO/NO₂ satellite data (OMI) to deduce ozone-NOx-VOC sensitivity. Therefore, the Jin et al. (2020) thresholds should only be used for satellite ratios and not be used to interpret ground ratios. Duncan et al. (2010) had the same intention of developing thresholds in order to use satellite data to determine ozone production sensitivity. However, unlike Jin et al. (2020), Duncan et al. (2010) calculated thresholds from CMAQ-modeling alone and then applied the model-based thresholds to satellite data. Errors in representing upper tropospheric HCHO and NO2 variability within CMAQ could introduce systematic biases in the relationship between surface and column HCHO/NO2 ratios. Thus, the Duncan et al. (2010) thresholds may be more appropriate to apply to boundary layer (and thus surface) HCHO/NO₂ ratios rather than satellite-derived column ratios.

Original Time-Averaging Interval	'Monthly' Mean HCHO/NO ₂
1-minute	1.124 ± 0.841
5-minute	1.089 ± 0.800
Hourly	1.026 ± 0.748
Daily	0.783 ± 0.520

 Table 4. Conversion of time-averaged data in Figure 10 to 'monthly' values

To assess the impact of the limited temporal sampling of the TROPOMI L2 data we also plotted a time series to compare the daily HCHO/NO₂ ratio values to the 1:00 pm hourly ratio values at the Spaceport Sheboygan EPA ground site. The Spaceport Sheboygan EPA 1:00 pm hourly ratio values more accurately represent the HCHO/NO₂ values calculated from TROPOMI observations as the Sentinel-5P satellite overpasses the Midwest United States at this time. Meanwhile, the Spaceport Sheboygan daily ratio values most resemble the ratio values calculated from EPA PAMS sites data because of the temporal resolution of HCHO measurements. As seen in *Figure 12*, the hourly 1:00 pm data points are greater than the daily data points. We averaged all the data points in the time series to get a 'monthly' value based on daily verses 1:00 pm composites. Table 5 shows that the monthly mean HCHO/NO₂ ratio of the hourly 1:00 pm data points is about 1.93 times larger than the monthly mean ratio of the daily data points (1.51 versus 0.78). If we adjust the EPA PAMS ratio values seen in *Figure 9* by this factor of 1.93, the multiplied ground-based

ratio values would be closer to the TROPOMI-based ratio values, reducing the differences by 13% on average. However, doing so does not completely close the numerical gap between the ground and satellite HCHO/NO₂ ratio values.



Figure 12. Time series plot of hourly 1:00 pm local and daily HCHO/NO2 ratio values at the Spaceport
Sheboygan EPA ground site

Table 5. Conversion of time-a	veraged data in Figure	212 to 'monthly' values
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Original Time-Averaging Interval	'Monthly' Mean HCHO/NO ₂
Hourly 1:00 pm local time data point	1.509088 ± 0.712567
Daily	0.782527 ± 0.520328

4. Summary & Conclusions

4.1 Summary of Task 3 Results

This study explored the use of satellite based estimates of the ratio of formaldehyde to nitrogen dioxide (HCHO/NO₂) as an indicator of ozone-NOx-VOC sensitivity in the Lake Michigan region. The satellite based HCHO/NO₂ values were interpreted using two different sets of thresholds for ozone production sensitivity, one from Duncan et al. (2010) and one from Jin et al. (2020). In general, we recommend the use of the Jin et al. (2020) thresholds for interpreting the satellite ratios and the Duncan et al. (2010) thresholds for interpreting the EPA PAMS surface ratios presented in this work.

The results demonstrate that binning satellite data onto a 12km grid allows one to see the spatial distribution of atmospheric NO₂ and HCHO on a monthly basis. Because TROPOMI retrievals of HCHO are noisier than NO₂, the data needed to be composited into monthly averages in order reduce the influence of noise in the HCHO retrievals. Results during the 2018 and 2019 ozone seasons show that the minimum HCHO/NO₂ ratios occur over NYC (1.64) and Chicago (1.92), which places both of these urban centers in VOC sensitive regimes based on Jin et al. (2020)

thresholds. Monthly composite results show that in the Lake Michigan region, the Chicago Metropolitan Area (CMA) is VOC sensitive, its surroundings and north along the Wisconsin shoreline up to Milwaukee are in the transition zone, and the rest of the region falls within the NOx sensitive ozone production regime based on the Jin et al. (2020).

During the ozone season and during Chicago ozone exceedance events, the Chicago CMA remains VOC sensitive, but the spatial extent of the transition zone that surrounds Chicago and extends north up to Milwaukee decreases during ozone exceedance events using the Jin et al. (2020) thresholds. Statistical tests show us that these higher ratios are due to higher HCHO levels rather than changes in NO₂. This is likely attributed to increased temperatures during the ozone exceedance events, which leads to increased biogenic VOC emissions and thus increased ozone production (Sillman & Samson, 1995).

Comparisons between ground-based EPA PAMS and satellite-based TROPOMI HCHO/NO₂ ratio values reveal large numerical differences, with the satellite ratios always being greater than the ground ratios. Part of the discrepancy is due to the lower temporal resolution of HCHO measurements at EPA PAMS sites, which have a sampling period of 8 or 24 hours. Despite having hourly NO₂ data, these data needed to be daily averaged in order to calculate HCHO/NO₂ ratios. We used LMOS 2017 data to show that because HCHO and NO₂ levels follow diurnal cycles, instantaneous HCHO/NO₂ ratio values calculated at 1:00 pm local time (indicative of TROPOMI ratios) can be 1.93 times greater than daily averaged HCHO/NO₂ ratio values (indicative of EPA PAMS ratios). This dampening of surface ratios (due to the averaging and sampling interval constraints of EPA PAMS measurements) can lead to incorrect determinations of ozone production sensitivity, especially when using the Duncan et al. (2010) thresholds to interpret the data. Another likely reason for the discrepancy is the fact that the ground data are indicative of surface ratios while satellites measure vertical column densities. Further research looking at the impacts of the vertical profiles of HCHO and NO₂ on comparisons between the satellite-based and ground-based HCHO/NO₂ ratios is needed to investigate this hypothesis.

Based on the results of our study, it is our conclusion that satellite-based TROPOMI HCHO/NO₂ ratios and ground-based EPA PAMS HCHO/NO₂ ratios require different thresholds for NO_x verses VOC sensitivities. Using the Jin et al. (2020) thresholds to interpret satellite ratios and using the Duncan et al. (2010) thresholds to interpret surface ratios leads to consistent interpretations of ozone-NOx-VOC sensitivity in the Lake Michigan region. However, due to sampling interval limitations at many EPA PAMS sites, only daily averaged HCHO/NO₂ ratios can be calculated, which are often different than instantaneously calculated ratios because of the diurnal cycles of HCHO and NO₂. The differences in value between daily averaged and instantaneously calculated HCHO/NO₂ ratios can lead to incorrect interpretations of ozone-NOx-VOC sensitivity. This highlights the need for more consistent and higher temporal resolution VOC measurements at EPA PAMS sites across the United States.

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6. Appendices

Appendix A: TROPOMI Data Acquisition

TROPOMI Version 1 tropospheric HCHO (DLR, 2019a, 2019b) and tropospheric NO_2 (KNMI, 2018, 2019) column L2 retrievals were downloaded for May to October, 2018 and 2019 from the NASA Goddard Earth Sciences Data and Information Services Center (GES DISC). The spatial resolution of the TROPOMI L2 retrievals was increased from 7 km x 3.5 km to 5.5 km x 3.5 km on August 6, 2019. The L2 files are provided in netcdf format. Table A1 summarizes the resolution, product name, specifications, and date availability of the TROPOMI data used in this study.

