This report documents preliminary results from the 2017 Lake Michigan Ozone Study (LMOS 2017). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and should not be construed as an official U.S. Government position, policy, or decision.
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Executive Summary

The 2017 Lake Michigan Ozone Study (LMOS 2017) was a collaborative, multi-agency field study of ozone chemistry and meteorology along the Wisconsin-Illinois Lake Michigan shoreline using a combination of aircraft, ground-based and ship-based measurements. The collection of measurement assets deployed is conceptually illustrated at right. The Lake Michigan region is seasonally impacted by episodes of high ozone concentrations. These episodes are influenced by complex meteorology and significant transport of pollutants. The overall goal of the study was to better understand ozone formation and transport around Lake Michigan to assist researchers and air quality managers who study, predict, and manage ozone concentrations in the region. Two particularly challenging issues that LMOS 2017 targeted were understanding the factors that determine the size, location, timing, and intensity of ozone-rich air masses, and understanding the details of the chemistry and meteorology that create the sharp gradients in ozone concentrations often observed between the lakeshore and nearby inland locations.

Field activities were conducted from May 22-June 22, 2017 and included two aircraft (one for remote sensing and one for in situ profiling), two ground based super sites (Sheboygan, WI and Zion, IL) outfitted with remote sensing and in situ measurements, three mobile sampling platforms measuring lakeshore-inland ozone concentration gradients or conditions on the lake surface, and additional ground-based remote sensing instruments collocated at several other shoreline monitoring locations. Air quality and meteorological forecasts provided flight planning guidance and in-field evaluation of model prediction skill during the study.

Section 1 of this report provides an overview of the LMOS 2017 study including a summary of objectives and an overview of the meteorology and lakeshore ozone concentrations during the field observation period. Section 2 provides a summary of the measurements conducted during the LMOS 2017 study, along with preliminary results. Section 3 provides a summary of preliminary comparisons of
photochemical model results with measurements highlighting the difficulties in predicting coastal ozone concentrations along the western shore of Lake Michigan. Section 4 provides initial recommendations for meteorological and photochemical model configurations to improve the prediction of ozone along the western shore of Lake Michigan.

**Key Findings:**

**Observed and Modeled Ozone.** Significant ozone events occurred during LMOS 2017, with exceedances of the 70 ppbv 8-hr ozone threshold on June 2, June 11-12, and June 14-16. The LMOS 2017 aircraft observed polluted layers with rapid ozone formation occurring in a shallow layer near the Lake Michigan surface. Modeling and observations show that this polluted layer over the lake is an important factor in ozone exceedance events, but that meteorological and photochemical model skill in forecasting these events needs improvement.

Specifically, airborne in situ profiling during selected events showed high ozone and nitrogen dioxide (NO$_2$) concentrations within the marine boundary layer over Lake Michigan, whose depth as determined by in situ temperature profiling ranged from ~50 to ~370 m above lake level depending on date, time of day, and location. Comparisons between model predictions and in situ airborne and surface ozone measurements showed that both National Weather Service (NWS) Community Multi-scale Air Quality (CMAQ) and high resolution (4km) Weather Research and Forecasting (WRF) with Chemistry (WRF-Chem) forecasts underestimated peak ozone concentrations and overestimated NO$_2$ concentrations during these events. Both NWS and WRF-Chem models showed persistent underestimates in terrestrial boundary layer (0-3km) ozone concentrations throughout the LMOS 2017 study. Preliminary emissions sensitivity studies using the WRF-Chem model suggest that both reductions in anthropogenic nitrogen oxide (NO$_x$) emissions and increases in anthropogenic volatile organic compounds (VOCs) improve model results for peak ozone during LMOS 2017; however, evaluation at the process level and replication in additional models is necessary. WRF physics sensitivity studies suggest that the ability to capture the inland penetration of the lake breeze circulation is dependent on accurate estimates of the Lake Michigan water temperatures and the physics options chosen to represent boundary layer mixing and land surface exchange processes.

**Sheboygan Ground Super-site.** At Sheboygan a valuable dataset of continuous wind, temperature, water vapor, and vertically-resolved aerosol profile was recorded. Meteorological characteristics of lake breeze penetration were captured in detail, including during the June 2 ozone exceedance event. In situ chemical measurements at Sheboygan of ozone, NO$_x$, formaldehyde, and NO$_x$ plus its reaction products (NO$_y$) at 1 minute and finer time resolution captured peak events, as well as diel cycles in precursors and oxidants, and wind-shift related changes. Chemicals (formaldehyde and NO$_2$) that can serve to indicate the chemical regime for ozone formation (i.e., NO$_x$ limited and volatile organic compound (VOC) limited) were measured at Sheboygan. Substantial variability in the indicators was recorded, suggesting a complex system with some NO$_x$ limited periods, and some VOC limited periods. However, lake breeze influence within this record is evident, and the chemical indicators at Sheboygan, when combined with the supporting datasets are promising for ongoing investigation.
An experimental network of four lower cost ozone monitors (2B-POM monitors) was spaced out over a 6 km area of Sheboygan to measure differences in concentrations with respect to distance from the lake. Intermittent data capture from these devices limits the drawing of detailed conclusions regarding spatial gradients.

**Zion Ground Super-site.** At Zion, IL, a dataset of continuous wind, temperature, and water vapor vertical profile was recorded. These instruments captured thermal and wind characteristics of lake breeze penetration in excellent detail, including during the June 2 ozone exceedance event. This should provide a useful dataset for future research and model evaluation. At Zion, a comprehensive suite of chemical and physical aerosol characterization was captured. This will be used in ongoing source apportionment analyses and to characterize local influences on the Zion monitoring station. During LMOS 2017, low levels of fine particulate matter dominated by organic matter were recorded, with PM2.5 enhancements often coinciding with ozone enhancements. During the largest lake breeze ozone event, elemental carbon concentrations were enhanced on a relative basis, consistent with a plume including significant combustion influence. Future organic source apportionment should be able to distinguish relative contributions from different combustion source types.

Continuous or semi-continuous measurements of ozone, NO, nitric acid, hydrogen peroxide, and many volatile organic compounds (VOC) and oxygenated volatile organic compounds (OVOC) were conducted. Some prominent VOC and OVOC compounds measured included benzene, toluene, isoprene, monoterpenes, methyl vinyl ketone, and methacrolein. Methyl vinyl ketone and methacrolein are oxidation products of isoprene, and can be useful indicators of biogenic influence. Preliminary analysis of these indicates that the field observation period can be divided into two periods – an initial period of low biogenic influence and higher anthropogenic influence (higher anthropogenic VOCs, low isoprene). After a transition period of about June 4-June 8, conditions shift to a higher biogenic influence with lower concentrations of anthropogenic VOCs.

Chemicals (nitric acid and hydrogen peroxide) that can serve to indicate the chemical regime for ozone formation (i.e., NO limited and VOC limited) were measured at Zion. Background conditions with westerly winds were mainly NO limited as expected given regional sources of VOCs exceeding regional NO sources. Lake breeze ozone events exhibited higher VOC sensitivity than other periods, and analyses of these is ongoing. As was the case for Sheboygan, the chemical regime for ozone formation at Zion had a complex time history; however, within this complexity, the lake breeze influence is clearly evident and this is expected to be useful in ongoing investigations.

**Ground-based remote sensing.** USEPA deployed remote sensing instruments for mixed layer height, cloud layer height, column NO₂, and column ozone (Vaisala CL51 ceilometers, and UV/visible Pandora spectrometers). The ceilometers were installed at Grafton, Milwaukee, and Zion. The Pandora spectrometers were installed at Sheboygan, Grafton, Milwaukee, Zion, and Schiller Park (Chicago). Data on mixed layer height, ozone column amounts, and NO₂ column amounts are being included in ongoing analyses such as comparison to models, comparison to aircraft in situ profiles, and comparison to other remote sensing instruments such as GeoTASO and satellites.
Aircraft measurements. Airborne sampling captured critical air pollution and meteorological features during LMOS 2017. The Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) flew 21 research flights on board the NASA LarC UC-12 aircraft. A light aircraft (Scientific Aviation) flew 22 research flights, measuring NO$_2$, ozone, carbon dioxide, methane, and meteorological parameters. Preliminary analysis of these datasets indicates that they captured their research objectives well, including strong spatial gradients associated with point and area sources, spatial gradients associated with oxidative aging of plumes, chemical and thermal stratification over Lake Michigan, and weekday-weekend differences in NO$_x$ emissions. A preliminary comparison between Pandora, aircraft, and GeoTASO NO$_2$ profiles has been completed and indicates satisfactory agreement.

Other mobile platforms. Three additional mobile platforms operated during LMOS 2017 at the surface: (i) the Geospatial Monitoring of Air Pollution (GMAP) mobile vehicle sampled ozone in transects parallel and perpendicular to the shore, (ii) mobile meteorological and ozone sampling was performed, and (iii) an instrumented research ship operated out of Sheboygan with daily measurements of a number of relevant chemical and meteorological parameters. Finally, an aerosol and cloud research-grade remote sampling system, AirHARP was tested from the NASA LarC UC-12 aircraft. Analysis of these datasets and integration with the other model- and observation-based analyses is ongoing.
Acknowledgments

The LMOS 2017 Science Team acknowledges the NASA Airborne Science Program and the NASA GEOstationary Coastal and Air Pollution Events (GEO-CAPE) Mission Pre-formulation Science Working Group for supporting the airborne remote sensing instruments, NSF (award number 1712909) and NOAA GOES-R Program Office for supporting the measurements at the Zion ground site, EPA and NOAA GOES-R program office for supporting the measurements at the Sheboygan ground site, and the Electric Power Research Institute (EPRI) for supporting the Scientific Aviation airborne in situ measurements.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor should they be construed as an official National Oceanic and Atmospheric Administration or U.S. Government position, policy, or decision. The United States Environmental Protection Agency’s Office of Research and Development partially performed and funded the research described within this report. This report should be considered a draft report and has not undergone a full EPA review. As such the report is not yet approved for full external publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

List of Cooperating Organizations

Research institutions: National Oceanic and Atmospheric Administration (NOAA), National Aeronautics and Space Administration (NASA), U.S. Environmental Protection Agency (EPA), University of Wisconsin-Madison, University of Iowa, University of Minnesota, University of Northern Iowa, University of Wisconsin-Eau Claire, University of Maryland Baltimore County, Scientific Aviation.

Air quality management agencies: Lake Michigan Air Directors Consortium (LADCO), Wisconsin Department of Natural Resources (WDNR), Illinois Environmental Protection Agency (IEPA), and Indiana Department of Environmental Management.

Review

This report was released to internal stakeholders on July 19, 2018. Comments were collected by LADCO and referred to Brad Pierce and Charles Stanier. Comments were submitted by EPA Region V, by staff from the states of Michigan, Illinois, and Wisconsin, by the Electric Power Research Institute, and by staff from LADCO. Comments were addressed and the list of comments and their responses (16 pages) is available upon request from LADCO, or from the corresponding authors Brad Pierce and Charles Stanier.
Section 1. Mission and Study Period Overview

1.1. Background: Ozone in the Lake Michigan Region

Counties around Lake Michigan have a long history of recording ozone concentrations that exceed the level of the National Ambient Air Quality Standards (NAAQS). Since the promulgation of the first ozone NAAQS in 1979, lakeshore counties in Wisconsin, Illinois, Indiana and Michigan have been designated nonattainment with each subsequent standard. While ozone concentrations have decreased substantially due to implementation of an array of measures controlling emissions of ozone precursors (WDNR, 2017), two Lake Michigan areas are currently designated nonattainment for the 2008 ozone NAAQS: the Chicago nonattainment area and Sheboygan County, WI. Additionally, lakeshore areas in all four states were recently designated nonattainment for the 2015 ozone NAAQS.

The persistent high ozone episodes affecting the region have been shown to be influenced by high precursor emissions from large transportation, urban, and industrial sources in upwind parts of the airshed coupled with the complex meteorology associated with the land-water interface of the Lake Michigan shoreline.

Two types of meteorological patterns are associated with elevated lakeshore ozone concentrations in the region:

1) Synoptic scale meteorology transports high concentrations of ozone and ozone precursors northward from source regions to the south and southeast, and

2) Mesoscale meteorology (via land-lake breeze circulation patterns) carries precursors over the lake at night and in the early morning, where they react to form ozone after sunrise. Daytime winds then shift to bring the high ozone onshore.

High pressure systems have been shown to generate meteorological conditions favorable to elevated ozone as they move through the eastern U.S. from west to east during late May to early September (Dye et al., 1995; Hanna and Chang, 1995; Haney et al., 1989). These systems are typified by hazy, sunny skies with generally weak, clockwise-rotating winds and a relatively shallow boundary layer, which inhibits the vertical mixing and dilution of near-surface pollution concentrations. These meteorological conditions contribute to the buildup of ozone precursors and facilitate the chemical production of new ozone. The highest ozone concentrations in the Lake Michigan region result when polluted air from upwind, high emissions regions is transported northward along the western edge of a high pressure system, adding to locally produced ozone (Ragland and Samson, 1977). On high ozone days, the lowest lakeshore ozone concentrations are typically found in the areas with high emissions of nitrogen oxides (NOx), such as in central Chicago and northwestern Indiana. The highest concentrations are found downwind of the high NOx sources in rural and suburban coastal areas. During classic Lake Michigan ozone transport episodes ozone plumes are observed moving northward from the southern end of the lake over the course of the day, carried by southerly winds.
Synoptic meteorological conditions often work in combination with lake-induced mesoscale meteorological features to produce the highest ozone concentrations in this region (Dye et al., 1995). Other coastal regions in the U.S. share related marine/lake enhanced ozone. Modeling by U.S. EPA (2016) projected that 9 of the 12 counties in the eastern U.S. that will not attain the 2015 ozone NAAQS by 2025 are located on coastlines. The coastal high ozone phenomenon has been documented for Lake Michigan, the Gulf of Mexico/Houston, the Chesapeake Bay/Maryland, and Lake Erie/southwestern Ontario (Lyons and Cole, 1976, Dye et al. 1995, Foley et al. 2011, Goldberg et al. 2014, Loughner et al 2014, Cleary et al. 2015)

Historically, the highest ozone concentrations in the Lake Michigan region have been found along the lakefront (Figure 1.1.2). The sharp temperature gradients between the warm land and cold lake drives the thermally-driven circulation cell called the “lake breeze” as described above, which runs approximately perpendicular to the Lake Michigan shoreline (Figure 1.1.3). As this figure shows, the lake breeze is generally preceded by an early morning land breeze, driven by relatively warm temperatures over the lake and subsidence over land. The land breeze carries ozone precursors emitted from coastal urban and industrial areas out over the lake, where they can react in the presence of sunlight to form ozone. Heating of the land surface in the afternoon leads to a reversal of the flow pattern and the lake breeze then transports the elevated ozone from over the lake into coastal areas. These mesoscale lake breeze patterns can overlap with southerly synoptic winds that carry ozone-rich air to impact coastal sites northward along the lakefront.
Figure 1.1. Map of ozone design values and LMOS 2017 ground site locations. Ozone design values (fourth-highest monitored eight-hour average ozone concentration at that monitor in a three-year period, ppbv) for 2014-2016 for the Lake Michigan region along with the location of the primary ground sites hosting measurements for the Lake Michigan Ozone Study 2017 (LMOS 2017).