Data	Product Name	Specifications	Date Availability
HCHO Lower Res	Sentinel-5P TROPOMI Tropospheric Formaldehyde HCHO 1-Orbit L2 7km x 3.5km (S5P_L2HCHO 1)	Sentinel-5P TROPOMI Version - 1 Spatial Res - 7 km x 3.5 km Process Level - 2	2018-05-14 to 2019-08-06
HCHO Higher Res	Sentinel-5P TROPOMI Tropospheric Formaldehyde HCHO 1-Orbit L2 5.5km x 3.5km (S5P_L2_HCHOHiR 1)	Sentinel-5P TROPOMI Version - 1 Spatial Res - 5.5 km x 3.5 km Process Level - 2	2019-08-06 to present
NO2 Lower Res	Sentinel-5P TROPOMI Tropospheric NO2 1-Orbit L2 7km x 3.5km (S5P_L2NO2 1)	Sentinel-5P TROPOMI Version - 1 Spatial Res - 7 km x 3.5 km Process Level - 2	2018-04-30 to 2019-08-06
NO2 Higher Res	Sentinel-5P TROPOMI Tropospheric NO2 1-Orbit L2 5.5km x 3.5km (S5P_L2NO2HiR 1)	Sentinel-5P TROPOMI Version 1 Spatial Res - 5.5 km x 3.5 km Process Level - 2	2019-08-06 to present

Table A1. TROPOMI data information

Appendix B: Exceedance days for LADCO Non-Attainment Areas

Ozone exceedance days for LADCO non-attainment areas were provided by Donna Kenski (LADCO). Table B1 provides a list of exceedance days in 2018 and 2019 and the number of sites within the non-attainment area with exceedances. Exceedance days require least 1 monitor within the non-attainment area to have MDA8 > 70 ppbv ozone. Only exceedance days with concurrent TROPOMI HCHO and NO₂ data are included.

Chicago		Cincinna	ti	Cleveland	i	Columbu	IS	Detroit		Louisvill	e	Sheboyg	an	St. Lou	is	Western Mic	higan
33 days	#	19 days	#	18 days	#	3 days	#	21 days	#	14 days	#	12 days	#	24 days	#	14 days	#
20180524	12	20180525	6	20180517	2	20180525	1	20180524	1	20180607	2	20180524	2	20180523	1	20180525	3
20180525	13	20180527	1	20180525	5	20180713	1	20180525	6	20180608	3	20180525	1	20180524	10	20180527	3
20180526	12	20180607	2	20180528	4	20190715	1	20180527	1	20180615	3	20180526	1	20180528	13	20180528	1
20180527	15	20180608	2	20180529	2			20180528	6	20180616	1	20180527	1	20180601	4	20180529	3
20180528	12	20180615	7	20180616	2			20180529	4	20180617	1	20180629	2	20180605	5	20180531	2
20180529	1	20180616	4	20180617	2			20180607	2	20180628	1	20180630	1	20180606	12	20180615	1
20180607	1	20180617	1	20180629	4			20180608	2	20180713	5	20180708	1	20180608	6	20180617	2
20180615	9	20180628	1	20180630	1			20180617	2	20180714	4	20180712	1	20180615	2	20180709	3
20180616	3	20180629	1	20180709	2			20180629	5	20180810	1	20180713	1	20180711	2	20180713	3
20180628	1	20180713	4	20180710	2			20180703	1	20180914	1	20180804	2	20180712	7	20180802	1
20180629	2	20180714	8	20180713	1			20180708	1	20190628	1	20190709	1	20180713	8	20190702	2
20180703	5	20190626	1	20180714	4			20180709	2	20190710	1	20190725	1	20180801	2	20190705	1
20180708	3	20190710	3	20180715	7			20180713	6	20190713	2			20180803	6	20190710	3
20180709	9	20190713	3	20190628	2			20180715	2	20190805	2			20180911	1	20190728	1
20180711	3	20190714	3	20190629	1			20180804	5					20190629	4		
20180713	6	20190805	3	20190710	2			20190627	4					20190713	11		
20180715	7	20190819	2	20190713	2			20190701	2					20190717	1		
20180803	1	20190910	1	20190804	1			20190710	4					20190719	1		
20180804	2	20190920	1					20190715	2					20190720	1		
20180813	1							20190727	1					20190721	1		
20180814	1							20190812	1					20190805	8		
20190605	2													20190819	2		
20190626	1													20190918	2		
20190628	1													20190919	6		
20190629	4																

Table B1. Identified ozone exceedance days for LADCO non-attainment areas

20190703	1								
20190705	1								
20190708	1								
20190709	11								
20190713	1								
20190725	2								
20190802	1								
20190803	2								

Investigating the O₃-NO_x-VOC Sensitivity of Plumes Advecting over Lake Michigan during LMOS 2017

Final Memo for Task 4: O₃-NO_x-VOC Sensitivity Analysis

September 30, 2020

Michael P. Vermeuel and Timothy H. Bertram

Background:

For this task we explore the use of indicator ratios for describing the sensitivity of ozone (O₃) production to volatile organic compounds (VOC) and NO_x (NO_x = NO + NO₂) emissions in select coastal regions along Lake Michigan. First, we review the photochemistry of tropospheric O₃ formation that serves as the chemical basis for the utility of select indicator ratios: the Sillman indicator ratio of hydrogen peroxide to nitric acid (H₂O₂/HNO₃), the fraction of radicals (*Q*) lost to NO_x reactions (*L_N*) presented as L_N/Q , and the ratio of formaldehyde to nitrogen dioxide (HCHO/NO₂).

The Sillman Indicator: H₂O₂/HNO₃

The photochemical production of O_3 is regulated by concentrations of NO_x and hydrogen oxide radicals (HO_x = OH + HO₂) and relies on the catalytic cycling of NO_x between NO and NO₂ and of HO_x between the hydroxyl radical (OH), the hydroperoxyl radical (HO₂) and organic peroxy radicals (RO₂) (Jacob, 1999). Chain termination of the O₃ cycle depends on the relative abundances of HO_x and NO_x. At the limit of high HO_x and low NO_x, the major chain terminating reactions are:

$$HO_2 + HO_2 + M \to H_2O_2 + O_2 + M$$
 (R1)

$$HO_2 + RO_2 \to ROOH + O_2 \tag{R2}$$

where H_2O_2 and ROOH are hydrogen peroxide and hydroperoxides, respectively, and M is any non-reactive species that stabilizes the product through collisions. In this chemical regime, the steady state concentration of HO_x is insensitive to changing NO_x and O_3 production increases linearly with NO_x . Because of this, when R1 and R2 dominate chain termination, O_3 production is said to be NO_x -sensitive.

In contrast, when peroxy radical $(HO_2 + RO_2)$ removal is dominated by reactions with NO_x, chain termination primarily results in formation of nitric acid (HNO₃) and alkyl nitrates (RONO₂),

$$OH + NO_2 + M \to HNO_3 + M \tag{R3}$$

$$RO_2 + NO + M \rightarrow RONO_2 + M$$
 (R4)

If the HO_x -NO_x cycle is primarily terminated through R3+R4, O₃ production is VOC-sensitive. In this regime, the rate of O₃ formation increases with increasing VOC and is suppressed by increasing NO_x (Milford et al., 1989).

Due to their status as chain termination products for these two limiting regimes, H₂O₂ and HNO₃ can be employed as indicator species. Specifically, the quantities H₂O₂/HNO₃ (concentration ratio) and $P_{\text{H2O2}}/P_{\text{HNO3}}$ (production ratio) can serve as time-integrated or instantaneous indicators of the sensitivity of O₃ production to VOC or NO_x emissions (Sillman, 1995; Tonnesen & Dennis, 2000). Sillman et al. (1990) first showed the utility of such indicators by modeling the sources and sinks of odd hydrogen along with the corresponding O₃ production. A linkage between P_{H2O2} , P_{HNO3} , and NO_x vs VOC limited O₃ production, as defined by the coupled HO_x-NO_x reactions, can be established by assuming that HO_x is in steady-state and HO_x production equals HO_x loss ($P_{\text{HOx}} = L_{\text{HOx}}$) (Lurmann et al., 1986; Sillman et al., 1990).

To arrive at a robust indicator value utilizing these termination species, photochemical simulations with varying rates of anthropogenic and biogenic emissions as well as changing meteorological conditions have been previously performed for several test scenarios. Models of O₃-NO_x-VOC sensitivity utilizing the indicator ratios of H₂O₂/HNO₃ and P_{H2O2}/P_{HNO3} have shown that the transition from VOC-sensitive to NO_x-sensitive O₃ production occurs in the regime where the concentration ratio value is between 0.06-0.35 at peak O₃ concentrations (Sillman & West, 2009; Sillman, 2002; Tonnesen & Dennis, 2000). However, there is still a need to explore how these values map to traditional definitions of NO_x- and VOC- sensitive O₃ production in more complex environments. The ratio of ($P_{ROOH}+P_{H2O2}$)/ P_{HNO3} could be used as a measure of the sensitivity of P_{O3} to changing NO_x and VOC emissions in spatially and temporally evolving air masses as it is the ratio of two instantaneous production rates (Schroeder et al., 2017). In areas of moderate to high biogenic VOC (BVOC) emissions, the production of ROOH contributes as a terminal sink to HO₂, allowing this ratio to be approximated as:

$$\frac{P(H_2O_2) + P(ROOH)}{P(HNO_3)} = \frac{k_1[HO_2]^2 + k_2[HO_2][RO_2]}{k_3[OH][NO_2]}$$
(E1)

Radical Loss to NO_x : L_N/Q

The indicator L_N/Q is analogous to $(P_{ROOH}+P_{H2O2})/P_{HNO3}$ and focuses on radical production rates (Q) and the fraction of radicals removed by reactions with NO_x (L_N) . When L_N is estimated as R3 and Q is calculated from the combined rates of radical initiation stemming from O₃ and carbonyl photolysis (Kleinman, 2005), the ratio L_N/Q can be calculated as:

$$\frac{L_N}{Q} = \frac{k_3[OH][NO_2]}{A[O_3] + B[RH]}$$
(E2)

where *A* and *B* are effective rate coefficients that account for sources of HO_x from photolysis of O₃ and carbonyls respectively (Lurmann et al., 1986; Sillman et al., 1990). It has been proposed that when L_N/Q is less than 0.5, P_{O3} is NO_x-sensitive and when L_N/Q is greater than 0.5, P_{O3} is VOC-sensitive (Kleinman et al., 2001). The transition region or cutoff value for VOC-NO_x sensitivity depends on the contribution of organic nitrates to L_N , thus allowing the cutoff value of 0.5 to vary by as much as 0.2 depending on the environment (Kleinman, 2005). Calculations of

 L_N/Q are ideal for an urban plume as they convey information on the sensitivity regime of an air parcel that generally transitions from high NO_x at the source to low NO_x some distance away. Relating P_{O3} and the sensitivity regime using this indicator requires both constrained quantities of measured chemical species in HO_x-NO_x cycling as well as confident predictions of meteorology and chemical unknowns. For that reason, L_N/Q is underutilized and not included in many fieldbased analyses (Kleinman et al., 2000; Mazzuca et al., 2016).

A Satellite-based indicator: HCHO/NO₂

While field measurements of chemical species provide a chemically detailed and high-temporal resolution suite of constraints for accurate box modeling of O₃ sensitivity, a required dense network of field measurements over a heterogenous urban/rural surface such as the Lake Michigan coastline is costly and impractical. Satellite measurements allow for publiclyaccessible measurements of the VOC formaldehyde (HCHO) and of the NO_x species NO₂, making remote sensing products an easier way to investigate surface emissions of VOC and NO_x and ultimately the O₃ sensitivity regime in a particular region. Tonnesen & Dennis (2000) used in situ observations of HCHO and NO₂ to diagnose multiple local photochemical regimes using the ratio HCHO/NO₂. In their work, they determine that an environment is VOC-sensitive if HCHO/NO₂ is <0.8 and NO_x-sensitive if HCHO/NO₂ is >1.8, with any values in between 0.8 and 1.8 considered a "transition" environment. Duncan et al. (2010), using a combination of box modeling and chemical transport modeling of southern California, showed that this transition region falls between 1 and 2 and applied this classification to satellite measurements. Schroeder et al. (2017), through box modeling of data from Houston, TX, found that the ratio of $(P_{ROOH}+P_{H2O2})/P_{HNO3}$ is proportional to HCHO/NO₂ and can be used to locate ridgelines in isopleths of P_{O3} , giving an average value of $(P_{ROOH}+P_{H2O2})/P_{HNO3} = 0.37$ as the transition value for VOC to NO_x sensitivity which corresponds to a wide range of values for HCHO/NO₂. Since the production of HCHO is dependent on the available NO_x in an environment, a chemical feedback occurs that creates a nonlinearity in HCHO/NO₂ and requires individual calculations of O₃ sensitivities for unique environments (Wolfe et al., 2016). Souri et al. (2020) further supported this idea by calculating isopleths of P_{O3} bound by HCHO and NO₂, locating the ridgeline in P_{O3} , then finding the corresponding value for $(P_{ROOH}+P_{H2O2})/P_{HNO3}$ at that ridgeline (i.e. the transition value). This allows for calculation of a site-specific $(P_{ROOH}+P_{H2O2})/P_{HNO3}$ indicator as well as a dynamic transition range of [HCHO] = $m[NO_2] + b$ where m is the slope of the line and b is the y-intercept (further explained in the discussion).

Research Statement

In the work that follows we present a trajectory box modeling analysis using a combination of modeled, assimilated, and observed constraints in the Lake Michigan region in June 2017. We identified five days when chemical surface emissions and lake-breeze meteorology lead to high O₃ events ([O₃]>70 ppbv) along the coastline. Each day (June 02, 04, 11, 12, and 15) delivered plumes that were sourced in unique regions (urban, rural, mix), advected over Lake Michigan, and arrived at a Lake Michigan Ozone Study 2017 (LMOS 2017) ground measurement supersite

in Zion, IL. We assess the chemistry along the plume trajectory and the evolution of O_3 sensitivity regimes using $(P_{ROOH}+P_{H2O2})/P_{HNO3}$, L_N/Q , and HCHO/NO₂. This allows for the prescription of either NO_x- or VOC-sensitivity and of transition values at different sites along the heterogenous Lake Michigan coastline and offers further insight into the evolution of indicator transition values from source to endpoint. This study shows that prescribing VOC- or NO_x-sensitivity at a particular site depends more on the displacement in the starting value of an indicator from the site's calculated transition value rather than the magnitude of the value itself.