Figure 1.1.3. Conceptual model of land/lake breeze circulations responsible for enhanced ozone production along the shores of Lake Michigan (Foley et al., 2011).
1.2. Objectives of LMOS 2017

The Lake Michigan Ozone Study 2017 (LMOS 2017) was conducted to address persistent violations of the ozone NAAQS in the coastal communities along the western shore of Lake Michigan. LMOS 2017 leveraged joint aircraft, ground-based, ship-based and mobile lab measurements to significantly expand observations of ozone and its precursors around Lake Michigan during the early summer of 2017. The study was designed to collect field measurements to address the following questions related to enhancements in ozone concentrations observed in coastal regions along Lake Michigan:

1) What is the relative contribution of inter- and intra-state nitrogen oxides (NOx) and volatile organic compound (VOC) emissions and emissions sources on ozone production rates along Lake Michigan?

2) To what extent do lake breeze circulations affect ozone production?

3) How far inland does ozone rich air penetrate during ozone events?

4) What is the spatio-temporal distribution of ozone and its precursors over Lake Michigan?

5) How can remote sensing products (e.g., measurements of nitrogen dioxide, NO₂, and formaldehyde, HCHO) be used to constrain ozone predictions?

6) How well do regional models capture ozone production chemistry as assessed through evaluation of critical measurement indicators?

1.3. Overview of the LMOS 2017 Mission

LMOS 2017 was conducted from May 22 through June 22, 2017, and was designed to collect measurements to investigate high ozone episodes in coastal communities along the western shore of Lake Michigan. Aircraft, ship, mobile lab, and ground-based stations were used to build an extensive dataset for studying ozone, its precursors, and particulate matter. The LMOS 2017 measurement strategy was designed to collect onshore and offshore measurements during lake-breeze-driven ozone exceedance events and to characterize the magnitude and variability of urban emissions on hourly, daily, and weekly timescales. The LMOS 2017 measurements were designed for use in evaluating chemical transport model skill in simulating critical aspects of coastal and lake meteorology, oxidant concentrations, VOC and total reactive nitrogen (NOy) speciation, the spatial and vertical distribution of ozone precursors, and fine particulate matter (PM2.5) sources. Figure 1.4.1. Schematic showing the types of measurements involved in LMOS 2017, including two types of aircraft measurements, ship-based measurements, ground-based measurements and mobile platforms. Figure 1.4.1 and Table 1.3.1. LMOS Science Team PIs show the range of measurements made during LMOS 2017.
Figure 1.4.1. Schematic showing the types of measurements involved in LMOS 2017, including two types of aircraft measurements, ship-based measurements, ground-based measurements and mobile platforms.
### Table 1.3.1: LMOS Science Team PIs

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<tr>
<td>Brad Pierce</td>
<td>NOAA (now at University of Wisconsin SSEC)</td>
<td>Science Director, Flight Planning Team Lead, RAQMS Modeling</td>
</tr>
<tr>
<td>Stephanie Shaw</td>
<td>Electric Power Research Institute (EPRI)</td>
<td>Representative of EPRI to LMOS 2017</td>
</tr>
<tr>
<td>Charles Stanier</td>
<td>University of Iowa</td>
<td>Zion Site co-Principal Investigator, Zion Representative to Flight Planning Team</td>
</tr>
<tr>
<td>Betsy Stone</td>
<td>University of Iowa</td>
<td>Zion Site co-Principal Investigator</td>
</tr>
<tr>
<td>James Szykman</td>
<td>USEPA and NASA Langley</td>
<td>EPA Measurements Lead (Sheboygan, Ceilometers, Pandora)</td>
</tr>
<tr>
<td>Luke Valin</td>
<td>USEPA</td>
<td>EPA Measurements</td>
</tr>
<tr>
<td>David Williams</td>
<td>USEPA</td>
<td>Shipborne Measurements</td>
</tr>
<tr>
<td>Tim Wagner</td>
<td>University of Wisconsin SSEC</td>
<td>Sheboygan Meteorology Measurements (SPARC)</td>
</tr>
</tbody>
</table>
Table 1.3.2. Summary of measurements made during LMOS 2017.

<table>
<thead>
<tr>
<th>Location</th>
<th>Measurement*</th>
<th>Research Institution*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Sites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spaceport Sheboygan</td>
<td>Remote sensing of meteorology</td>
<td>UW-Madison</td>
</tr>
<tr>
<td></td>
<td>In situ measurements of pollutants</td>
<td>U.S. EPA ORD</td>
</tr>
<tr>
<td>Zion, IL</td>
<td>Remote sensing of meteorology</td>
<td>Univ. Northern Iowa</td>
</tr>
<tr>
<td></td>
<td>Detailed in situ chemical measurements</td>
<td>Univ. Iowa, UW-Madison,</td>
</tr>
<tr>
<td></td>
<td>Routine measurements of ozone</td>
<td>Univ. Minnesota</td>
</tr>
<tr>
<td>Various†</td>
<td>Remote sensing of pollutants and boundary layer height</td>
<td>U.S. EPA ORD</td>
</tr>
<tr>
<td>Sheboygan transect</td>
<td>In situ measurements of ozone at four locations</td>
<td>U.S. EPA ORD</td>
</tr>
<tr>
<td>Airborne Platforms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lakeshore region</td>
<td>Airborne remote sensing of NO₂ (GeoTASO)</td>
<td>NASA</td>
</tr>
<tr>
<td></td>
<td>Airborne remote sensing of clouds (AirHARP)</td>
<td>Univ. Maryland, Baltimore County</td>
</tr>
<tr>
<td></td>
<td>Airborne in situ profiling of pollutants and meteorology</td>
<td>Scientific Aviation</td>
</tr>
<tr>
<td>Shipboard Platform*</td>
<td>In situ measurements of pollutants and meteorology</td>
<td>U.S. EPA ORD</td>
</tr>
<tr>
<td></td>
<td>Remote sensing of pollutants and boundary layer height</td>
<td>U.S. EPA ORD</td>
</tr>
<tr>
<td>Mobile Platforms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northeast IL and Southeast WI</td>
<td>In situ measurements of pollutants (GMAP)</td>
<td>U.S. EPA Region 5</td>
</tr>
<tr>
<td>Grafton to Sheboygan</td>
<td>In situ measurements of ozone and meteorology</td>
<td>UW-Eau Claire</td>
</tr>
</tbody>
</table>

*NO₂ = nitrogen dioxide, GeoTASO = Geostationary Trace gas and Aerosol Sensor Optimization instrument, AirHARP = Airborne Hyper Angular Rainbow Polarimeter, GMAP = Geospatial Mapping of Pollutants, UW = University of Wisconsin, EPA = Environmental Protection Agency, ORD = Office of Research and Development.

† These measurements were made at Spaceport Sheboygan, Zion, two Wisconsin DNR monitoring locations (Grafton and Milwaukee SER) and one Illinois EPA monitoring location (Schiller Park).

* Shipboard measurements are still being quality controlled and are not discussed in this initial report.

Aircraft measurements included remote measurements of NO₂ and potentially HCHO columns from the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) spectrometer, and cloud and aerosol measurements from the Airborne Hyper-Angular Rainbow Polarimeter (AirHARP), which flew on the NASA King Air aircraft. In situ trace gas and meteorological measurements were made using instruments onboard a Mooney Aircraft operated by Scientific Aviation. Twenty-one GeoTASO and 22 Scientific Aviation flights were conducted during the LMOS 2017, with most of these flights coordinated between the NASA and Scientific Aviation aircraft. Flight planning meetings were conducted each morning during the aircraft deployment to determine the flight plan for the day based on meteorological and chemical forecasts. Primary flight objectives were to 1) conduct regional scale coastal surveys along the western shore of Lake Michigan during ozone exceedance events, 2) conduct...
local Chicago, IL, and Milwaukee, WI, flights to characterize the urban NO$_2$ emissions, and 3) conduct
local Sheboygan, WI, and Zion, IL, survey flights to characterize coastal gradients in air pollutants and
meteorological fields. The NASA King Air aircraft flew “raster” patterns to obtain maps of NO$_2$ column
abundances. Scientific Aviation flew low level transects to sample the marine boundary layer along with
in situ spirals to measure vertical profiles at selected waypoints. On most of the deployment days, the
two aircraft flew over the same area at the same time to provide the best overlap between the two
types of measurements.

Ground-based measurements included enhanced in situ and remote sensing measurements,
and two mobile measurement platforms. The enhanced in situ measurements were made at two
primary ground sites along the western shore of Lake Michigan: Spaceport Sheboygan in downtown
Sheboygan, WI, and the Illinois Environmental Protection Agency (IEPA) Zion monitoring site (AQS ID 17-
097-1007) just south of the Wisconsin-Illinois state line (Figure 1.1.2 and
These two sites are each located near the monitors that consistently measure the highest ozone concentrations in the region. Measurements at the Sheboygan site were focused on vertically resolved coastal winds, aerosols, temperature, water vapor and surface measurements of ozone, ozone spatial patterns, NOx, NOy, and formaldehyde (a marker of oxidation chemistry). Measurements at the Zion site focused on vertically resolved coastal winds, temperature, water vapor, aerosol optical depth and surface measurements of ozone, select ozone precursors, NOx, VOCs, oxygenated VOCs, nitric acid, hydrogen peroxide, and aerosol characterization. Additional ground based remote sensing instruments were deployed at the Wisconsin Department of Natural Resources (WDNR) Grafton (AQS ID 55-089-0008) and Milwaukee SER (AQS ID 55-079-0026) sites, as well as at IEPA’s Schiller Park monitoring site (AQS ID 17-031-3103). Mobile ground based measurements of ozone and ozone precursors were made along the shoreline and along inland transects near Zion, IL and Sheboygan, WI to investigate the extent that high ozone penetrates inland during ozone episodes.

The LMOS 2017 data are being used in conjunction with a number of different meteorological and photochemical models (Table 1.3.3). The LMOS 2017 data are being used to evaluate the skill of the models in an extended manner that is not possible when just traditional ground-based chemical and meteorological stations are used. The LMOS 2017 dataset contains chemical species and meteorology fields that are not routinely measured, observed vertical profiles of ozone and NO2, and measurements of the structures of the lake boundary layer and lake breeze. Furthermore, LMOS 2017 produced a rare dataset of chemical measurements over the lake, instead of just on land. Models are also being used to help interpret the measurement dataset, through visualization of air mass trajectories and spatio-temporal patterns of air pollutants, and through emissions sensitivity experiments.

The LMOS team is working toward providing best-practices recommendations on applying models for simulating high ozone concentrations along the shores of Lake Michigan. These recommendations will include details on the model configurations, temporal and spatial resolutions needed to simulate the dynamical and chemical drivers of high ozone. The LMOS 2017 team is also studying sensitivity of ozone model skill to biogenic emissions. The LMOS 2017 project was designed in anticipation of long-term use of the resulting data products for future model evaluation and model development projects.

### Table 1.3.3. Models being evaluated using LMOS 2017 data.

<table>
<thead>
<tr>
<th>Model</th>
<th>Research Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>WRF-CHEM</td>
<td>Univ. Iowa</td>
</tr>
<tr>
<td>NAM-CMAQ</td>
<td>NOAA</td>
</tr>
<tr>
<td>WRF-Met</td>
<td>NOAA</td>
</tr>
<tr>
<td>CMAQ</td>
<td>UW-Madison</td>
</tr>
</tbody>
</table>

### 1.4. Meteorology during LMOS 2017

The measurements collected during LMOS 2017 were designed to capture the key features of the meteorological and chemical conditions during the study period. This section begins with a
comparison of the observed monthly mean meteorological conditions to historic climatological trends in
the region. These comparisons are significant because they frame the meteorological conditions of
LMOS 2017 in the context of the historically observed connections between weather and air quality in
the region. The prevailing synoptic patterns that occurred during each week of LMOS 2017 are then
presented to lend insight into the conduciveness of the meteorological conditions for ozone formation.

The NOAA National Centers for Environmental Information (NCEI) Synoptic Discussion for May
2017 (https://www.ncdc.noaa.gov/sotc/synoptic/201705) states that the weather over the contiguous
United States (CONUS) was dominated by a highly variable jet stream circulation resulting in above-
normal precipitation across much of the eastern half of the country and cooler than normal
temperatures across much of the central U.S. (Figure 1.4.1). Precipitation was above average over
Wisconsin and maximum surface temperatures were below average over Wisconsin and NE Illinois
ridge dominated the western half of the U.S. resulting in warmer- and drier-than-normal weather in the
west. An upper-level trough over the eastern half of the country resulted in cooler- and wetter-than-
normal weather in the eastern U.S. (Figure 1.4.2). Precipitation was above average over Wisconsin and
below average over Illinois during June 2017. Temperatures were near average in northern Wisconsin
and above average in southern Wisconsin and Northern Illinois during June 2017.

Weekly (Sunday to Saturday) composite 850 millibar (mb) heights, 2 meter (m) temperatures, 2
m relative humidity, and 2 m temperature anomaly maps from the North American Regional Reanalysis
(NARR) (Mesinger, et al, 2006) data are presented here to summarize the synoptic conditions of the
LMOS 2017 study period. These images were generated using the web tools provided by the
NOAA/ESRL Physical Science Division web site (http://www.esrl.noaa.gov/psd/). The 2 m temperature
anomalies are relative to the 1979 to 2017 mean. Figures 1.4.3 through 1.4.7 show the composite
synoptic conditions for each of the 5 weeks of the study, beginning on Sunday, May 21, 2017, and
ending on Saturday, June 24, 2017.
Figure 1.4.1. National maps of departure from climatological means of precipitation and temperature for May 2017. Total Precipitation (left) and Maximum Temperature (right) Percentiles relative to the 1895-2017 ranking period from the NOAA National Centers for Environmental Information Synoptic Discussion for May 2017 (https://www.ncdc.noaa.gov/sotc/synoptic/201705).

Figure 1.4.2. Same as Figure 1.4.1 for June 2017 (https://www.ncdc.noaa.gov/sotc/synoptic/201706)

Figure 1.4.3 shows that a large amplitude trough in the 850 mb heights over the Northern Plains resulted in cooler than normal temperatures over the Central Plains during the first week of LMOS 2017 (May 21-27, 2017). Mean 2 m temperatures ranged from 291K (64°F) in northern Illinois to 288K (59°F) in southern and central Wisconsin. The mean 2 m relative humidity ranged from 80-85% over Wisconsin, Michigan and the Great Lakes with slightly lower (70-80%) relative humidity over Illinois and Indiana. The 2 m temperature anomaly map shows that Wisconsin, Illinois, and Indiana had near normal to slightly below normal temperatures, while temperatures over Lake Michigan were up to 2K (4°F) below normal.