Methodology:

The trajectory model used in this study is described extensively in Vermeuel et al. (2019), with a more brief description and updates explained here. A trajectory box model was built in MATLAB that incorporates the Framework for 0-D Atmospheric Modeling (F0AM) (Glenn M. Wolfe et al., 2016) to calculate mixing ratios and reaction rates of important compounds involved in O₃ production along air parcel trajectories. The model operates over a domain spanning 41 to 45°N latitude and 89 to 85°W longitude and is driven by analyzed winds with a model spatial resolution of 4 km and a temporal resolution of 1 hour. The volume of each photochemical box is set by the domain spatial resolution and the boundary layer depth outputs of the National Oceanic and Atmospheric Administration (NOAA) High-Resolution Rapid Refresh (HRRR) model (Smith et al., 2008). The chemistry used in each box is from the Master Chemical Mechanism (MCM v3.3.1) that can simulate up to 17,224 reactions amongst 5,832 chemical species with integrated photolysis rates (Saunders et al., 2003). In this applied model 2,756 species and 8,401 reactions were used to optimize performance while still covering the predominant species in urban chemistry.

To simulate the chemistry in an urban plume evolving along a trajectory towards Zion, IL, regional anthropogenic and biogenic emissions were incorporated along with observed meteorological parameters. Anthropogenic stationary and non-stationary emissions of hourly speciated NO_x and VOC were gathered from the EPA National Emissions Inventory (NEI) 2017 at 4 km resolution. VOC emissions are speciated into 21 compounds of different functional groups and bond order. Monitors of O₃ and NO_x from the EPA Air Quality System (AQS) were used to initialize box mixing ratios of O₃ and NO_x. Biogenic emissions of isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆) were calculated using a combination of model and ground-based constraints for equations estimating the net emission rate of BVOC in the Model of Emissions of Gases and Aerosols from Nature (MEGAN) found in Guenther, et al. (2006). Select ground-based measurements of VOC from the EPA Photochemical Assessment Monitoring Stations (PAMS) network were used to initialize VOC mixing ratios in box models, when applicable.

The physical factors required for estimating biogenic emissions as well as calculating chemical and photolytic rates were gathered for each grid in the model as follows. The MEGAN emissions used in this study use updated maps of land cover (Community Land Model v4) relative to the maps used in Vermeuel et al. (2019). Temperature, surface wind, relative humidity fields, and downward radiation were generated by the North American Land Data Assimilation System

(NLDAS) (Mitchell, 2004) that utilizes the Noah-Multiparameterization Land Surface Model (NOAH-MP LSM) (Niu et al., 2011). Daily leaf area index (LAI) was taken from the Moderate Resolution Imaging Spectrometer aboard the research satellite Terra.

Air parcel trajectories were determined from the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model running HRRR (Stein et al., 2015) at a resolution of 3 km. An air parcel path is generated by retrieving a backward trajectory from the NOAA Real-time Environmental Display sYstem (READY) (Rolph et al., 2017) with a start point at the surface (20 m) in Zion, IL and an end point determined based on availability of O₃ and NO_x monitors as well as distance from the shoreline. The chemical model is evaluated starting at the backward trajectory endpoint and moving forward toward the Zion site. The trajectories for June 02, 04, 11, 12, and 15 are displayed in Figure 1 along with locations of AQS NO_x and O₃ monitors and PAMS VOC monitors. Each circle is an hour along the trajectory, with trajectories ranging from 6 to 11 hours in length. The trajectories are overlaid on either calculated day-averaged isoprene emissions or late afternoon (16 CDT) NEI 2017 NO emissions.

Chemistry is solved along the trajectory by treating the first grid on the trajectory as a stationary point. Model constraints 24 hours prior are used to allow this first box to spin up for two days to reach steady state concentrations of chemical intermediates. O_3 and NO_x are constrained by monitor values at the source region and VOC emissions serve as constraints for VOC. Once the first box is at steady state after the spin-up period, the outputs are used as initial conditions for the first step in the trajectory. Box models are solved hourly along each point on the trajectory and the integrated mixing ratios of the entire trajectory are compared to the Zion field measurements. A horizontal dilution term is employed to represent advection and to avoid the unphysical build-up of pollutants in each box:

$$\frac{d[X]}{dt} = -k_{dil}([X] - [X]_b)$$
(E3)

where k_{dil} is a first order dilution rate constant, [X] is the chemical concentration within the box, and [X]_b is the background concentration. In the case of the evolving urban plume, k_{dil} is the rate of entrainment of background air and τ_{mix} (k_{dil}^{-1}) would be the e-folding time required to mix with the background. Over land τ_{mix} is 5 hours and over water τ_{mix} is 12 hours during the June 11 case and 24 hours over the other case days. The rate of k_{dil} is determined by the relative windspeeds over the lake (i.e. higher horizontal windspeed produces more advection and a higher k_{dil}). As discussed in Vermeuel et al. (2019) the k_{dil} term over the lake is an important sensitivity factor in modeling lake breeze chemistry.







Figure 1: HRRR parcel trajectories overlaid over either MEGAN isoprene emissions or NEI NO emissions for June 02 (a+b), June 04 (c+d), June 11 (e+f), June 12 (g+h), and June 15 (i+j). The time of arrival of each parcel at the supersite in Zion, IL is indicated on each map. All emissions maps are displayed as daily averages.

Discussion:

Figure 1 shows that each of the parcels analyzed are sourced from regions of varying relative magnitudes of biogenic (i.e. isoprene) and anthropogenic (i.e. NO) emissions. For example, trajectory on June 11 originates in regions of higher BVOC emissions than NO emissions, the trajectory on June 15 originate in regions with low BVOC emissions and high NO emissions, and the trajectory on June 02, 04, and 12 originate in a region that is a mix.

Updated June 02 Analysis

A detailed analysis of the June 02 trajectory is discussed in Vermeuel et al. (2019), but changes in model outputs due to updated constraints in NEI and MEGAN are addressed here. Figure 2

shows the modeled and measured O₃, NO_x, and VOC reactivity along the June 02 trajectory. VOC reactivity (VOCR) is calculated as

$$VOCR = \sum k_{OH+X_i}[X_i] \tag{E4}$$

where k_{OH+Xi} is the rate constant for a reaction of OH with a specific VOC and $[X_i]$ is the ambient concentration of the VOC. At Zion, $[O_3]$ was measured at the surface using a UV photometric monitor and $[NO_x]$ was measured using a chemiluminescence monitor. Discrete [VOC] was measured with canister samples collected three times a day and continuous VOC measurements were made using a proton-transfer time of flight mass spectrometer (PTR-MS). Implementation of updated emissions provides for a 6%, 28%, and 40% decrease in modeled $[O_3]$, $[NO_x]$, and VOCR, respectively.

Although implementation of new constraints drives the model further away from measurements at Zion, IL, there are still uncertainties in chemiluminescence measurements of NO_x and sourcing of VOCR at Zion. Uncertainty in NO_x arises from the reported NO_2 not being a true NO_2 measurement and likely containing a larger fraction of NO_y that is converted to NO on the molybdenum oxide (MoO) catalytic converter (Fehsenfeld et al., 1987; Williams et al., 1998; Xu et al., 2013) prior to detection *via* chemiluminescence. Uncertainty in VOCR arises from the sourcing of VOCs that were measured at Zion. Since the supersite was located in a state park consisting of marshes, dunes, grassland prairies, and forests of black oak amongst mixed vegetation, there is the potential for a considerable contributions to measured VOC from hyperlocal VOC production. Without high-temporal measurements of VOC in the source regions, it is difficult to attribute all of the measured VOC to the source region. However, since Zion has low onsite NO_x emissions sources, it can be assumed that all NO_x is from the source region during a lake breeze.



Figure 2: Time series of a.) O_3 , b.) NO_x , and c.) VOCR along the June 02 trajectory. The model solutions using NEI 2016v1 and an updated MEGAN model (solid black line) and the model implementation in Vermeuel et al. (2019) (dashed green line) are presented alongside measurements at Zion (solid blue circle).

Initial Results and Model Validation of Backward Trajectory Analysis for June 04, 11, 12, and 15 Model solutions along the trajectories for June 04, 11, 12, and 15 have not been presented in previous publications and will be presented here. Figure 3 shows model O₃, NO_x, H₂O₂, and HNO₃ along the parcel trajectory that begins at 8:00 CDT on June 4 in northern Chicago and ends at 18:00 CDT in Zion, IL. Lines are the model solutions and stars are measurements from ground monitors. For June 04, 11, 12, and 15 ground monitors of O₃ and NO_x were present, allowing for validation at both the source and endpoint regions. For June 04, model O₃ and NO_x are in excellent agreement with ground monitor measurements (Fig. 2a and 2b), H₂O₂ is in poor agreement (about an order



Figure 3: Model solutions of a.) O_3 (red line), b.) NO_x (blue line), c.) H_2O_2 (red line), and d.) HNO_3 (green line) along the parcel trajectories with measurements at the source and Zion, IL (stars) on June 04, 2017. Measurements of H_2O_2 at the endpoint are divided by 10. The sensitivities of ΔO_3 ($O_{3,Zion}-O_{3,source}$) to changes in anthropogenic VOC (red circles), biogenic VOC (green circles), all VOC (blue circles), and NO_x only (yellow triangles) is presented in e.).

of magnitude lower than measurements; Fig. 2c), and HNO_3 is in reasonable agreement with measurements (Fig. 2d). We present this as reasonable agreement due to challenges in both measuring and modeling HNO_3 .

As discussed in Vermeuel et al. (2019), the model and measurement disagreement in HNO_3 could be due to: 1) The model having a fixed, but potentially inaccurate, HNO3 gas-particle partitioning rate constant (k_{uptake}) of 6 x10⁻⁵ s⁻¹ although experimental observations of HNO₃ uptake coefficients allow k_{uptake} to aerosol particles to be between 10^{-5} - 10^{-1} , quickly reaching equilibrium with the aerosol phase. 2) HNO₃ deposition velocities, (v_d ; cm s⁻¹) follow a diel cycle that can exceed 3 cm s⁻¹ in forested regions (Nguyen et al., 2015) and can exceed 7 cm s⁻¹ in urban areas (Nunnermacker et al., 1998; Pierson et al., 1988). The model does not differentiate between forested and urban regions over land and uses a fixed parameterization (Johnson, 2010) for calculating v_d in lowmoderate winds (<2 ms⁻¹) over the lake ($v_d = 0.1$ cm s⁻¹). Inaccuracies in land cover type, spatial variability of wind speed over the lake, and experimentally determined land v_d can contribute uncertainty in dry deposition rates. 3) Our trajectory model has only one vertical level in the mixed layer, forcing all HNO₃ to be evaluated in this single layer. The measurements were made at 5 m, significantly lower than the average height of the mixed layer. A strong vertical gradient in HNO₃, driven by surface deposition, would lead to a model-measurement disagreement. It has been shown that HNO₃ mixing ratios increase by about a factor of 1.3 with height due to a decrease in dry deposition further away from the surface, introducing a small source of uncertainty. (Huebert & Robert, 1985; Lee et al., 1993; Pryor et al., 2002). In addition to modeling uncertainties, observational uncertainty can occur from HNO₃ partitioning into the aqueous phase of an inlet or remaining on inlet walls, making transmission difficult to characterize for a long study that may experience variable inlet conditions (Bowermaster & Shaw, 1981; Neuman et al., 1999).

The model and measurement disagreement in H_2O_2 could potentially be due to the presence of an isobaric compound at the detected mass for H_2O_2 or hyperlocal production of H_2O_2 due to the presence of vegetation onsite. This makes it difficult to compare H_2O_2 produced at the source to H_2O_2 at the endpoint particularly when the endpoint is in the afternoon when emissions of BVOC and P_{H2O2} is high and during periods later in the month when [BVOC] and [H_2O_2] is high at Zion. These periods of high BVOC allows for sustained H_2O_2 due to its relatively short lifetime that is primarily controlled by dry deposition and photolysis.

Figure 3e presents model sensitivities of ΔO_3 to emissions of VOC and NO_x. E is the factor which the emissions are scaled by for determining the sensitivity (e.g. E_{VOC}=2 implies double the emissions of VOC in the source region and throughout the trajectory). To determine the extent to which biogenic and anthropogenic VOCs control VOC emissions and ΔO_3 , cases are tested by scaling either anthropogenic VOC only (red circles), biogenic VOC only (green circles), or both (blue circles). For each sensitivity test, the emission denoted is being changed and all other emissions are held constant. For example, the red trace shows the case where only anthropogenic VOC emissions are being changed and biogenic VOC and NO_x emissions remain at the base case values. In the case of June 04, biogenic VOC has a stronger control on ΔO_3 although anthropogenic and biogenic VOC are close in influence. For all cases, increasing VOC while holding NO_x constant increases the amount of O₃ produced along the trajectory (ΔO_3). E_{NOx} is scaled in the source region by multiplying the constrained time series of ground monitor [NO_x] during the source region spin up by the factor 0-3. During the trajectory, there is no ground monitor constraint so NEI emissions of NO_x are scaled by E_{NOx} . According to Figure 3e O₃ production has passed its peak from NO_x emissions, showing that increasing NO_x in this space inhibits the production of O₃ and decreasing NO_x by up to half of the base emissions would slightly increase the production of O₃.

Figure 4 shows the same analysis for the June 11 case study. For June 11, the "base case" required doubling the NO_x emissions and halving the MEGAN BVOC emissions to arrive at reasonable values that matched ground monitors. This is most likely due to overestimation of parameterized BVOC emissions that drew down O₃ and NO_x. Although this treatment allows for agreement of O₃ and NO_x it may not correctly reflect VOC at the source region (discussed further in the memo). As shown in Figure 4, model O₃ and NO_x are in good agreement with measurements, H₂O₂ is in poor agreement with measurements, and HNO₃ is in reasonable (within 1.5 ppbv) agreement with measurements. This case study shows the lowest observed ΔO_3 (11 ppbv) as compared to the other studies ($\Delta O_{3,max} = 44$ ppbv), potentially due to low source mixing ratios of precursors as well as fast mixing over the lake on that day (horizontal windspeed > 6 m s⁻¹ over trajectory region). Figure 4e shows that in this implementation, ΔO_3 is equally controlled by biogenic and anthropogenic VOC and precedes the E_{NOx} value for peak ΔO_3 . Increasing NO_x slightly will continue increasing O₃ production, however the region will become NO_x-inhibiting at an E_{NOx} > 1.5.



Figure 4: Model solutions of a.) O_3 (red line), b.) NO_x (blue line), c.) H_2O_2 (red line), and d.) HNO₃ (green line) along the parcel trajectories with measurements at the source and Zion, IL (stars) on June 11, 2017. Measurements of H_2O_2 at the endpoint are divided by 10. The sensitivities of ΔO_3 ($O_{3,Zion}-O_{3,source}$) to changes in anthropogenic VOC (red circles), biogenic VOC (green circles), all VOC (blue circles), and NO_x only (yellow triangles) is presented in e.).

Figure 5 presents model trajectory solutions for the June 12 case. As shown in Figure 5, model O_3 and NO_x are in excellent agreement with measurements, and H_2O_2 and HNO_3 are in poor agreement. Figure 5e shows ΔO_3 is controlled more by anthropogenic VOC and is at E_{NOx} for peak ΔO_3 . Increasing NO_x beyond the base case will decrease O_3 production along this trajectory.