Figure 1.4.4 shows that during the second week of the study (May 28-June 03, 2017) the trough over the Northern Plains moved to the NE resulting in near normal 2 m temperatures and somewhat dryer air over most of the Midwest. Mean 2 m relative humidity ranged from 55-65% over Illinois to 70-75% over Wisconsin with somewhat drier air over southern Lake Michigan. Mean 2 m temperatures rose to 294K (69°F) in central Illinois but remained near 288K (59°F) in central Wisconsin, resulting in sharper temperature gradients and increased (3-5 m/s) mean westerly 2 m wind speeds (not shown) over much of Wisconsin.

As shown in Figure 1.4.5, a weak ridge dominated the Central Plains during the third week of LMOS 2017 (June 04-10, 2017) resulting in above average temperatures (294K or 69°F) over southern and central Wisconsin. Figure 1.4.6 shows that during the fourth week of the study (June 11-17, 2017) a large amplitude ridge formed over the SE U.S. leading to a broad region of above average temperatures over the central and eastern U.S. This ridge resulted in significantly (4-5K or 8-10°F) above average temperatures over Iowa, Wisconsin, Michigan, and northern Illinois. Mean 2 m temperatures reached 300K (80°F) in central and northern Illinois and 297K (75°F) in southern Wisconsin. The warmer
temperatures and higher (80%) 2 m relative humidity in NE Wisconsin resulted in frequent afternoon cloudiness and occasional convective precipitation over eastern Wisconsin during this period.

Figure 1.4.7 shows that the final week of the campaign (June 18-24, 2017) returned to an 850 mb geopotential height pattern that was similar to the second week of the study, resulting in below normal temperatures over Minnesota and NW Wisconsin. These cooler temperatures north of the study region, coupled to near normal temperatures in Illinois, produced strong surface temperature gradients and somewhat stronger (2-4m/s) westerly 2 m winds over eastern Wisconsin and east-central Illinois (not shown).

Figure 1.4.3. CONUS meteorological overview for the week starting May 21. 850mb geopotential height (upper left, m), 2m air temperature (upper right, K), 2m relative humidity (lower left, %), and 2m air temperature anomaly (lower right, K) during May 21-27, 2017 (Week 01 of LMOS 2017)
Figure 1.4.4. CONUS meteorological overview for the week starting May 28. 850mb geopotential height (upper left, m), 2m air temperature (upper right, K), 2m relative humidity (lower left, %), and 2m air temperature anomaly (lower right, K) during May 28-June 03, 2017 (Week 02 of LMOS 2017).
Figure 1.4.5. CONUS meteorological overview for the week starting June 4. 850mb geopotential height (upper left, m), 2m air temperature (upper right, K), 2m relative humidity (lower left, %), and 2m air temperature anomaly (lower right, K) during June 04-10, 2017 (Week 03 of LMOS 2017).
Figure 1.4.6. CONUS meteorological overview for the week starting June 11. 850mb geopotential height (upper left, m), 2m air temperature (upper right, K), 2m relative humidity (lower left, %), and 2m air temperature anomaly (lower right, K) during June 11-17, 2017 (Week 04 of LMOS 2017).
**Figure 1.4.7.** CONUS meteorological overview for the week starting June 18. 850mb geopotential height (upper left, m), 2m air temperature (upper right, K), 2m relative humidity (lower left, %), and 2m air temperature anomaly (lower right, K) during June 18-24, 2017 (Week 05 of LMOS 2017).

### 1.5. Lakeshore Ozone During LMOS 2017

This section briefly summarizes the ozone concentrations observed during LMOS 2017. The study period began with fairly low lakeshore hourly ozone concentrations (< 60 ppbv) through the end of May. June was more promising for investigating elevated ozone at the lakeshore with three distinct high ozone periods occurring before the end of the study on June 22. Figure 1.5.1 shows timeseries of surface ozone during LMOS 2017 at the three lakeshore monitors (shown in blue and purple) that typically measure the highest ozone concentrations on the western shore of the lake. The figure also shows concentrations at nearby, inland monitors (shown in green), which typically have lower ozone concentrations. Peak lakeshore ozone concentrations remained below 60 ppbv until June 2, 2017, when all five of these monitors measured hourly ozone levels well above 70 ppbv. As shown in Figure 1.5.2, measured maximum daily eight hour average (MDA8) ozone exceeded 70 ppbv at most of the lakeshore monitors from Northern Indiana to NE Wisconsin.

Figure 1.5.1 shows that on June 4 the ozone monitors near the IL-WI border measured hourly ozone concentrations above 70 ppbv. A second, multiday period of high lakeshore ozone concentrations...
occurred at these monitors between June 10-12. The Zion, IL; Chwaukee, WI; and Kohler-Andrae, WI, monitors all observed hourly ozone concentrations above 70 ppbv on each of these days. The Chwaukee, WI, monitor exceeded 70 ppbv MDA8 on June 12 and the Kohler-Andrae, WI, monitor exceeded 70 ppbv MDA8 on June 11 and 12.

A third, multiday period of high lakeshore ozone concentrations occurred between June 14-16 with most of the sites shown in Figure 1.5.1 measuring hourly ozone above 70 ppbv on each of these days. On June 15 only the Zion, IL, and Chwaukee, WI, monitors measured hourly ozone concentrations above 70 ppbv. The Zion, IL, and Chwaukee, WI monitors exceeded 70 ppbv MDA8 on June 15 and the Kohler-Andrae, WI, monitor exceeded 70 ppbv MDA8 on June 16.

Figure 1.5.1. Time series of one-hour surface ozone concentration (ppbv) during May 22 – June 22, 2017. Upper panel shows time series at Chiwaukee Prairie (CP), Kenosha Water Tower (WT), and Zion (Zion). Lower panel shows time series at Sheboygan Kohler-Andrae (KA) and Haven (Haven) sites. The lakeshore monitors are shown in blue and purple, and the inland (3.2 to 3.6 miles) monitors are shown in green.
During some of these ozone episodes (e.g., June 2\textsuperscript{nd} in both areas and June 11\textsuperscript{th} and 16\textsuperscript{th} in Sheboygan), high ozone concentrations reached the inland monitors, located 3.2 to 3.6 miles from the lakeshore. On other days (e.g., June 10\textsuperscript{th} and June 12\textsuperscript{th} in Sheboygan and June 15\textsuperscript{th} in Kenosha), only the lakeshore monitors were impacted by high ozone. On these days, concentrations at the inland monitors...
remained low. These figures demonstrate that the LMOS 2017 campaign included a variety of types of ozone episodes.

The MDA8 ozone concentrations at Chiwaukee and at Kohler Andrae were fairly typical, compared to values for May 15-July 15 from other years, as shown in Figure 1.5.3. The highest levels of ozone (MDA8 exceeding 85 ppb) are rare events, with typical years having either zero or one day in that time period at over 85 ppb. LMOS did not capture such events at Chiwaukee or at Kohler Andrae.

Figure 1.5.3. Ozone concentrations during LMOS were representative of climatological values.
Section 2. Summary of LMOS Observations and Key Results

This section presents an overview of the observations collected during LMOS 2017 and a summary of the key results from the initial analysis of the data from the different measurement platforms. The results presented here are preliminary and are largely based on the field data collected during the study that are still undergoing quality assurance checks, calibration adjustments, and zero adjustments. Additional results will become available as the intercomparison of data from the different measurement platforms and research groups evolves, as the observational datasets from the study are harmonized, and as model-observation comparisons are completed. Data collected during LMOS is archived at the NASA Langley Research Center (LaRC) Airborne Science Data for Atmospheric Composition (https://www-air.larc.nasa.gov/missions/lmos/).

2.1. Spaceport Sheboygan, WI Measurements

2.1.1. Overview

To investigate the lake breeze dynamics and local production of ozone during LMOS 2017 a suite of ground-based remote sensing and in situ instruments were deployed at Spaceport Sheboygan (43°44’46.55”N, 87°42’29.09”W) (Figure 2.1.1) in Sheboygan, WI. The Spaceport Sheboygan ground site is located approximately 0.25 km from the Lake Michigan shoreline, approximately 3.5 km north of the Edgewater coal-fired power station, and approximately 8.5 km north of the Wisconsin Department of Natural Resources (WDNR) Sheboygan Kohler-Andrae (KA) air quality monitor. This site served as the main LMOS 2017 research station for the UW-Madison Space Science and Engineering (SSEC) and the U.S. EPA Office of Research and Development research groups.

Understanding the temporal evolution of photochemical regimes for ozone production at the local scale via direct observations can provide important insights for model performance as the MDA8 O₃ concentrations are sensitive to the changes in NOₓ and VOC precursors throughout the day. The EPA measurement suite at Spaceport Sheboygan focused on a limited set of trace gas measurements (Table 2.1.1). These measurements can be used both to provide insight into the local photochemical conditions during LMOS 2017 through the use of chemical indicators and to evaluate chemical transport model simulations of the study period. The ratio of formaldehyde (HCHO) and NO₂ measurements can be used to assess the local photochemical regime driving O₃ production. A HCHO/NO₂ ratio < 0.8 indicates that the ozone production chemistry is radical limited, a ratio > 1.8 indicates NOₓ limited conditions, and ratios between indicate a transition state between the two conditions (Sillman, 1995; Sillman 1998; Tonnesen and Dennis, 2000). At the same time, SSEC collected an extensive suite of meteorological measurements. The combined set of EPA and SSEC measurements will be used to assess air mass changes and the associated ozone production conditions within the air masses.
2.1.2. Methods

The SSEC Portable Atmospheric Research Center (SPARC, Wagner et al. 2016) is a movable meteorological research laboratory that hosts in situ and remote observations of conditions at and above the surface. SPARC observations include continuous ground-based temperature and water vapor profiles from the SSEC Atmospheric Emitted Radiance Interferometer (AERI) (Knuteson et al. 2004a,b), aerosol backscatter measurements from the SSEC High Spectral Resolution LIDAR (HSRL) (Shipley et al, 1983), and Doppler Lidar wind measurements. A data logger and other instrumentation feeds are synchronized to a GPS receiver in order to coordinate internal clocks to facilitate precise intercomparisons of the data between instruments.

Figure 2.1.1. Location of the LMOS ground based measurements in Sheboygan, WI. The SPARC trailer was located on the NE side of SpacePort Sheboygan and the EPA trailer was located on the SW side of Spaceport Sheboygan.

The U.S. EPA research trailer is a mobile research laboratory designed to host a combination of in situ and remote sensing observations with a primary emphasis on the measurement of key trace gas species related to ozone chemistry. Table 2.1.1 provides a summary of the EPA measurement suite deployed in Sheboygan, including the portable 2B-POM ozone measurements that were deployed further inland to assess ozone gradients. With the exception of the 2B-POM ozone instruments, all other in situ instruments were housed within the temperature-controlled EPA mobile research laboratory for the study. The instruments in the EPA mobile lab were calibrated according to manufacturer’s operation manuals and in accordance with the Federal Reference Method (FRM; 40 CFR part 50, Appendix F and D). During LMOS 2017 automated zero and span checks were performed every other night to monitor the validity of the calibration and control for drifts or variations in the span and zero response. Details regarding generation of span and zero gases, dilution air, inlet materials and
placement, filtration of particles, and data acquisition are available upon request and will be included with final reports.

Table 2.1.1. Summary of EPA Measurements at Sheboygan, WI, during LMOS 2017

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Measurement Principle</th>
<th>Model/Manufacturer</th>
<th>Time Resolution</th>
<th>Relevant Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_3$</td>
<td>Scrubberless Ultraviolet Photometric (SL-UV)</td>
<td>2B Technology M211</td>
<td>10-seconds</td>
<td>EQOA-0514-215</td>
</tr>
<tr>
<td></td>
<td>Ultraviolet Photometric</td>
<td>2B Personnel Ozone Monitors</td>
<td>1-minute</td>
<td>EQOA-0815-227</td>
</tr>
<tr>
<td>NO/NO$_2$/NO$_x$</td>
<td>Cavity attenuated phase shift spectroscopy (CAPS)</td>
<td>Teledyne T500U</td>
<td>10-seconds</td>
<td>EQNA-0514-212</td>
</tr>
<tr>
<td></td>
<td>$O_3$ Chemiluminescence with Molybdenum converter</td>
<td>Teledyne T200U</td>
<td>10-seconds</td>
<td>RFNA-1194-099</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>$O_3$ Chemiluminescence with external Molybdenum converter at 10m</td>
<td>Teledyne T200U</td>
<td>10-seconds</td>
<td>NA</td>
</tr>
<tr>
<td>HCHO</td>
<td>Quantum Cascade Laster (1765 cm-1)</td>
<td>Aerodyne Research</td>
<td>1- seconds</td>
<td>Herndon et al., 2007</td>
</tr>
<tr>
<td>$O_3$/NO$_2$/HCHO column densities</td>
<td>Sun-sky radiances 280-525nm</td>
<td>NASA Goddard Pandora Spectrometer</td>
<td>Total columns every 80-s</td>
<td>Herman et al., 2009</td>
</tr>
<tr>
<td>*WS, WD, T, RH, BP, Prec.</td>
<td>Various</td>
<td>Vaisala WXT520 with ultrasonic wind sensors</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* WS-wind speed, WD-wind direction, T-temperature, RH-relative humidity, BP-barometric pressure, Prec.-precipitation

In addition to measurements at Spaceport Sheboygan, the EPA placed three ozone monitors (2B-POMs) at approximate distances of 0.65 km, 3 km, and 6 km from the lakeshore, as shown in Figure 2.1.2. The purpose of these ozone monitors was to investigate potential concentration gradients over the domain, particularly during high ozone days and lake breeze-driven ozone events.
Location of the 2B-Personal Ozone Monitors in relation to the lake shore and the main Spaceport Sheboygan research site.

2.1.3. Results and Discussion

Over the study period the hourly ozone concentrations measured at the Spaceport Sheboygan research site reached over 70 ppbv for sustained periods on June 2, 11, 12, and 16 (Figure 2.1.3). Time series of NO$_2$ and HCHO are also plotted in Figure 2.1.3. The time series of NO$_2$ and HCHO concentrations show the relative levels of these precursors are different for the high ozone days. Figure 2.1.4 shows the time series of the HCHO/NO$_2$ ratio and wind direction at the Spaceport Sheboygan research site. The HCHO/NO$_2$ ratio indicates that ozone production during the June 2 and 16 high ozone events was radical or VOC limited (HCHO/NO$_2$ <0.8). Ozone production on June 11 and 12 was NO$_x$ limited (HCHO/NO$_2$>1.8). The presence of the two different local photochemical regimes driving ozone production at Spaceport Sheboygan indicates the potential for different causes of the high observed ozone.
Figure 2.1.3. Time series of O$_3$, NO$_2$ and HCHO mixing ratios as measured at the Spaceport Sheboygan research station during LMOS.

Figure 2.1.4. Time series of the ratio of HCHO/NO$_2$ mixing ratios and wind direction measured at the Spaceport Sheboygan research station during LMOS. HCHO/NO$_2$ ratios falling below the dark blue line plotted at 0.8 indicates a radical limited environment, while ratios above the orange line at 1.8 indicate a NO$_x$ limited environment.