Figure 5: Model solutions of a.) O_3 (red line), b.) NO_x (blue line), c.) H_2O_2 (red line), and d.) HNO₃ (green line) along the parcel trajectories with measurements at the source and Zion, IL (stars) on June 12, 2017. Measurements of H_2O_2 at the endpoint are divided by 10. The sensitivities of ΔO_3 ($O_{3,Zion}-O_{3,source}$) to changes in anthropogenic VOC (red circles), biogenic VOC (green circles), all VOC (blue circles), and NO_x only (yellow triangles) is presented in e.).

Figure 6 presents model trajectory solutions for the June 15 case. As shown in Figure 6, model O_3 and NO_x are in excellent agreement with measurements, and H_2O_2 is in poor agreement and HNO_3 in reasonable agreement with measurements. Figure 6e shows ΔO_3 is sensitivity to VOC is completely controlled by anthropogenic VOC with no response in ΔO_3 when changing biogenic VOC emissions, which is in agreement with the site being located in a primarily urban region. In

addition, the base case of NO_x emissions in this region allow for peak ΔO_3 . Increasing NO_x beyond the base case will decrease O₃ production along this trajectory. These findings fit the characteristics of the source location (the urban center of Chicago; Figure 1j) where NO_x emissions are high and significant BVOC sources are limited. It should also be noted that O₃ was already high (65 ppbv) in the source region prior to advection over Lake Michigan, suggesting high O₃ production in Chicago prior to transport to Zion via lake breeze meteorology.



Figure 6: Model solutions of a.) O_3 (red line), b.) NO_x (blue line), c.) H_2O_2 (red line), and d.) HNO₃ (green line) along the parcel trajectories with measurements at the source and Zion, IL (stars) on June 15, 2017. Measurements of H_2O_2 at the endpoint are divided by 10. The sensitivities of ΔO_3 ($O_{3,Zion}-O_{3,source}$) to changes in anthropogenic VOC (red circles), biogenic VOC (green circles), all VOC (blue circles), and NO_x only (yellow triangles) is presented in e.).



The ΔO_3 for this trajectory was 19 ppbv over 6 hours (or an average P_{O3} of 3.2 ppbv hr⁻¹)

Figure 7: Time series of modeled (line) and measured (circle) VOCR (red) and NO_x (blue) for a.) June 02, b.) June 04, c.) June 11, d.) June 12, and e.) June 15.

Figure 7 provides a summary of the VOCR and NO_x time series for June 02, 04, 11, 12, and 15. For all the days, VOCR is underestimated in the model as compared to measurements at Zion. As discussed earlier, this is most likely due to hyperlocal production of BVOC at the Zion site driving an onsite VOCR uninfluenced by parcel source regions upwind of the site. Uncertainties in the source region VOCR may be dependent on time of day, boundary layer height, and position of O_3 and NO_x monitors in relation to the starting point of the HRRR trajectory. Modeled source VOCR

is highest for June 02 and 04 (VOCR > 5 s⁻¹). This is partially a function of time of day and boundary layer height, which is lowest at night, allowing for VOC to accumulate in the absence of photochemistry. A lower boundary layer height increases surface mixing ratios as it decreases the height of the box pollutants are emitted into. The nearer to sunrise a parcel initiates its trajectory, the more likely the parcel samples higher VOC and NO_x that has accumulated during overnight. The effect of timing and boundary layer height is also evident in time series of NO_x. June 02 and 04 experience the highest model NO_x at 22 and 20 ppby, respectively and their parcel trajectories begin at the earliest hour, 8:00 CDT. To allow for best agreement in O₃ and NO_x it was required that June 04 simulations utilized the EPA Meteorology-Chemistry Interface Processor (MCIP) boundary layer heights, instead of HRRR outputs, which were as low as 200 m at night. The position of NO_x and O_3 monitors in relation to the parcel starting point introduced some uncertainty in the model due to the requirement of using distanced O₃ and NO_x monitor concentrations. Although there is no NO_x ground monitor site at the source region for the June 02 case study, the monitor at the source region on June 04 validates this high NO_x due to nighttime accumulation and limited photolysis at this hour. The variability in source VOCR (1-5.9 s⁻¹) and high VOCR at Zion, IL requires VOC measurements in the source region to validate these claims.

Figure 8 presents the contributions of speciated VOC to a.) model VOCR at the source region and b.) measured VOCR in Zion, IL. Figure 8a shows that a large fraction (>50%) of the modeled VOCR in the source regions of June 02 and 04 are from isoprene and HCHO, the latter of which can have mixed anthropogenic and biogenic sources. As discussed earlier, these high modeled VOCR are partially a function of low morning boundary layer heights and time of day, in addition to VOC speciation at the site. Model VOC during June 11 and 12 contain both biogenic and anthropogenic species and June 15 is comprised of all anthropogenic species. Figure 8b shows that VOCR on all days at the Zion site are dominated by isoprene, further supporting the idea that the presence of reactive BVOC during the period when parcels arrive at Zion are primarily due to local emissions from the park site. The unknowns presented in Figures 7 and 8 highlight the merit in having more VOC measurements in source regions along coastal Lake Michigan to better speciate VOC and their contribution to O_3 production.



Figure 8: Contributions of select chemical species to VOCR at the a.) source region and b.) Zion during the case studies. The "other" category includes toluene, benzene, ethane, ethene, butene, and propane. In panel b. it is assumed that [HCHO] = 2 ppbv.

Sensitivity Analysis Based on the ΔO_3 Isopleth Ridgeline

Figure 9 presents ΔO_3 isopleths for the different test cases under varying E_{NOx} and E_{VOC} . Included are the base cases where E_{NOx} and $E_{VOC} = 1$ (grey circles) and the ridgelines for each day. June 02 and 04 show the highest potential ΔO_3 for the given range of sensitivities and are both strongly VOC-sensitive and NO_x-inhibiting at the source region. June 11 and 12 show weak NO_x-inhibition (sensitivity in the y direction from the base case) and are considered closer to NO_x-sensitive chemistry. June 15 is NO_x-inhibiting from the base case and would be considered VOC-sensitive.



Figure 9: Isopleths of ΔO_3 ($\Delta O_3 = O_{3,Zion} - O_{3,Source}$) with fitted ridgelines (black lines) and the base case where $E_{NOx} = E_{VOC} = 1$ (grey circle) shown for a.) June 02, b.) June 04, c.) June 11, d.) June 12, and e.) June 15.

Figure 10 summarizes the results in Figure 9 by placing all the ridgelines on one figure and presenting their positions relative to the base case of E_{NOx} and $E_{VOC} = 1$ (grey circle). Cases where

the base case is above the ridgeline are considered more VOC-sensitive (06/02, 06/04, 06/15) and cases where the base case is below the ridgeline are considered more NO_x-sensitive (06/11, 06/12).



Figure 10: A first approximation of each ridgeline shows that at the source region, the cases of 06/02, 06/04, and 06/15 exhibit more VOC-sensitive chemistry and the cases of 06/11 and 06/12 exhibit more NO_x-sensitive chemistry.

The intercepts and slopes of each line can provide further information on the sensitivity regimes of each case. A higher intercept implies a more NO_x -sensitive regime since it determines the y position relative to the base case. In the studied cases, ridgelines with a higher slope tend to be more VOC-sensitive, although this needs to be considered in combination with the y-intercept of the fit. Table 1 presents a summarized analysis of these linear fits for each day along with the O₃-NO_x-VOC sensitivity as determined by the position of the base case relative to the ridgeline.