Figure 2.1.5 and 2.1.6 show data collected by instruments within the SPARC trailer on the June 2 and June 11 high ozone days. In addition to producing high ozone at the Spaceport Sheboygan site, these days also saw ozone exceedances at the Sheboygan KA monitor. In each figure, the panels show time height cross sections with the Doppler lidar wind profiles overlaid on top of the AERI Optimal Estimation (AERIoe) (Turner and Löhner, 2014) retrievals of potential temperature (top) or HSRL aerosol backscatter (bottom). Times are in UTC and cover the range from 12 midnight to 12 midnight (CDT). Sunrise is approximately 10 UTC (5:00am CDT).

The temperature profile in Figure 2.1.5 shows that before sunrise on June 2, a very stable nocturnal boundary layer exists in the lowest 100m, as indicated by temperatures that are cooler at the surface than aloft. After sunrise, diurnal heating warms the surface and the boundary layer becomes unstable, and vertical mixing erodes the stable nocturnal boundary layer beginning at around 13 UTC. Another indication that the boundary layer is deepening is the increase in the depth of aerosol backscatter seen in the bottom panel at around the same time. Before 15 UTC (10:00am CDT) the
inversion is mixed out, and rapid increase in boundary layer depth is observed after that time. Shortly after 17 UTC (noon CDT), the Doppler lidar indicates a shift in the wind direction from westerly to easterly and then southerly. Since Sheboygan sits on the southern side of a point, flow from the east or south originates in the lake. As the air sitting over the lake is substantially cooler than the air over land, the lake breeze generates a new inversion through advection of a shallow layer of cold air onshore. Note that the winds and temperature inversion are slightly offset in the vertical. This offset is a result of the 140 m dead zone where the Doppler lidar cannot perform wind measurements coupled with the fact that the lake breeze inversion builds from the surface upward. The afternoon southerly winds that extend up to approximately 600 m persist throughout the rest of the day and into evening.

The darker colors in the HSRL lidar profile on June 2 indicate very clean (i.e. free of aerosols) air prior to 21:30 UTC (4:30pm CDT). After 21:30 UTC, air within the lake breeze inversion that is southerly in origin shows higher aerosol backscatter than the air immediately above the lake breeze inversion and may indicate polluted air that has been transported over the lake from the south.

In contrast, on June 11 the AERI temperature retrievals show no evidence of a nocturnal boundary layer during the early morning hours, strong westerly winds above 400 m during the evening of June 10 and early morning of June 11, and associated turbulent mixing, likely inhibited the formation
of the stable surface layer. The arrival of the lake breeze at 14:30 UTC (9:30am CDT) is evident in the AERI temperature profiles as a shallow inversion layer. The Doppler Lidar shows winds switching from westerly to southwesterly at 17 UTC (12 noon CDT). By 22 UTC (5:00pm CDT), the maritime inversion is gone. The HSRL Lidar also shows very different behavior on June 11, 2017, with advection of more polluted (higher aerosol backscatter) air above 400m from the west during the early morning hours and advection of less polluted (lower aerosol backscatter) air from the southwest during the daytime and early evening.

![Sheboygan AERIoe Temperature 20170611](image)

![Sheboygan HSRL Aerosol Backscatter 20170611](image)

**Figure 2.1.6.** Visualization of boundary layer evolution (winds, temperature, and aerosol backscatter) for June 10 and 11, 2017 at Sheboygan, WI. AERI potential temperature (K, upper panel) and HSRL backscatter (log$_{10}$(m$^{-1}$ sr$^{-1}$), lower panel) with Doppler winds during the period from 5 UTC on June 10 to 5 UTC on June 11, 2017 (12 midnight to 12 midnight CDT).

Intermittent data capture issues were experienced with all of the 2B-POM instruments. The data capture rate for each ozone instrument used in this study for a 5-minute average ozone concentration was 95.8% at Spaceport Sheboygan, 22.2% at Sheboygan Chamber of Commerce, 27.3% at Sheboygan Fire Department, and 27.3% at Kohler Public Works. A regression of the 5-minute data from the inland 2B-POMs against the Spaceport Sheboygan data is shown in Figure 2.1.7. While the low data capture rate will limit the utility of this data to investigate the dynamics of the ozone gradients, the regressions appear to indicate the furthest site inland from the lakeshore, Kohler Public Works, experiences ozone values 5-6% lower than the close lakeshore site, Spaceport Sheboygan. This difference reflects losses due to deposition, ozone titration by nitrous oxide (NO), other chemical ozone destruction reactions, or dilution due to enhanced vertical mixing. When ozone concentrations at Spaceport Sheboygan are
greater than 70 ppbv, however, the observed concentrations at Sheboygan Fire Department are even larger. The sampling limitations from these instruments experienced during LMOS 2017 inhibit drawing additional conclusions from these data.

Figure 2.1. Comparison of 2B-POM ozone from Sheboygan Fire Department, Kohler Public Works, and Spaceport Sheboygan sites. Linear regression of 5-minute 2B-POM ozone concentrations measured at Sheboygan Fire Department (SFD) and Kohler Public Works (KPW) against Spaceport Sheboygan (SPS) 5-minute average ozone (all coincidences).

2.2. Zion, IL, Measurements

2.2.1. Overview

The Zion, IL site was selected to focus on gas phase chemistry of the urban plume from the Chicago-Naperville-Elgin, IL-IN-WI Metropolitan Statistical Area (MSA). By selecting a site at the northern end of the MSA, we believed we would intercept ozone formation at its early stages during episodes characterized by synoptic winds from the south. This was supported by preliminary modeling – sometimes the site would represent relatively fresh emissions, while at other times air would be moderately processed through oxidative aging and ozone formation, as indicated by H$_2$O$_2$/HNO$_3$ and HCHO/NO$_2$ ratios from photochemical grid models and remote sensing. Sampling this variability, and
testing the extent to which models reproduce this variability, was part of the study design. Gas chemistry was sampled together with a number of supporting measurements to provide meteorological context and allow source apportionment (through particulate matter source apportionment using Positive Matrix Factorization, PMF). Finally, the site was far enough to the northeast of O’Hare Airport that in situ profiles by light aircraft could be performed above the site without too many air traffic control concerns.

Site access, available space and power, and a long-term ozone record were favorable at the Zion, IL site. Furthermore, at 0.95 km from the lake with no major sources between the monitoring site and the lake, the Zion site was favorable for capturing the lake breeze and for sampling air “fresh” off the lake.

Continuous or semi-continuous measurements of ozone, NOx, nitric acid, hydrogen peroxide, and many volatile organic compounds (VOC) and oxygenated volatile organic compounds (OVOC) were conducted. Some prominent VOC and OVOC compounds measured included benzene, toluene, isoprene, monoterpenes, methyl vinyl ketone, and methacrolein.

Volatile organic compounds (VOCs) play several key roles in the atmosphere: their oxidation leads to the formation of ozone and organic aerosol; they affect the nitrogen cycle by interacting with atmospheric NOx; and they modulate the atmosphere’s oxidizing capacity and therefore the lifetimes of greenhouse gases and other pollutants. VOC measurements were performed at Zion during LMOS 2017 with the aim of understanding the role of different VOC species for ozone formation, determining the importance of biogenic versus anthropogenic emissions for VOC reactivity in this region, and quantifying indicator species that can be used to diagnose photochemical age and VOC versus NOx limitation for ozone formation.

Over the past two decades, a wide array of observation-based approaches has been utilized to study the impact of changing VOC and NOx emissions on ozone production rates and efficiency. During LMOS 2017 the experimental approach to investigate this area focused on two areas: 1) comparison of radical production rates (Q) with radical loss rates to NOx (LN) as an indicator of VOC vs. NOx limited regimes (2005), and 2) the direct use of hydrogen peroxide (H2O2) and nitric acid (HNO3) as indicators for VOC and NOx sensitivity in ozone production (1995).

In the first approach, radical production was calculated using the current version of the Master Chemical Mechanism (http://mcm.leeds.ac.uk/MCM) in a box model framework constrained by observations collected during LMOS 2017. In coastal Lake Michigan during summer, most of the radical loss is likely to NOx through the reaction of nitrogen dioxide with the hydroxyl radical (OH + NO2). This hypothesis is being tested with in situ measurements from the Zion, IL site, including biogenic hydrocarbons and a variety of N-containing oxidation products. To complement the chemical transport modeling analyses, the ratio LN/Q (radical loss to NOx versus total radical loss rate) are being examined to provide a direct observational constraint on VOC and NOx limitations to ozone production. A LN/Q ratio > 0.5 suggests that ozone production is limited by the availability of VOCs.
For the second approach, chemical indicators of ozone production sensitivity (e.g., $\text{H}_2\text{O}_2/\text{HNO}_3$) are being investigated. Specifically, Sillman suggested that the following chemical ratios indicate hydrocarbon-sensitive ozone chemistry: $\text{HCHO}/\text{NO}_2 < 0.28$, $\text{H}_2\text{O}_2/\text{HNO}_3 < 0.4$, and $\text{O}_3/\text{NO}_2 < 7$. The combination of instruments deployed at Zion, IL, during LMOS 2017 enable the assessment of these indicator ratios in relation to the radical-based approaches discussed above. The simplicity of the indicator ratio technique makes it a promising tool for assessing VOC and NO$_x$ sensitivity if it is proven to be reliable in characterizing the ozone chemistry in coastal Lake Michigan air masses.

### 2.2.2. Methods

**Concentration and Bulk Composition of PM$_{2.5}$**

Fine particulate matter (PM$_{2.5}$) was collected and is undergoing chemical analysis to facilitate characterization of air mass characteristics at Zion during polluted and non-polluted conditions, and to provide input data for receptor-based source apportionment (Positive Matrix Factorization).

PM$_{2.5}$ was collected during LMOS 2017 using two medium-volume air samplers (3000B, URG Corp., Chapel Hill, NC) for daytime (8:00AM-8:00PM CDT) and nighttime (8:30PM-7:30AM CDT). PM$_{2.5}$ mass was determined gravimetrically using a high-precision balance (Mettler-Toledo XP26). Elemental and organic carbon (EC and OC) were measured by thermal-optical analysis following the ACE-Asia base case protocol (Schauer et al., 2003). Water soluble cations and anions were determined by water-extraction and ion exchange chromatography with suppressed conductivity detection as described by Jayarathne et al. (2014). Planned future analysis includes quantitation of organic species via Gas Chromatography Mass Spectrometry (GC-MS), organosulfates via Liquid Chromatography Mass Spectrometry (LC-MS), and metals using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Once measured, these species will be used with positive matrix factorization in order to determine sources contributions to fine particulate matter in Zion, IL, with an emphasis on understanding the distribution of primary/secondary and biogenic/anthropogenic sources. PMF analyzes the co-variation of chemical species over time and identifies factors based on a constrained weighted least-squares matrix. Data inputs include detailed bulk chemical and speciation measurements and measurement uncertainties and will include organic molecular markers of primary sources, SOA tracers, inorganic ions, and metals. The model outputs factors and their relative contributions to ambient measurements that will be interpreted as aerosol sources using elemental and molecular tracers and regional source characteristics, as done previously by Stone’s group for urban and rural sites.

**Observation-based approach for determining the sensitivity of O$_3$ production rate and efficiency to NO$_x$ and VOCs.**

Hydrogen peroxide ($\text{H}_2\text{O}_2$) and nitric acid ($\text{HNO}_3$) mixing ratios were measured by the Bertram group (U. Wisconsin), using chemical ionization time-of-flight mass spectrometry [Bertram et al., 2011] utilizing $\text{O}_2^-$ and $\text{I}^-$ reagent ion chemistry (Figure 2.2.1). $\text{H}_2\text{O}_2$ and $\text{HNO}_3$ sensitivities and inlet transmission were determined in the field through standard additions of isotopologues of $\text{H}_2\text{O}_2$ and $\text{HNO}_3$. For LMOS 2017, we mounted the detection axis of the mass spectrometer to the roof of the sampling trailer, to avoid the use of an extensive inlet and associated sampling losses for both molecules. The primary focus
during LMOS 2017 was H₂O₂ and HNO₃, however the TOF mass analyzer measured a broader distribution of molecules beyond H₂O₂ and HNO₃ (e.g., N₂O₅, ClNO₂, select organic acids).

High-resolution proton-transfer time-of-flight mass spectrometry VOC measurements

VOC measurements by Proton Transfer Reaction Quadrupole Interface Time-of-Flight Mass Spectrometry (PTR-QiTOF, Ionicon Analytik, GmbH) were made at 1-Hz time resolution from the roof of the Zion trailer using a 0.5” OD / 0.375” ID PFA Teflon inlet line that was wrapped and heated to ~50°C to minimize VOC-wall interactions and avoid water condensation inside the air-conditioned laboratory. All downstream wetted sampling surfaces (including valves) were likewise composed of PFA Teflon. The sampling line was equipped with a 10 µm filter that was replaced every ~2-3 days. A rotary vane pump (1023 Series, Gast Manufacturing Inc.) was used for sampling, yielding flow rates of approximately 40 L/min with an inlet residence time of approximately 3 s.

Measurement blanks (5 minutes) were performed hourly using zero air generated by passing ambient air through a Pt-bead catalyst (3.2 mm diameter; Sigma Aldrich) heated to 400°C. Calibration curves (4-point) were performed daily for a set of 28 VOCs by dynamic dilution of certified, gravimetrically-prepared, ppm-level compressed standards (Apel-Reimer Environmental Inc.). Instrumental settings were selected for optimal combination of high sensitivity, high mass resolution, and low humidity-dependence. The time-of-flight analyzer was operated over an m/z range of 0-337 (extraction period 32.5 µs), with the mass axis calibrated continuously via addition of a diiodobenzene internal standard. Peak fitting and integration was performed with the PTR-MS VIEWER 3.2.8. post-processing software. All subsequent data processing was performed using a custom set of R routines.
Meteorological Observations

A profiling microwave radiometer and acoustic wind profiler, or sodar, from the University of Northern Iowa were stationed at the Zion field site. Microwave emissions by atmospheric oxygen at any altitude are proportional to local temperature and density of oxygen, allowing for retrieval of the temperature vertical profile. Microwave emissions by water vapor are proportional to vapor density and temperature, allowing for retrieval of water vapor profiles. The echo from acoustic pulses emitted into the atmosphere will experience a frequency shift that is directly proportional to the motion of the air. Radiometer measurements extend upward to 10 km, while the sodar determines wind profiles every 10 m from 30 to 200 m above ground level (AGL). Temperature and water vapor retrievals from the radiometer and wind measurements from the sodar were used to characterize the structure of the atmospheric boundary layer and the development of the lake breeze during LMOS 2017.

2.2.3. Results and Discussion

An overview of hourly averaged ozone, NO\textsubscript{x}, and PM\textsubscript{2.5} measurements from the Zion, IL, site is shown in Figure 2.2.2 and in Figure 2.2.3. Ozone exceeded 70 ppbv on June 2, 4, 10, 11, 12, 14, 15 and 16. The onset of the largest ozone episode at Zion (June 2) was correlated with increases in NO\textsubscript{x}, but the peak ozone on June 2 appeared depleted in NO\textsubscript{x}. PM\textsubscript{2.5} on June 2 behaved qualitatively similar to NO\textsubscript{x} – with an increase at the onset of the ozone increase – but then with lower PM2.5 at the time of the peak ozone. During the period of June 11-17, PM\textsubscript{2.5} and ozone concentrations peak at the same time of day.