Case	Slope	Intercept	Ridgeline Sensitivity
06/02	0.30	0.34	More VOC-sensitive
06/04	0.22	0.5	More VOC-sensitive
06/11	0.23	1.1	More NO _x -sensitive
06/12	0.24	0.85	More NO _x -sensitive
06/15	0.31	0.48	More VOC-sensitive

Table 1: Linear Fits of △O₃ Ridgelines

Indicator-based Assessment of Sensitivity

Since it has been previously shown that sensitivity regimes for O₃ production within a parcel evolve with time due to a changing chemical environment (Vermeuel et al., 2019) and that the ranges and magnitudes of transition regimes are also dependent on the environment and on chemical feedbacks (Schroeder et al., 2017; Souri et al., 2020), an indicator-based approach is required to accurately evaluate the sensitivity regimes for each trajectory. This is achieved by generating an isopleth of P_{O3} , rather than ΔO_3 , with x and y bounds of a VOC and NO_x species (HCHO and NO_2) rather than an emission factor of each. This allows analysis of a more instantaneous sensitivity for each hour in a trajectory rather than as the integral of the entire trajectory controlled by source emissions as presented in Figure 9. Figure 11 shows isopleths of net $P_{O3}(P_{O3}-L_{O3})$ as a function of HCHO and NO₂. Values presented in Figure 11 are taken from any point in a trajectory on the specified day. To generate a wide combination of values presented in each subpanel, solutions are taken from model sensitivity runs where E_{VOC} and E_{NOx} are varied from 0 to 3. For example, Figure 11a is the result of time-aligned solutions of HCHO, NO₂, and P_{O3} for every model run simulated for June 02 where E_{VOC} and E_{NOx} are varied from 0 to 3. The ridgeline of each isopleth gives the transition region for each case study trajectory, which corresponds to a linear fit relating HCHO and NO2 (black line). Since HCHO has a complex, nonlinear dependence on NO_x (Wolfe et al., 2016), this provides a more appropriate definition of the HCHO/NO₂ transition value, rather than a fixed value. An isopleth of $\frac{P(H_2O_2) + P(ROOH)}{P(HNO_3)}$ as a function of HCHO and NO₂ produces linear contours which can be overlaid on each subpanel. Noted on each subpanel in Figure 11 are the corresponding values of $\frac{P(H_2O_2)+P(ROOH)}{P(HN_3)}$ at that ridgeline, linking HCHO/NO₂ to a more robust indicator.



Figure 11: P_{O3} isopleths as a function of HCHO and NO₂ for a.) June 02, b.) June 04, c.) June 11, d.) June 12, and e.) June 15. Denoted on each subpanel are the linear fit of each ridgeline as a function of [HCHO] and [NO₂] (black line) as well as the corresponding value of $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$ at that ridgeline.

The new case-dependent transition values can be applied to each case study trajectory to determine the source region's O_3 -NO_x-VOC sensitivity and the point in time along the trajectory when a change in sensitivity occurs, if applicable. An example of this application is presented in Figure

12 for the June 02 trajectory. Figure 12a presents the modeled time series of HCHO/NO₂ (blue line) and the instantaneous VOC to NO_x transition value (red line) for each hour along the trajectory as determined by the fit of the isopleth ridgeline in Figure 11a. At the start of the trajectory the O₃-NO_x-VOC sensitivity is very VOC-sensitive (HCHO/NO₂ is less than transition value) and as time progresses, the model approaches the transition value but fails to reach it.



Figure 12: Modeled (blue) and transition (red) values for the indicators a.) HCHO/NO₂, b.) $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$, c.) L_N/Q , and d.) net P_{O3} on June 02, 2017.

Figure 12b presents the modeled and transition values for $\frac{P(H_2O_2)+P(ROOH)}{P(HN_3)}$ as determined by the overlapping isopleth ridgeline of $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$ =0.18. The modeled time series behaves similarly to the HCHO/NO₂ indicator time series, where the sensitivity regime begins as very VOC-sensitive then progresses towards the transition region. Figure 12c presents the modeled and transition values for L_N/Q, where the transition value for L_N/Q is assumed to be 0.5. It is important to note that for this analysis, time series are evaluated only between 9:00 to 18:00 CDT to avoid uninterpretable solutions of L_N/Q (in the absence of photolysis Q<<1 and L_N/Q>>1). For the June 02 trajectory, all three indicators agree that the source region sensitivity is very VOC-sensitive

with O₃ production chemistry evolving towards more NO_x-sensitive along the trajectory but never arriving at NO_x-sensitive chemistry. Figure 12d shows the net P_{O3} (net $P_{O3} = P_{O3} - L_{O3}$) for June 02. Note this is a chemical term and does not account for physical loss or horizontal dilution. Net P_{O3} peaks around 11:00, plateaus, and declines around 14:00 CDT, indicative of photochemistry dependent on available solar radiation.

Figure 13 presents the same analysis as in Figure 12, but considers the June 04 case study. Noted on Figure 13a is the HCHO/NO₂ value at which the parcel crosses from VOC- to NO_x-sensitive chemistry (HCHO/NO₂ = 1.23). Noted in Figure 13b is the value of $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$ as determined from the isopleth ridgeline in Figure 11b and in Figure 13c is the value of L_N/Q where the parcel crosses from VOC- to NO_x-sensitive chemistry ($L_N/Q = 0.56$). This analysis provides a new definition for HCHO/NO₂ and L_N/Q for this specific trajectory. The fact that not every panel crosses the transition region at exactly the same hour is due to the agreement in the fit of the ridgeline across P_{O3} and $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$. The potential error in this agreement creates a disagreement in the transition-crossing hour of up to 0.5 hours.

Figures 14, 15, and 16 repeat this analysis for the June 11, 12, and 15 case study days, respectively. A summary of each case study day and ways to interpret this analysis is presented in the summary section that follows each figure.



Figure 13: Modeled (blue) and transition (red) values for the indicators a.) HCHO/NO₂, b.) $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$, c.) L_N/Q, and d.) net P_{O3} on June 04, 2017.



Figure 14: Modeled (blue) and transition (red) values for the indicators a.) HCHO/NO₂, b.) $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$, c.) L_N/Q, and d.) net P_{O3} on June 11, 2017.



Figure 15: Modeled (blue) and transition (red) values for the indicators a.) HCHO/NO₂, b.) $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$, c.) L_N/Q, and d.) net P_{O3} on June 12, 2017.



Figure 16: Modeled (blue) and transition (red) values for the indicators a.) HCHO/NO₂, b.) $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$, c.) L_N/Q, and d.) net P_{O3} on June 15, 2017.

Summary

Comparison of Transition Values for each Case Study

Table 2 presents a summary of starting and ending values for the indicators as well as for VOCR and NO_x along the case trajectory. Also presented is the sensitivity as determined from the ΔO_3 ridgelines in Figure 9 and Table 1. For all trajectories in this analysis $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$ exhibits a range of 7e-4 to 2.3, HCHO/NO₂ from 0.18 to 2.4, and L_N/Q from 0.15 to 0.91. Upon comparison of indicators at their respective starting and ending point, it is difficult to assess whether or not each source or endpoint region is in a more VOC- or NO_x-sensitive regime if the transition values of $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$ =0.37, HCHO/NO₂=1-2, and L_N/Q=0.5 are used. For example, June 12 and June 15 have the same starting $\frac{P(H_2O_2)+P(ROOH)}{P(HN_3)}$ yet June 12 was determined to be more NO_x-sensitive in the source region and June 15 more VOC-sensitive in the source region although both values are the same (0.004) and far from the transition value of 0.37. Additionally, June 02, 04, 12, and 15 all have HCHO/NO₂ values that fall within a range of 0.2 and L_N/Q values greater than 0.8 (where L_N/Q is VOC-sensitive), making it difficult to differentiate the source sensitivity regime of each.