![Figure 2.2.2. Hourly-averaged O\textsubscript{3} and NO\textsubscript{x} measurements at the Zion site.](image-url)
Figure 2.2.3. Hourly-averaged ozone and estimated PM$_{2.5}$ at the Zion site.

The wind rose of hourly wind measurements collected by IL EPA at the Zion, IL site is shown in Figure 2.2.4, and can be contrasted to the ozone conditional probability function in Figure 2.2.5. Winds from the SE were much more likely (0.15-0.2 fraction) to have O$_3$ > 70 ppbv. Low ozone (blue) occurred during weak westerly winds, likely due to weak offshore flow. High ozone corresponded to high wind speeds from the SE.

Figure 2.2.4. Zion wind rose for the duration of the study, based on 1-min averages. The colors show the wind speed and the distance from the center shows the frequency of winds from that direction. The feature from the southeast is mainly due to the lake breeze effect at Zion.
Figure 2.2.5. Left: Ozone vs. wind direction and speed and Zion, IL. Ozone conditional probability function, showing the fraction of 1-min ozone measurements above 70 ppbv as a function of wind direction. Right: ozone (color scale in ppm) vs. wind direction vs. wind speed (radial position in m/s).

At Zion during LMOS 2017, PM$_{2.5}$ mass averaged 5.1 µg m$^{-3}$, 12-hour averaged concentrations ranged from 0.7 to 13 µg m$^{-3}$ and hourly PM$_{2.5}$ averaged between ~0.5 and ~16 µg m$^{-3}$. A summary of PM$_{2.5}$ mass concentrations and its chemical constituents are shown in Table 2.2.1. The most significant contributor to PM$_{2.5}$ mass was organic matter (OM, calculated as 1.8 x OC), followed by the secondary ions sulfate, nitrate, and ammonium. Figure 2.2.6 shows that the PM$_{2.5}$ concentrations were highest during the June 2 ozone event and were also elevated during the June 10-17 elevated ozone period compared to non-event periods; however, the relative composition of PM was generally consistent in terms of ion composition. The average OC:EC ratio was 12.25, suggesting a large contribution from secondary organic aerosol. Notably, the OC:EC ratio was substantially lower (at 6.9) during the June 2 ozone event. The higher EC measurements on this day indicate a larger influence of combustion emissions. Future analyses will focus on characterizing organic species, particularly source tracers, to better define the sources of PM$_{2.5}$.
Table 2.2.1. Summary of ambient concentrations of PM$_{2.5}$ organic and elemental carbon (EC and OC) and inorganic ions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Range (µg m$^{-3}$)</th>
<th>Mean ± SD (µg m$^{-3}$)</th>
<th>% PM$_{2.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>0.69 – 12.94</td>
<td>5.08 ± 2.9</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>&lt;0.05 – 0.78</td>
<td>0.22 ± 0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>OC</td>
<td>&lt;0.5 – 4.73</td>
<td>1.79 ± 1.0</td>
<td>37.1</td>
</tr>
<tr>
<td>OM</td>
<td>&lt;0.9 – 8.52</td>
<td>3.23 ± 1.8</td>
<td>66.7</td>
</tr>
<tr>
<td>Sodium</td>
<td>&lt;0.02 – 0.12</td>
<td>0.04 ± 0.03</td>
<td>0.3</td>
</tr>
<tr>
<td>Potassium</td>
<td>&lt;0.004 – 0.10</td>
<td>0.04 ± 0.03</td>
<td>0.6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>&lt;0.001 – 0.05</td>
<td>0.01 ± 0.01</td>
<td>0.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;0.02 – 0.19</td>
<td>0.06 ± 0.05</td>
<td>0.9</td>
</tr>
<tr>
<td>Ammonium</td>
<td>&lt;0.003 – 0.83</td>
<td>0.31 ± 0.18</td>
<td>6.6</td>
</tr>
<tr>
<td>Fluoride</td>
<td>&lt;0.003 – 0.03</td>
<td>0.01 ± 0.01</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrate</td>
<td>&lt;0.04 – 0.80</td>
<td>0.19 ± 0.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulfate</td>
<td>&lt;0.03 – 3.05</td>
<td>0.82 ± 0.5</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Figure 2.2.6. The concentration of major bulk components of PM$_{2.5}$ during the high ozone event, high ozone period, and background. Na$^+$, K$^+$, Mg$^{2+}$, and F$^-$ were all below 0.1 µg/m$^3$.

Figure 2.2.7 shows the time series of H$_2$O$_2$ and HNO$_3$ mixing ratios measured at Zion. Typical midday HNO$_3$ mixing ratios ranged from 1-8 ppbv exhibiting a strong diel profile. Typical midday H$_2$O$_2$...
mixing ratios ranged from 0.5 – 8 ppbv and were strongly correlated with isoprene mixing ratios, where
the largest concentrations were observed following leaf-out in early June. In contrast to HNO₃ diel
profiles, the H₂O₂ diel profiles were much more muted, perhaps indicating lower dry deposition rates.
Preliminary analysis of HNO₃ and H₂O₂ mixing ratios highlight a complex sampling environment, where
the lake breeze during high O₃ events is associated with low H₂O₂/HNO₃ ratios, indicating VOC-limited O₃
production (i.e., below ratio-based indicators such as Sillman’s hydrocarbon sensitive region of
H₂O₂/HNO₃ < 0.4). In contrast, the regional background is characterized by elevated H₂O₂/HNO₃ ratios,
suggestive of NOx-limited O₃ production. Ozone plumes arriving at Zion in day-time lake breezes were
generally VOC-limited according to the indicator ratios. This was the case even late in June when
biogenic VOCs were present in higher concentrations, and thus contributing a source to H₂O₂. This
observation is consistent with plumes enriched in NOx and O₃, depleted of hydrocarbons on a relative
basis, coming ashore from the lake during some high O₃ hours. Ongoing work will focus on the role of
atmospheric mixing at the lake/land boundary between VOC-limited (urban plume) and NOx-limited
(regional background) air.

Figure 2.2.7. Time series of HNO₃ (top) and H₂O₂ (bottom) mixing ratios as measured at the Zion ground station during LMOS.
Analysis of the PTR-QIOTOF VOC measurements, including application of finalized humidity corrections and time-resolved blank and calibration factors, is ongoing. Figure 2.2.8 shows a preliminary time series for observations of isoprene, methyl vinyl ketone (MVK) plus methacrolein (MACR), monoterpenes, and toluene. MVR and MACR are prominent oxidation products of isoprene. Mixing ratios of isoprene and its oxidation products MVK+MACR were low during the first half of LMOS 2017, and significantly higher during the second half. Anthropogenic species such as toluene show the reverse trend, with more elevated concentrations seen early in the study. Future analyses will focus on evaluating the ability of chemical transport models to simulate the observed patterns of VOC abundance, reactivity, and photochemical age for the LMOS 2017 period.

Figure 2.2.8. Measured mixing ratios of isoprene, MVK+MACR, monoterpenes, and toluene at the Zion field site during LMOS-2017. June 1 is Julian day 152.

By examining Zion time series, particularly those in Figure 2.2.8, we identify a transition between an initial period of low biogenic influence (isoprene, MVK, and MACR are low initially) and higher anthropogenic influence (toluene and other anthropogenic VOCs, not shown). A sharp transition date is not evident, but the first large isoprene peak is on Julian date 155 (June 4) and the last large
nocturnal toluene peak is on Julian data 159 (June 8). Peroxide and nitric acid concentrations (Figure 2.2.7) generally increase along with the biogenic VOCs.

The highest 8-hour and 1-hour average ozone concentrations at Zion occurred on June 2. Meteorological observations collected at Zion that day are displayed in Figure 2.2.9. Orange shading highlights winds with an onshore (easterly) component; green shading indicates offshore (westerly) winds. Southwesterly winds are abruptly replaced by southeasterly winds at all levels between hours 14 and 15 UTC (9 and 10 a.m. CDT) as a deep lake breeze arrived at Zion. The wind shift was accompanied by a rapid drop in surface temperature and a sharp decrease of mixed layer depth. The lake breeze persisted at all levels until sunset at about 1 UTC (8 p.m. CDT), then eroded near the surface while persisting aloft.

Figure 2.2.10 shows that a shallower and shorter-lived lake breeze was observed at Zion on June 11. This date was also characterized by high ozone levels at Zion (1-hour averages above 70 ppbv). The lake breeze arrived just before 18 UTC (1 p.m. CDT), accompanied by a drop in surface temperature and a rapid decrease in mixed layer depth. The lake breeze did not extend as high as that observed on June 2, but depressed both the surface temperature and mixed layer depth for a longer period. Mixed layer depth and surface temperatures briefly recovered as the lake breeze dissipated around 00 UTC (7 p.m. CDT) on June 12.
Figure 2.2.9. Radiometer and sodar measurements at Zion on June 2, 2017. Top: color shading indicates winds (m/s) with a westerly (green) or easterly (orange) component. Middle: mixed layer depth (m). Bottom: surface temperature (°C). Time (UTC) extends from midnight CDT (hour 5 on 2017-06-02) to 11:55 p.m. CDT (hour 4 on 2017-06-03) on June 2.
Figure 2.2.10. Radiometer and sodar measurements at Zion on June 11, 2017 (as in Fig. 2.2.9). Time (UTC) extends from midnight CDT (hour 5 on 2017-06-11) to 11:55 p.m. CDT (hour 4 on 2017-06-12) on June 11.

2.3. Pandora/Ceilometer Measurements

2.3.1. Overview

In addition to several remote sensing profiling instruments deployed by research groups at Spaceport Sheboygan and Zion, the EPA deployed three ceilometers (Vaisala CL51) and five ground based UV/visible grating spectrometers (Pandoras). The ceilometers were installed at two WI DNR monitoring sites, Grafton and Milwaukee SER, and the Zion research site which is also an IEPA monitoring site. The Pandora spectrometers were installed at Spaceport Sheboygan, Grafton, Milwaukee SER, Zion, and Schiller Park in Chicago.
The primary objective of the ceilometers was to provide additional characterization of mixing heights across the study domain to better understand the lake breeze impacts on mixed layer height (planetary boundary heights) for model evaluation. The primary objective of the Pandora instruments was to provide column totals for NO$_2$ – which are useful as a contrast to in situ surface measurements; further they can be compared to GeoTASO NO$_2$ columns, in situ aircraft profiles, to satellite remote sensing NO$_2$, and to NO$_2$ columns from photochemical models. Secondary objectives of Pandora were column totals for ozone and HCHO.

2.3.2. Methods

The mixed layer height measurements were obtained with the Vaisala CL51 via single-wavelength (910 nm) laser aerosol backscatter and use of Vaisala BLView 1.0 software package. The BL-view software identifies up to three separate aerosol layers based on a gradient method applied to aerosol backscatter signals, with the lowest layer most often identified as the mixing height.

Remote sensing for trace gas column amounts was performed using ground-based Pandora spectrometers developed at NASA Goddard Space Flight Center (https://acd-ext.gsfc.nasa.gov/Projects/Pandora/index.html). Pandora spectrometers were placed at Schiller Park (IL EPA), Zion (IL EPA/LMOS 2017 super site), Milwaukee (WI DNR NCore), Grafton (WI DNR) and Spaceport Sheboygan (LMOS 2017 super site), in efforts to cover conditions representative of the Lake Michigan shoreline environment. The Pandora instrument is a UV-VIS spectrometer system designed to measure direct sun with a 2.1° field of view with a diffuser and 1.6° field of view without the diffuser. For direct sun measurements the sensor head attached to a tracker follows a specific solar azimuth and zenith direction that changes from East in the morning to West in the evening to track the sun (Herman et al., 2009). The spectra measured by the Pandora spectrometers are collected by the local host computer and then transferred to a central data processing system at 5-minute intervals, provided internet access, where the data is processed via a set of common algorithms. The standard set of data products is total column NO$_2$, HCHO and ozone (Herman et al, 2009, Spinei 2018). Both the total column ozone and NO$_2$ algorithms are considered validated algorithms, while the total column HCHO is still in validation stage.

The Scientific Aviation (SA) concentrations sampled by the Mooney light aircraft during ascending and descending spirals over Spaceport Sheboygan were used to calculate sub-columns of NO$_2$ over the Spaceport Sheboygan research site. The SA sub-columns were calculated from the measured NO$_2$ between approximately 1km- 3km AGL and the EPA ground-based NO$_2$ measurement, with the NO$_2$ concentration linearly interpolated between the lower aircraft value and the EPA ground measurement. The SA data are referred to as sub-columns even though they include data from both the surface measurement and the SA aircraft profile.

2.3.3. Results and Discussion

CL51 measurements indicate that the average mixed layer height during the LMOS 2017 period was similar at Zion, Milwaukee SER, and Grafton (Figure 2.3.1, black lines), growing on average from less than 1 km before 6 AM local time to approximately 1.5 km around 6 PM before lowering. The observations indicate that the mixed layer height at Zion is slightly lower than at the other sites,
reflecting more prevalent lower-level stratifications (gray lines). The most striking feature of the dataset is the large range of day-to-day (gray, red and blue lines) and hourly variations, with observed mixing layer heights under 200 m observed at all three sites. These variations are driven by the competition between continently influenced air (deeper mixing due to daytime heating and subsequent convection) and stratified marine layers with shallow mixed layer depths. Also, in practice, the Vaisala BLView1.0 algorithm for detecting mixed layer height may not detect shallow stratified layers of aerosol backscatter that occur within a much deeper continental offshore flow aloft. As noted previously, the conditions associated with the June 2 and 12 high ozone days, are distinct. The same can be said for the mixing conditions based on CL51 measurements on those days (red and blue lines).

Figure 2.3.1. All LMOS CL51 First Mixed Layer Height measurements (km AGL) between 15 May and 25 June 2017 by time of day (CST, gray lines). Data from 2 June (red) and 12 June (blue) are highlighted. The average is also shown (black solid line).

A comparison of the Pandora total vertical column and the SA sub-columns shows good agreement (Figure 2.3.2), when the two outliers are removed from the regression. A review of the two outliers show that these measurements are from May 27 and June 14, when the Pandora instrument likely sampled a large NO\textsubscript{2} plume during the SA spiral, which primarily sampled outside the plume. The offset in the regressions reflects the contribution of stratospheric and tropospheric NO\textsubscript{2} to the Pandora observation that is above the aircraft. The agreement between the Pandora data and the aircraft dataset lends confidence and caution to both datasets: in 9 of 11 spirals directly overhead of Spaceport Sheboygan both instruments are sampling representative airmasses with high-quality measurements, but in 2 of 11 samples, the atmosphere is sufficiently stratified such that there is not appropriate overlap. Not shown here, the quality of the regression substantially degrades when including Sheboygan inland, near the airport, and Sheboygan offshore samples, indicating again that the NO\textsubscript{2} distributions over Sheboygan vary locally, as demonstrated in the GeoTASO data (e.g., Figure 2.4.4)
Figure 2.3.2. Comparison of in situ NO$_2$ columns (x axis) and Pandora total column (y axis). The two outliers are May 27 and June 14 when Pandora likely sampled a large plume with more weight than did the SA. Profiles are restricted in to within +/- 0.035 deg of Spaceport Sheboygan research site. This restricts the profiles to the Sheboygan onshore profiles. Furthermore, only profiles extending 2000 m or greater vertically and without missing data were included. Regression is reduced mean axis.