Case	P(H2O2) + P(ROOH)/ P(HNO3)	HCHO/ NO ₂	L _N /Q	VOCR	NOx	∆O3 Ridgeline Sensitivity
06/02	7e-4	0.38	0.88	5.3	22.0	More VOC-
	0.05	0.69	0.83	1.3	4.2	sensitive
06/04	7e-4	0.18	0.91	5.8	18.8	More VOC-
	0.38	1.5	0.51	0.78	1.3	sensitive
06/11	0.073	0.67	0.61	0.96	3.4	More NO _x -
	1.4	1.9	0.21	0.44	0.9	sensitive
06/12	0.004	0.23	0.87	1.3	7.7	More NO _x -
	2.3	2.4	0.15	0.9	1.0	sensitive
06/15	0.004	0.30	0.89	1.0	9.5	More VOC-
	0.64	1.6	0.37	1.7	1.5	sensitive

Table 2: Summary of Trajectory Start (top) and End (bottom) Values

A more appropriate treatment of O₃-NO_x-VOC sensitivity would be to consider how far in magnitude the starting indicator values are from their respective transition values and the time required to reach that transition value. Table 3 presents the transition values from Figures 12-16 along with the starting hour of each trajectory and the hours required to reach each transition region as determined by the hour in the trajectory at which the Sillman indicator reaches the new calculated transition value. At a first approximation, it can be estimated that if all parcels begin as VOC-sensitive, the degree of VOC-sensitivity can be approximated by the time it takes to reach the transition value. For example, on June 11 it takes only 1.5 hours to reach the transition point to evolve from VOC- to NOx-sensitive which suggests that the source region initiates the trajectory as more NO_x-sensitive compared to other parcels that take 4+ hours. The June 02 case takes ≥ 10 hours (all indicators never reach the transition point) which suggests that the source region initiates the trajectory as very VOC sensitive. This type of analysis would work best if all trajectories started at the same time of day. This is because the analysis becomes convoluted when one takes into account the start time with $P(H_2O_2)$, P(ROOH), and Q potentially biased low closer to the morning hour in periods of lower photolytic rates and high accumulated NO₂ that push loss of OH to higher values of P_{HNO3} and L_N. For example, the June 12 and 15 cases take roughly the same amount of time to reach their transition values, but the June 12 trajectory starts at 9:00 CDT and the June 15 trajectory starts at 12:00 CDT. Differentiating between the sensitivity regimes of those days solely

based on hours to transition may be incorrect. For this reason, we suggest prescribing sensitivities based on the displacement in magnitude of the starting indicator value from the indicator transition value, as the transition values have been specifically defined for a range of scenarios within the conditions of each trajectory (e.g. source region, time of day, length of trajectory, time over the lake versus time over land).

Case	P(H ₂ O ₂) + P(ROOH)/ P(HNO ₃)	HCHO/ NO ₂	L _N /Q	Hour Start	Hours to transition
06/02	0.18	-	-	9	>10
06/04	0.25	1.23	0.56	9	7
06/11	0.17	0.96	0.56	10	1.5
06/12	0.13	0.83	0.60	9	3.5
06/15	0.14	0.96	0.63	12	3

Table 3: Transition Values

Table 4 summarizes each case day in terms of differences between the transition values and starting values of select indicators and of differences between endpoint values and starting values of VOCR, NO_x, and O₃. Table 4 allows for the estimation of sensitivity thresholds for the source regions along the Lake Michigan coastline as a whole. The cases of June 12 and June 15 have been shown to be similar based on the proximity of their base case to the ΔO_3 isopleth ridgelines in Figure 9, their near-same initial indicator values in Table 2, and their comparable hours to transition in Table 3. Inspection of Table 4 shows that their distance from transition values are similar as well as their decrease in VOCR and NO_x along the trajectory. Considering all of those assessments we can assign the June 12 and June 15 cases as scenarios with O₃-VOC-NO_x sensitivity within the transition regime and prescribe VOC-sensitive as having a $\Delta \frac{P(H_2O_2) + P(ROOH)}{P(HNO_3)} > 0.14$ and a Δ HCHO/NO₂>0.60. This assigns the June 02 and June 04 cases as VOC-sensitive in the source region and the 06/11 case as NO_x-sensitive. These cases also produce the largest changes in VOCR, NO_x, and O₃ along the trajectory while spending the most time over Lake Michigan (>10 hours). The combination of a high input of precursors at the start of the parcel trajectory and the length of time the parcel spends over the slowly diluting lake leads to high production of O₃ during the parcel trajectory. The other case days assume that the production of O_3 was already high at the source region and the transport of the parcel over the lake had a smaller contribution to the high witnessed O₃ at Zion, IL.

Table 4: Summary of Distance of Indicator Transition Values from End Values and Distance of Precursor End Values from Start Values

	Transition Val Value	ue – Starting	End Value –			
Case	Δ[P(H ₂ O ₂) + P(ROOH)/ P(HNO ₃)]	Δ[HCHO/ NO2]	ΔVOCR	ΔΝΟ _x	ΔΟ ₃	∆Indicator Sensitivity
06/02	0.18	>1.06	-4.0	-17.8	44.6	VOC- sensitive
06/04	0.25	1.05	-5.0	-17.5	44.7	VOC- Sensitive
06/11	0.10	0.29	-0.52	-2.5	12.2	NO _x - sensitive
06/12	0.13	0.60	-0.40	-6.7	24.1	Transition
06/15	0.14	0.60	-0.70	-8.0	18.6	Transition

Conclusions:

This memo has highlighted the use of indicators in determining the O_3 -NO_x-VOC sensitivity at pollutant source regions along the Lake Michigan coastline as well as at throughout the trajectory of a parcel advecting over the lake. We present a simple box model that can be used in a trajectory analysis when coupled to HRRR backward trajectory retrievals. This box model was used for five case study days during LMOS 2017: 06/02, 06/04, 06/11, 06/12, and 06/15. The model was validated by comparing model solutions to ground monitor measurements of O_3 and NO_x at the beginning and end of a parcel trajectory. The model was also validated by showing reasonable agreement between the model and endpoint measurements of HNO₃ at a supersite in Zion, IL. The model did not agree with endpoint measurements of H_2O_2 as well as calculations of VOC reactivity, pointing to either an inadequate understanding in the sourcing of VOCs at the Zion site or poorly constrained VOCs at the start of the trajectory.

A primary O₃-NO_x-VOC sensitivity analysis was performed by generating isopleths of ΔO_3 (where $\Delta O_3 = [O_{3,endpoint}-O_{3,source}]$) under varying emissions of anthropogenic NO_x and VOC. A more instantaneous sensitivity analysis was performed by generating isopleths of P_{O3} under varying HCHO and NO₂. This allowed for the comparison of three indicators, $\frac{P(H_2O_2)+P(ROOH)}{P(HNO_3)}$, HCHO/NO₂, and L_N/Q in determining the sensitivity regimes of each case study as well as defined new, case-specific transition region values for each indicator. All case studies aside from 06/02 transitioned from more VOC-sensitive at the source region to NO_x-sensitive at Zion, IL with peak net P_{O3} regularly between 11 and 15 CDT, indicative of photochemistry that occurs during the day. In order to more definitively determine the source sensitivity for each case, we propose taking the difference of each starting indicator value from the case-specific transition region values. This

analysis allows for the prescription in the source region of two VOC-sensitive days (06/02 and 06/04), one NO_x-sensitive day (06/11), and two days in the transition region (06/12 and 06/15).

In order to completely validate the model used in this analysis, it is required that VOCs are quantified in the source region to validate whether the disagreement in VOCR is due to source or endpoint unknowns. In addition, it is recommended that more CO monitors are utilized and implemented to determine the parcel dilution factor (τ_{mix}) that can strongly control O₃ production at periods in the trajectory when the parcel is advecting over Lake Michigan.

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