The average NO$_2$ column measurements during LMOS 2017 generally indicate (Figure 2.3.3) that NO$_2$ columns are largest over Schiller Park, which is located just east of O’Hare International Airport, and are small to moderate elsewhere. The most notable feature of the Pandora dataset is the departure of NO$_2$ column observations above the average at four sites during one ozone episode (Friday 2 June red) versus observations that are average or smaller than average during the second ozone episode (Monday 12 June, blue). This finding is consistent with the more general observation than the dynamical and chemical factors affecting ozone concentrations are different on these two days.

Despite the relatively short data record, day-of-week variations exist in the NO$_2$ measurements (Fig.2.3.3, black solid line versus dashed). Over Schiller Park, Zion and Milwaukee, NO$_2$ columns were larger on Monday-Friday (black solid line) than on Saturday-Sunday (black dashed line), likely reflecting weekend decreases of NO$_x$ emissions. Over Grafton and Sheboygan, there is little day-of-week variation of NO$_2$ columns. The sources of NO$_x$ in Sheboygan may have a different day-of-week profile than typical of urban settings because it is a weekend tourist destination and downwind of a base-load coal-fired power plant. Neither of these emissions influences typically have large day-of-week variations.
2.4. GeoTASO Measurements

2.4.1. Overview

The Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) is an airborne hyperspectral mapping instrument built by Ball Aerospace (Leitch et al., 2014) and is being used as an airborne testbed for future high-resolution trace-gas observations from geostationary sensors such as TEMPO. This instrument has two spectrometers capable of quickly measuring spectra ranging from ~300-400 nm in the UV channel with a spectral resolution of 0.43 nm and ~400-700 nm in the Visible channel with a spectral resolution of 0.88 nm (Nowlan et al., 2016). Spectra within the 435-460 nm window are used to retrieve integrated atmospheric column amounts of nitrogen dioxide (NO₂). Preliminary results are described below. In the future, retrievals of column HCHO may also assist in the analysis of photochemistry around Chicago and along the western shore of Lake Michigan.

2.4.2. Methods

During LMOS, GeoTASO was operated on the NASA LaRC UC-12 aircraft. Figure 2.4.1 (right) shows GeoTASO integrated into the forward port of the aircraft. This aircraft configuration was flown for 21 research flights based out of Madison, Wisconsin from May 22 - June 21 in support of LMOS 2017 and its objectives. Figure 2.4.1 (left) depicts how light from the sun travels through Earth’s atmosphere and is scattered/reflected up to the nadir-viewing window aboard the aircraft. The light captured by the instrument’s telescope is guided through an arrangement of mirrors, gratings, and beam splitters into each spectrometer. The 45° nadir field-of-view, as depicted by the swath in Figure 2.4.1 (left), provides...
an across-track ground width of over 7 km from a nominal altitude of 28,000 ft. Flight plans were
designed to create raster maps, defined as a series of parallel flight legs spaced 6 km apart to provide
gapless coverage over regions of interest. Each flight had between 1-3 rasters.

Figure 2.4.1. Depiction of GeoTASO sampling strategy and photo of GeoTASO instrument. GeoTASO’s sampling strategy
(left) including its 45° swath width with a swath sample taken every 250 ms along the aircraft flight line (from Nowlan et al.,
2016) and GeoTASO integrated onto the NASA LaRC UC-12 (right: Photo credit: Matt Kowalewski, USRA/NASA GSFC).

Flight Planning

Prior to the campaign, a ‘playbook’ of flight plans (shown in Figure 2.4.2) was developed for
accomplishing a range of science objectives depending on the cloud/air quality forecasts during LMOS
2017. These flight plans are grouped into two categories: urban emissions sampling and coastal mapping
surveys. Emissions sampling flights were designed to observe time-varying emissions over the areas of
Chicago (8 flights/1-2 repeated rasters per flight) and Milwaukee (1 flight/3 repeated rasters). The
coastal mapping plans, oriented around the two supersites (Sheboygan and Zion), were designed to
observe large local point sources (such as power plants) as well as the regional influence from upwind
sources such as Chicago and Milwaukee. The goal of this mission was to capture how these emissions
are influenced by coastal dynamics, especially in the presence of lake breeze events. The yellow plan
(Figure 2.4.2, left) maps the entire extent of the western shore between the two supersites. The other
two plans focused on each supersite individually and the smaller areas of these plans allowed for
multiple repeated rasters per flight (up to three times over Sheboygan and two times over Zion).

Quick look NO₂ retrievals were prepared during LMOS 2017 within 24-48 hours of a flight. Due
to this timely turnaround, the science team was able to get a better grasp on what GeoTASO could
capture and flight plans were sometimes adjusted slightly from the ones shown in Figure 2.4.2. These
adjustments included adding/subtracting flight lines and shifting the flight lines to cover areas
forecasted to best accomplish the LMOS 2017 science objectives.
Figure 2.4.2. Flight plans within the LMOS ‘playbook’ separated by coastal mapping surveys of the western shore (left) and emissions sampling over Chicago and Milwaukee (right). Red targets indicate the location of Pandora Spectrometers used for validating GeoTASO NO\textsubscript{2} retrievals.

**NO\textsubscript{2} Retrieval**

NO\textsubscript{2} differential slant columns (DSCs) were retrieved from GeoTASO spectra via Differential Optical Absorption Spectroscopy (DOAS) within the spectral window of 435-460 nm. The DOAS technique provides a column amount relative to a reference scene, which ideally is unpolluted and cloud-free. The resulting DSCs of each observation can be thought of as incremental columns relative to the reference spectrum location and time, primarily showing contributions from local pollution sources. The DSCs are also sensitive to changes in the stratosphere, however the stratospheric column is relatively constant over the LMOS domain and the influence on the DSCs is a function of solar zenith angle. The native spatial resolution for these observations is 250 m x 250 m. From there, co-adding to larger spatial resolution increases signal-to-noise ratio (SNR). For this report, we’ve selected 750 m x 750 m spatial resolution as the best balance between improving the SNR and conserving fine spatial resolution. All the results below and in the Appendix are shown at this spatial resolution.

The NO\textsubscript{2} DSC data are available from the NASA Archive (https://www-air.larc.nasa.gov/missions/lmos/index.html) and mapped in the Appendix. The first publicly available GeoTASO NO\textsubscript{2} differential slant column data from LMOS was released in August 2018.

2.4.3. **Results and Discussion**

Figure 2.4.3 shows how the preliminary NO\textsubscript{2} DSCs compare to the coincident retrievals of the network of ground-based Pandora Spectrometers (Herman et al., 2009) installed along the western
shore of Lake Michigan during LMOS 2017 (shown in Figure 2.4.2). Since Pandora’s measurement reflects both tropospheric and stratospheric contributions, for a troposphere only comparison, the Pandora stratospheric contribution is estimated and subtracted. The stratospheric contribution was estimated using OMI Stratospheric Vertical Column over the Lake Michigan region during the time period of the study multiplied by Pandora’s AMF. Circles show the average GeoTASO DSC within a 750-m radius of the Pandora site and the average Pandora data within 5 minutes of GeoTASO’s overpass. Horizontal bars show standard deviation of GeoTASO DSCs within the 750-m radius. Vertical bars show the standard deviation of Pandora data within the ± 5-minute coincidence window.

The plots show two different ranges. Figure 2.4.3 (left) includes one large outlier over Schiller Park on June 1st (>50x10^{15} molecules cm^{-2}). Both instruments captured this occurrence. All coincidences, including the one outlier, correlate quite well (r^2=0.89). When excluding the outlier, correlation is still quite high with r^2=0.67 and slope near 1 (Figure 2.4.3 right). The points with large variance bars are also from the Schiller Park site in Chicago, which is located near O’Hare airport and likely experiences very localized spatiotemporal variability of NO\textsubscript{2} due to both ground and air traffic. The rest of the sites were far less polluted and stayed below 10x10^{15} molecules cm^{-2}. These results provide confidence that GeoTASO captured the magnitude of NO\textsubscript{2} columns within the LMOS 2017 study region.

GeoTASO captured consistent spatial patterns from area and point emissions sources during the LMOS 2017 flights. While examples of all flights are found in the Appendix, Figure 2.4.4 shows a few zoomed in examples from Chicago (left), Pleasant Prairie Power Plant (lower right), and Sheboygan (upper right). Along the more rural western shore of the lake, the large power plants were often observed by GeoTASO as distinct plumes. The areal extent of these plumes varied widely from day to day. The typical spatial pattern in Chicago showed peaks near downtown and the industrial area in NW
Indiana. This pattern was consistent through most of the Chicago flights, however the magnitude and extent of these plumes were dependent on meteorology and day of week. Figure 2.4.5 shows the difference between consecutive weekend/weekday sampling over the Chicago area on June 18 and 19, 2017. Also shown on this figure are the in situ NO$_2$ vertical profiles from the Scientific Aviation aircraft offshore and downwind of Chicago. Both days had similar meteorological conditions and spatial patterns. As Sunday transitioned into the work week on Monday, there was a large increase in the magnitude of NO$_2$ columns over the Chicago metropolitan area. On Monday June 19 the enhancement in the NO$_2$ column was confined to the lowest 500-600m of the atmosphere, with one profile measured by the in situ aircraft approaching $12 \times 10^{15}$ molecules cm$^{-2}$.

Figure 2.4.4. GeoTASO NO$_2$ differential slant column maps for May 22 and June 15, 2017. DSC maps: May 22nd Chicago Raster during mid-morning (left). June 15th morning raster in Sheboygan (hole in data due to clouds) (upper right). June 7th morning raster over Pleasant Prairie (lower right). The left color bar corresponds to the Chicago map, and the right color bar corresponds to both maps on the right.
Future work will include processing DSCs into vertical columns. This requires the calculation of the air mass factor (AMF), which is defined as the ratio of the slant column/vertical column. AMFs are calculated according to Palmer et al. (2001) as the product of the normalized vertical distribution of NO$_2$ (modeled by University of Iowa’s WRF-Chem simulations for the duration of the study period) and scattering weights calculated by VLIDORT (Spurr, 2006). Cloud contamination can easily be filtered by radiance levels observed by GeoTASO. These data can be used for assessing emission inventories, air quality modeling evaluation, as well as linking how local and transported emissions can influence the air quality along the coast of Lake Michigan.

2.5. Scientific Aviation Measurements

2.5.1. Overview

Scientific Aviation (SA) was contracted by the Electric Power Research Institute (EPRI) to participate in LMOS 2017 with airborne in situ profiling of O$_3$, NO$_2$, CO$_2$, CH$_4$, altitude, T, RH, winds, and pressure. The majority of the SA flights were conducted in close coordination with the NASA airborne remote sensing measurements and provided vertical profiles over and offshore from selected ground sites (Sheboygan and Zion), offshore profiles east of Milwaukee and Chicago, and onshore background profiles. Low level flight legs were also conducted within the marine boundary layer.

2.5.2. Methods

In situ NO$_2$ measurements were conducted using an Aerodyne cavity attenuated phase shift (CAPS) NO$_2$ monitor with a sensitivity (S/N=3) less than 1.0 ppbv for 1 second and 0.1 ppbv for 10 second
averages. \( \text{O}_3 \) was measured with a 2B Model 202 monitor with a precision (1-sigma, rms noise) of 1.5 ppbv for \( \text{O}_3 \) less than 75 ppbv, or 2% for \( \text{O}_3 \) greater than 75 ppbv. A Picarro instrument was used to measure \( \text{CO}_2/\text{CH}_4 \) with a precision (1-sigma over 30 seconds) of less than or equal to 200 ppbv for \( \text{CO}_2 \) and less than or equal to 2 ppbv for \( \text{CH}_4 \). Temperature and relative humidity (RH) were measured with a Vaisala HMP60 probe with a temperature accuracy of +/- 0.5 Celsius over temperature range of 10-30 Celsius, and a relative humidity accuracy of +/- 3% for 0-90% and +/- 5% for 90-100% relative humidity over a temperature range of 0-40 Celsius.

SA flew a total of 21 flights during LMOS 2017 plus 1 post mission flight on June 24, 2017, near Holland, MI. Each flight included ascending and descending spirals at predetermined waypoints from near 60 m AGL over water and from 1000 m AGL over land to 3 km with low level legs in between the spirals (Figure 2.5.1).

**Results and Discussion**

The two SA flights that occurred on days with ozone exceedances at both the Sheboygan KA monitor and the Zion monitor will be discussed here. Figure 2.5.2 shows \( \text{O}_3 \), \( \text{NO}_2 \), RH, and temperature for the SA flight on June 2. The SA aircraft took off from the Sheboygan County Municipal Airport at 19 UTC (noon CDT) and conducted ascending/descending spirals at Spaceport Sheboygan followed by ascending/descending spirals at the Sheboygan KA offshore waypoint. The SA aircraft then headed south and conducted low level profiling of the marine boundary layer past the Milwaukee offshore waypoint.
to the Zion offshore waypoint. Ascending/descending spirals were conducted at the Zion offshore and
onshore waypoints and then the SA aircraft headed north towards the Oak Creek Power Plant waypoint.
The SA aircraft proceeded northeast to the Milwaukee offshore waypoint and conducted
ascending/descending spirals before heading to the northwest past the Port Washington Power Plant
waypoint. The SA aircraft proceeded northeast and conducted ascending/descending spirals at the
Sheboygan KA waypoint before returning to the Sheboygan County Municipal airport at 23:48 UTC
(6:48pm CDT). Shallow layers of higher RH and colder temperatures at the Sheboygan KA and
Milwaukee offshore waypoints, as well as during the low level leg between the Milwaukee offshore and
Port Washington Power Plant waypoint, occurred during periods where the SA aircraft sampled the
shallow marine boundary layer. Hourly ozone ranged from 90-110 ppbv and NO\textsubscript{2} ranged from 4 to over
20 ppbv during these marine boundary layer sampling periods. The highest ozone measurements
occurred near the lake surface during the low level leg between the Milwaukee offshore spiral and the
Oak Creek Power Plant waypoint.
Figure 2.5.2. Three-dimensional (latitude, longitude, altitude) view of Scientific Aviation Flight on June 02, 2017, showing in situ \(O_3\) (upper left, ppbv), \(NO_2\) (upper right, log10(ppbv)), relative humidity (RH) (lower left, %) and temperature (lower right, K). Waypoints are indicated by red “+” symbols, land is indicated by black lines. The Sheboygan Haven WDNR monitor is the northernmost waypoint and Zion is the southernmost waypoint.

Figure 2.5.3 shows \(O_3\), \(NO_2\), RH and temperature for the SA flight on June 11. The SA aircraft departed at approximately 18 UTC (1:00pm CDT) and conducted ascending/descending spirals at the Sheboygan Haven, Sheboygan and Sheboygan offshore waypoints and then conducted a low level leg within the marine boundary layer between Sheboygan and Sheboygan KA offshore waypoints. Ascending/descending profiles were conducted at off-shore and onshore at Sheboygan KA followed by a low level leg to the Sheboygan background waypoint where a final ascending/descending spiral was performed prior to returning to Sheboygan County Municipal airport slightly prior to 22 UTC (5:00pm CDT). Shallow layers of higher RH and colder temperatures were observed within the marine boundary layer during the low level leg between Sheboygan offshore and at the Sheboygan KA offshore. Ozone...
mixing ratios were above 60 ppbv throughout the lowest 3 km except for a layer of slightly lower O₃ between 2 and 3 km. Ozone below 1km remained in excess of 70 ppbv except for the low level legs and spirals at Sheboygan Haven. Highest ozone was encountered following the descending spiral at the Sheboygan KA offshore waypoint where it reached up to 90 ppbv near the surface. NO₂ was generally less than 1 ppbv during most of the offshore flight legs except for very narrow enhancements at the beginning and end of the Sheboygan spirals. CO₂ mixing ratios in excess of 410 ppmv within these narrow NO₂ enhancements suggest that the aircraft sampled the plume from the Edgewater power plant, which is located between the Sheboygan and Sheboygan KA waypoints. A broad region of NO₂ between 1-2 ppbv was observed below 1 km during the Sheboygan Haven spiral and during the low level legs during and after the Sheboygan background spiral.

Figure 2.5.3. Three dimensional (latitude, longitude, altitude) view of Scientific Aviation Flight on June 11, 2017 showing in situ O₃ (upper left, ppbv) NO₂ (upper right, log10(ppbv)), relative humidity (RH) (lower left, %) and temperature (lower right, K). Waypoints are indicated by red “+” symbols, land is indicated by black lines. The Sheboygan Haven WDNR monitor is the northernmost waypoint and Zion is the southernmost waypoint.
2.6. Mobile Platform Measurements

2.6.1. Overview

Two mobile platforms were deployed during LMOS 2017 to investigate the chemical gradients between on shore stationary monitoring sites. The routes driven were to investigate E-W gradients and some N-S gradients in ozone concentrations (e.g., Figure 2.6.1). The EPA Region 5 Geospatial Monitoring of Air Pollution (GMAP) platform focused on the area around the Wisconsin-Illinois stateline, extending northward into southeastern Wisconsin. The UW-Eau Claire platform studied more northern lakeshore areas in Sheboygan and Ozaukee counties in Wisconsin.

2.6.2. Methods

GMAP was used to measure ozone concentrations on June 6, 8, 12, and 13 to better understand how ozone is produced and transported over Lake Michigan. A TEI49CPS was used to measure ozone and streamed to a Campbell Scientific CR850 data logger. Meteorology and GPS coordinates were measured and logged from the existing GMAP platform. The time stamp from the data logger was paired with the GMAP computer. The TEI49CPS was placed in the rear seat of the GMAP vehicle to maintain a temperature-controlled environment and minimize vibration, and a ¼ inch Teflon line was added to the GMAP mast. The 49CPS was checked against the US EPA Region 5 SRP SN6 before and after the study. The check followed standard procedures on “Standard Operating Procedures For Conducting Verifications Of Level 2 Ozone Transfer Standards” (R5-ARD-0005-r1). The criteria for acceptable results were determined for each point to be within 10.0%. All data points fell within the acceptable criteria pre- and post-campaign. Stationary collocation comparisons between the Zion ozone site (17-097-1007) and the GMAP ozone readings are included in Table 2.6.1.
Figure 2.6.1. Southern transects driven by the GMAP van. Transect segments are color coded, named, and numbered. See arrows for the number and overall direction of each segment. Arrow numbers correspond to the following transect segments: 1) West from Zion Illinois Beach State Park on 21st St., 2) East toward Zion Illinois Beach State Park on 21st St., 3) Illinois Beach State Park to Chiwaukee Prairie, 4) Chiwaukee Prairie to Kenosha, 5) Kenosha Lakeshore to Kenosha O3 monitor, 6) Kenosha O3 monitor to Lakeshore, 7) Kenosha Lakeshore to Racine O3 monitor, 8) Racine O3 monitor to Windpoint, 9) Windpoint to Belmar Ave.

Table 2.6.1. GMAP Zion collocation comparisons

<table>
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<tr>
<th>Date</th>
<th>Time (CDT)</th>
<th>GMAP Reading</th>
<th>Zion Reading</th>
<th>PPB Diff vs Zion</th>
<th>Percent Diff</th>
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<td>6/6/2017</td>
<td>10:18</td>
<td>32.3</td>
<td>31.8</td>
<td>0.5</td>
<td>1.6%</td>
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<td>6/7/2017</td>
<td>9:41</td>
<td>33.0</td>
<td>32.0</td>
<td>1.0</td>
<td>3.1%</td>
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<tr>
<td>6/8/2017</td>
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<td>45.2</td>
<td>45.5</td>
<td>-0.3</td>
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<tr>
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<td>57.3</td>
<td>0.0</td>
<td>0.0%</td>
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<tr>
<td>6/13/2017</td>
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<td>45.5</td>
<td>45.1</td>
<td>0.4</td>
<td>0.9%</td>
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</table>

The second mobile platform deployed for LMOS 2017 was the UW-Eau Claire automobile platform, equipped with a 2-B Technologies Personal Ozone Monitor and a handheld Kestrel weather sensor. This platform made regular measurement stops between the Grafton WDNR site and the Sheboygan Spaceport site to investigate N-S and shallow E-W gradients. The ozone measurements were taken at a height of 3 m for at least 5 minute increments at each location. The 15 stops are described in Table 2.6.2. On June 2, 3, 12, 13, and 17 the UW-Eau Claire vehicle drove the route of some combination of the stops (e.g. Stops 1-13 on June 2, Stops 10-15 multiple times on June 3 to correspond to ship and aircraft measurements made concurrently). Data from the ozone monitor was obtained using 1 minute averaged signal. The duty cycle of the Personal Ozone Monitor subtracts a background (scrubbed ozone) UV-signal from a whole air sample, which accounts for the UV absorption of water. However, drastically...
changing humidity can lead to higher standard deviations in this instrument, which is why the vehicle chose to stop at a single location to measure ozone.

Table 2.6.2. UW-Eau Claire automobile measurement stops

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>Site name</th>
<th>Colocation</th>
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<td>WI-DNR</td>
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<td>3 Western and Division</td>
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<td>4 Country Inn</td>
<td></td>
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<td>43.4347</td>
<td>-87.8338</td>
<td>5 High Point Beach Ln</td>
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<td>43.4993</td>
<td>-87.7937</td>
<td>6 Harrington Beach</td>
<td></td>
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<td>7 Harrington Beach Park</td>
<td>WI-DNR</td>
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<tr>
<td>43.5576</td>
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<td>8 Amsterdam Park</td>
<td></td>
</tr>
<tr>
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<td>-87.7497</td>
<td>9 Foster Road</td>
<td></td>
</tr>
<tr>
<td>43.6673</td>
<td>-87.7160</td>
<td>10 Kohler-Andrae Dunes</td>
<td>WI-DNR</td>
</tr>
<tr>
<td>43.6728</td>
<td>-87.7273</td>
<td>11 Straight out W of KA</td>
<td></td>
</tr>
<tr>
<td>43.6735</td>
<td>-87.7206</td>
<td>12 Corner near KA entrance</td>
<td></td>
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<tr>
<td>43.7079</td>
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<td></td>
</tr>
<tr>
<td>43.7459</td>
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<td>14 Spaceport</td>
<td>LMOS Spaceport Supersite</td>
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<tr>
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<td>43.7614</td>
<td>-87.7490</td>
<td>16 HSHS St. Nicholas Hospital</td>
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</tbody>
</table>

2.6.3. Results and Discussion

Figure 2.6.2 through Figure 2.6.4 are timeseries of the measured ozone concentrations over individual transects on different days during LMOS 2017. Gradients inland were observed on June 8th and 12th. On June 8th, when ozone concentrations were 50-70 ppbv, the gradient concentration increased inland (Figure 2.6.2). On June 12th, when ozone levels were higher (50-80 ppbv), the ozone gradient decreased inland, particularly in the nearly 6 mile transect from the Kenosha ozone monitor to the lake shore (Figure 2.6.3, transect 6) and Windpoint to Belmar (Figure 2.6.4, transect 9), with a nearly 30 ppbv gradient towards Lake Michigan.
Figure 2.6.2. Ozone concentration (ppbv) for GMAP Zion Illinois Beach State Park 21st St Transect – West (Transect 1) on June 8, 2017 as a function of time (UTC).

Figure 2.6.3. Ozone concentration (ppbv) for GMAP Kenosha O₃ monitor to Lakeshore (Transect 6) on June 12, 2017 as a function of time (UTC).
Figure 2.6.4. Ozone concentration (ppbv) for GMAP Windpoint to Belmar Ave Transect (Transect 9) on June 12, 2017 as a function of time (UTC).

The observations from the UW-Eau Claire mobile monitor reflected increasing ozone concentrations through the afternoon of June 2 (Figure 2.6.5). The spatial gradient moving north along the lakeshore observed in Figure 2.6.5 does not necessarily reflect a north-south gradient, but is interpreted as a growth in ozone abundance over the afternoon in which the measurements were taken, noting the time when the automobile started at the southern sites and when the automobile arrived in Sheboygan.

On June 3, several trips were conducted between the Sheboygan supesite and Kohler-Andrae State Park WDNR site because of the concurrent ship and aircraft measurements on that day. Figure 2.6.6 depicts the ozone measurements from the multiple trips with an arrow which demonstrates the general direction of the automobile. On this day, a very shallow incursion of lake air came on land later in the afternoon, which was observed as higher ozone (>50 ppbv) and lower ambient temperatures than sites inland. Panel 4 of Figure 2.6.6 shows that sites inland from the Sheboygan shoreline supersite measured ozone 20 ppbv less than that observed at the shoreline. One interesting observation from that day was the onset of the lake breeze incursion. At the Kohler-Andrae shoreline location, observations of ozone remained higher throughout the afternoon near 60 ppbv. At 21:20 UTC (4:20pm CDT) the incursion of lake air on land started to occur, where inland observations of ozone were high on the E-W highway directly outside of the Kohler-Andrae State Park entrance (measurement of 55 ppbv), but a measurement taken on a N-S street surrounded by trees remained lower at 42 ppbv measured within minutes of each other. The temperature readings at these two sites were also different, with colder air correlating to the higher ozone measurements inland. This observation shows the potential for complex flow patterns within the lake breeze incursion. There is not enough evidence from this monitoring.
platform to indicate that this was a lake breeze driven event. By 5:30-6:30 pm local time, the ozone measurements at sites 10-13 were ~60 ppbv with less sharp gradients at those sites, but a 20 ppbv drop off to sites 14-15 farther inland.

Figure 2.6.5. UW-Eau Claire automobile platform ozone measurements from June 2, 2017. Times are given in local time (CDT) and each point is a 5 minute average of 1 minute points ± 1 standard deviation.
Figure 2.6.6. UW-Eau Claire automobile platform ozone measurements from June 3, 2017. Times are given in local time (CDT) and each point is a 5 minute average of 1 minute points ± 1 standard deviation.
**Section 3. Summary of LMOS Model/Measurement Evaluations**

Meteorological and photochemical models have been used for forecasting, flight planning, and analysis of LMOS 2017 observations. As shown in Table 3.1, four models have been used for either forecasting/planning, and for post-study interpretation and analysis. Three of the models have results in this report. The fourth modeling system results will be in future reports.

**Table 2.6.1. Summary of forecast models used during LMOS.**

<table>
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<tr>
<th>Model</th>
<th>Group and Report Section</th>
<th>Horizontal Resolution</th>
<th>Chemistry?</th>
<th>Coupled Air Quality and Met?</th>
<th>Purposes</th>
</tr>
</thead>
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<td>Yes</td>
<td>Yes</td>
<td>Forecast; Post-Analysis (Sensitivity to Configuration and Emissions)</td>
</tr>
<tr>
<td>NWS, NAQFC NAM-CMAQ (operational CMAQ 5.0.2)</td>
<td>NWS/NOAA; section 3.2</td>
<td>12 km</td>
<td>Yes</td>
<td>No</td>
<td>Forecast; Evaluation of Operational Forecast</td>
</tr>
<tr>
<td>WRF v3.8</td>
<td>Univ. of Wisc.; section 3.3</td>
<td>4 km &amp; 12 km (in this report; 1.3 km in future reports)</td>
<td>No</td>
<td>NA</td>
<td>Sensitivity of Meteorology to Configuration</td>
</tr>
<tr>
<td>WRF v3.8, CMAQ v5.2.1</td>
<td>Univ. of Wisc.</td>
<td>4 km &amp; 1.3 km (in future reports)</td>
<td>Yes</td>
<td>No</td>
<td>Post-Analysis</td>
</tr>
</tbody>
</table>

The University of Iowa modeling group developed a WRF-Chem forecasting framework at 4 km horizontal resolution to support the flight planning during LMOS 2017, and has extended that modeling effort to post-analysis sensitivity studies. WRF-Chem is a widely used regional modeling system that simultaneously solves meteorological and photochemical equations in a coupled fashion. The coupled architecture of WRF-Chem makes it well suited for air quality forecasting, reduces memory and storage requirements relative to uncoupled models, and allows feedbacks between air quality and meteorological variables, such as aerosol particles influencing radiation.

Operational air quality forecasts from the National Weather Service (NWS) National Air Quality Forecasting Capability ([https://airquality.weather.gov/](https://airquality.weather.gov/) and [https://www.weather.gov/sti/stimodeling_airquality_predictions](https://www.weather.gov/sti/stimodeling_airquality_predictions)) were also used to support daily flight planning activities during LMOS 2017 and have been compared to observations in post-analysis. The operational forecast is based on NAM (meteorology) and CMAQ (photochemical grid model).
An additional LMOS-related modeling activity is focused on optimization of the WRF meteorological modeling system for prediction and regulatory scenario modeling of lake-breeze ozone events in the region. Various configurations and resolutions are being explored in order to provide a best configuration for future modeling. This can improve future products from WRF-Chem as well photochemical models driven by WRF meteorology (i.e., WRF + CMAQ, WRF + CAMx, etc.).

The optimized WRF configuration (above) is being used to drive WRF-CMAQ simulations by the University of Wisconsin-SSEC team, and those results will be presented in future reports.

3.1. WRF-CHEM Model

The University of Iowa modeling group developed a WRF-Chem forecasting framework to support the flight planning during LMOS 2017 and extended this framework for post-campaign analysis. This section describes the details of WRF-Chem forecasting and modeling system and provides preliminary evaluations of model and emission performance.

3.1.1. WRF-Chem domain

A single domain WRF-Chem v3.6.1 was used to simulate the atmospheric transport and chemistry around Lake Michigan during LMOS 2017. Figure 3.1.1 illustrates the domain and the underlying terrain map. The domain covers Minnesota, Iowa, Missouri, Wisconsin, Illinois, Michigan, Indiana, and Ohio (37.6-48.8°N and 95.45-81.46°E) with 4 km x 4 km horizontal resolution or 310x260 grids. The domain has 53 vertical levels with domain top at 50hPa (~11 layers within the lowest 1 km). Meteorological initial and boundary fields were retrieved from the National Center for Environmental Prediction (NCEP) Global Forecasting System (GFS) (National Centers for Environmental Prediction, National Weather Service, NOAA 2000). European Centre for Medium-Range Weather Forecasts Monitoring Atmospheric Composition and Climate reanalysis (MACC) (Inness et al. 2013) was used as chemical boundary conditions.

Figure 3.1.1. WRF-Chem domain: A. Chicago, B. Zion, C. Kenosha, D. Kohler Andre
Table 3.1 summarizes the major WRF-Chem configurations used for the forecast and post-analysis. These configurations remain constant for all WRF-Chem simulations.

Table 3.1. Summary of WRF-Chem configuration

<table>
<thead>
<tr>
<th>Category</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Horizontal resolution</strong></td>
<td>4km</td>
</tr>
<tr>
<td><strong>Vertical resolution</strong></td>
<td>53 layers (11 within the lowest 1km)</td>
</tr>
<tr>
<td><strong>PBL Scheme</strong></td>
<td>MYNN3</td>
</tr>
<tr>
<td><strong>Surface layer</strong></td>
<td>MYNN surface layer</td>
</tr>
<tr>
<td><strong>Land Surface</strong></td>
<td>5-layer thermal diffusion</td>
</tr>
<tr>
<td><strong>Microphysics</strong></td>
<td>Morrison double-moment scheme</td>
</tr>
<tr>
<td><strong>Shortwave radiation</strong></td>
<td>Goddard shortwave</td>
</tr>
<tr>
<td><strong>Longwave radiation</strong></td>
<td>RRTMG scheme</td>
</tr>
<tr>
<td><strong>Cumulus Parametrization</strong></td>
<td>Grell-Freitas scheme</td>
</tr>
<tr>
<td><strong>Gas-phase chemistry</strong></td>
<td>RACM-ESRL</td>
</tr>
<tr>
<td><strong>Biogenic emission</strong></td>
<td>MEGAN</td>
</tr>
<tr>
<td><strong>Lightening</strong></td>
<td>OFF</td>
</tr>
<tr>
<td><strong>Land use</strong></td>
<td>USGS</td>
</tr>
<tr>
<td><strong>SST</strong></td>
<td>No SST update</td>
</tr>
</tbody>
</table>

Gas phase chemistry in WRF-Chem was simulated using the Regional Atmospheric Chemistry Mechanism using Earth System Research Laboratory (RACM-ESRL) (Stockwell et al. 1997) with an updated reaction table for gas phase chemistry. RACM-ESRL (Kim et al. 2009) is an updated version of the RACM mechanism and includes 23 photolysis and 221 chemical reactions (Ahmadov et al. 2015). The Modal Aerosol Dynamics Model/Secondary Organic Aerosol Model (MADE/SORGAM) was used to simulate aerosol thermodynamics and chemistry.

Anthropogenic emissions for the WRF-Chem simulation were estimated with the 2011 National Emission Inventory (NEI-2011) with 4 km x 4 km horizontal and hourly temporal resolution regridded to the LMOS 2017 modeling domain. In the base anthropogenic emission inventory (NEI11-0.72 NOx) NOx emissions were reduced by 28% to account for the reduction in NOx emission from 2011 to 2017 (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data). Reductions were applied uniformly (proportional to NEI-2011 emission) across the domain (Fig. 3.1.1). Actual reductions would have a non-uniform spatial profile.

We used the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 to estimate biogenic emissions (Guenther et al. 2012). The base runs used anthropogenic hydrocarbons from NEI 2011. Adjustment of NEI 2011 to account for documented reductions in bottom up anthropogenic hydrocarbons was not performed. Different emissions scenarios (based on NEI-2011) were tested to capture the sensitivity of ozone concentrations to NOx, hydrocarbon (HC), and isoprene emissions. Table 3.1.2 summarizes the emissions scenarios designed for this study.
### Table 3.1.2. Emission scenarios designed for LMOS forecasting and post-analysis system

<table>
<thead>
<tr>
<th>Name</th>
<th>Mode</th>
<th>Emission</th>
<th>Period and description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR_base</td>
<td>Forecast</td>
<td>NEI11-0.72NOX</td>
<td>Duration of campaign/Daily re-initialization</td>
</tr>
<tr>
<td>FR_pert</td>
<td>Forecast</td>
<td>NEI11-0.22NOX</td>
<td>Duration of campaign/Daily re-initialization</td>
</tr>
<tr>
<td>0.72NOx (base)</td>
<td>Post-analysis</td>
<td>NEI11-0.72NOX</td>
<td>05-20 to 06-22 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.22NOx</td>
<td>Post-analysis</td>
<td>NEI11-0.22NOX</td>
<td>05-30 to 06-04 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.72NOx_5HC</td>
<td>Post-analysis</td>
<td>NEI11-0.72NOx-5HC</td>
<td>05-30 to 06-22 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.72NOx_10HC</td>
<td>Post-analysis</td>
<td>NEI11-0.72NOx-10HC</td>
<td>05-30 to 06-05 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.5NOx_5HC</td>
<td>Post-analysis</td>
<td>NEI11-0.5NOx-5HC</td>
<td>05-30 to 06-04 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.5NOx_2HC</td>
<td>Post-analysis</td>
<td>NEI11-0.5NOx-2HC</td>
<td>05-30 to 06-04 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.72NOx_2iso</td>
<td>Post-analysis</td>
<td>NEI11-0.72NOx-2isop</td>
<td>05-20 to 06-21 Daily initialization of met at 00Z</td>
</tr>
<tr>
<td>0.72NOx_MOZ</td>
<td>Post-analysis</td>
<td>NEI11-0.72NOx</td>
<td>05-30 to 06-03 Daily initialization of met at 00Z MOZART chem mechanism</td>
</tr>
</tbody>
</table>

#### 3.1.2. University of Iowa forecast system

During LMOS 2017 WRF-Chem forecasts were used as aids during the flight planning briefings. Two separate 72-hr forecasts (simulation start time 6Z) were initialized every evening and the workflow is depicted in Figure 3.1.2. The NEI11-0.72NOx emissions were used in the base simulation (FR_base). The NOx emissions were further reduced by 50% (total reduction of 78%) and used in a second forecast simulation to account for uncertainties of NOx emissions in the NEI-2011 and to test the sensitivity of ozone concentrations to NOx. MACC reanalysis data were used for the chemical initial and boundary conditions for each forecast.
Several analysis products were made available during LMOS 2017 and uploaded to the University of Iowa LMOS website: https://bio.cgrer.uiowa.edu/LMOS/. Spatial plots of 11 chemical species, 4 columns, and 10 meteorological products were available at four pressure levels and the full domain or zoomed onto Lake Michigan. The cross-sectional plots with cloud and NO$_2$ contours overlaid on color contours of 10 chemical species were produced for three west-east and two north-south transects of the domain. Also, 11 ground sites were chosen to show curtain plots and time series graphs of nine chemical species, relative humidity, and temperature. Examples of these products are shown in Figure 3.1.3.

3.1.3. Post-analysis

This section summarizes the WRF-Chem simulations. The goals of the analyses presented here are to evaluate the ability of the model and emissions inventory to reproduce observations and to test the sensitivity of simulated ozone concentrations to changes in NO$_x$, HC, and isoprene emissions. The model was evaluated against observations from the Zion supersite, hourly ozone mixing ratios, hourly PM$_{2.5}$, and hourly METAR station meteorology downloaded using the EPA Remote Sensing Information Gateway (RSIG, ozone, PM$_{2.5}$, and metar fields, RSIG3D version 20170410, www.epa.gov/rsig), and in
situ observations from Scientific Aviation flights. Table 3.1.2 is a summary of the emission scenarios tested for the WRF-Chem sensitivity analyses. Meteorological fields in the post-analysis run were re-initialized with NCEP meteorological fields every 24 hours (starting 00Z or 19:00 local time). Each cycle simulated 30 hours and the first 6 hours were discarded as a spin-up.

**Meteorological performance**

Preliminary evaluation of meteorological performance indicates that WRF-Chem successfully captured much of the synoptic variability of onshore flow. Performance is shown for the reanalysis configuration of the model, not for the forecast version used for flight planning. The model generally reproduced the temperature observations but frequently under-predicted observed maximum temperatures. Observed wind speed and direction were also generally reproduced by the model. Table 3.1.3 includes a summary of wind speed and direction statistics at five different stations for the period of 2017-05-22 to 2017-06-21. On average, the model better captured wind speed at inland sites and over-predicted wind speed at sites closer to the shore such as Zion, Sheboygan, and Manitowoc. The modeling team is continuing to investigate the sensitivity of meteorological skill to selection of boundary condition, initial condition, land surface model parameterization, and nudging. The goal is to reduce transport errors on ozone episode days as much as possible, so that model-observation errors can be interpreted mainly as a function of non-transport model processes including chemistry and emissions. Commonly used meteorological performance benchmarks such as those in Emery et al. (2001) need to be interpreted carefully in the context of coastal ozone modeling performance. Depending on the temporal and spatial averaging choices and met station selection, models may appear skilled in terms of traditional benchmarks, yet not be sufficient for ozone modeling skill.

Table 3.1.3. Summary of wind speed and statistics at along the shore (Zion, Sheboygan, Manitowoc) and inland (Midway and O’Hare) stations for the duration of 2017-05-22 to 2017-06-21.

<table>
<thead>
<tr>
<th>All Days</th>
<th>wspd avg (m/s)</th>
<th>wspd std (m/s)</th>
<th>wdir avg (deg)</th>
<th>wdir std (deg)</th>
<th>avg U (m/s)</th>
<th>avg V (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midway (41.8,-87.9)</td>
<td>Model 4.22</td>
<td>1.82</td>
<td>250.71</td>
<td>78.54</td>
<td>1.67</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>OBS 4.45</td>
<td>2.32</td>
<td>249.41</td>
<td>89.95</td>
<td>1.13</td>
<td>0.43</td>
</tr>
<tr>
<td>O’Hare (42.0,-87.9)</td>
<td>Model 4.28</td>
<td>1.86</td>
<td>255.49</td>
<td>76.56</td>
<td>1.81</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>OBS 4.28</td>
<td>2.47</td>
<td>262.50</td>
<td>89.66</td>
<td>1.05</td>
<td>0.14</td>
</tr>
<tr>
<td>Zion (42.4,-88.0)</td>
<td>Model 5.10</td>
<td>2.14</td>
<td>257.47</td>
<td>80.51</td>
<td>2.03</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>OBS 3.22</td>
<td>2.29</td>
<td>228.44</td>
<td>93.80</td>
<td>0.58</td>
<td>0.52</td>
</tr>
<tr>
<td>Sheboygan (43.8,-87.85)</td>
<td>Model 5.15</td>
<td>2.26</td>
<td>264.24</td>
<td>74.86</td>
<td>2.35</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>OBS 3.84</td>
<td>2.50</td>
<td>248.62</td>
<td>88.41</td>
<td>1.16</td>
<td>0.45</td>
</tr>
<tr>
<td>Manitowoc (44.1,-87.7)</td>
<td>Model 5.09</td>
<td>2.23</td>
<td>264.12</td>
<td>79.36</td>
<td>2.16</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>OBS 3.61</td>
<td>2.32</td>
<td>243.10</td>
<td>90.58</td>
<td>1.07</td>
<td>0.54</td>
</tr>
</tbody>
</table>
Ozone and NO\textsubscript{x} performance

This section summarizes the WRF-Chem performance through comparison with ozone observation from IL EPA monitors at Zion (42.5N, -87.81W) and Chicago (42.1N, -87.9W) and NO\textsubscript{x} observations at the LMOS 2017 Zion supersite. The appendix includes an evaluation of WRF-Chem performance in capturing ozone, NO\textsubscript{2}, and relative humidity along the Scientific Aviation flights. WRF-Chem generally reproduced the diurnal variability in observed ozone, however consistently under-predicted the observed maximum ozone values. NO\textsubscript{x} was over-predicted in the base simulation. During the last two weeks of the campaign (from June 10 to June 22) WRF-Chem had high biases for NO\textsubscript{x}. Figure 3.1.4 shows time series of modeled ozone and NO\textsubscript{x} vs. observations collected during LMOS 2017.
Figure 3.1.4. Samples of WRF-Chem model output and sensitivity. LEFT panels (A, B, & C) Model output (red) vs. observations (black) for ozone in Chicago and Zion, and for NOx at Zion. MIDDLE panels (D, E, & F) sensitivity of ozone (D, E) and NOx (F) to hydrocarbon emissions. RIGHT panels (G, H, & I) sensitivity of ozone (G, H) and NOx (I) to changes in NOx emissions.
The sensitivity of ozone to changes in emissions was tested by modifying NO\textsubscript{x}, HC, and isoprene emissions. The sensitivity simulations were conducted for a short period (May 30 – June 4) to focus on the June 2 high ozone event. During this event, WRF-Chem showed an underestimation bias in ozone of \(~50\) ppbv at Zion and \(~30\) ppbv at the Chicago site. In a reduced NO\textsubscript{x} sensitivity, NO\textsubscript{x} emissions (from all sources) were decreased by 50\% (0.22NO\textsubscript{x}). This sensitivity resulted in \(~20\) ppbv increase in ozone concentrations at Zion site and \(~10\) ppbv reduction in ozone concentrations at the Chicago site. A pair of HC sensitivities increased the HC emissions across the board by a factor of 5 (5HC) and 10 (10HC). Increasing the HC emissions by a factor of 5 (0.72NO\textsubscript{x} 5HC and 0.5NO\textsubscript{x} 5HC) increased the simulated ozone by \(~50\) ppbv at Zion and \(~5\) ppbv at the Chicago site. Increasing the HC emissions by a factor of 10 (0.72NO\textsubscript{x} 10HC) produced additional simulated ozone at Zion but resulted in no significant change in ozone at the Chicago site (Figure 3.1.4). In another sensitivity experiment, biogenic isoprene emissions were doubled to assess the impact on predicted ozone. This had only a small impact on peak ozone concentrations. Ozone concentrations during the afternoon and evening of June 2 increased over much of the southern portion of Lake Michigan by up to about 6 ppbv. Isoprene concentrations, as well as isoprene oxidation products (formaldehyde, MVK, methacrolein) increased by up to a factor of two in the isoprene sensitivity experiment. It should be noted that isoprene was only increased within the domain shown in Figure 3.1.1 and not throughout the entire CONUS domain.

Table 3.1.4 shows hourly and MDA8 ozone statistics to quantify the changes in modeled ozone from each sensitivity experiment. The 0.72NO\textsubscript{x} 5HC simulation improved the model bias and correlation (R\textsuperscript{2}) at Zion for both hourly and MDA8 ozone, but did not improve model performance at the Chicago site. While not displayed in Table 3.1.4, the isoprene sensitivity produced slight (up to 3 ppbv) increases in modeled ozone during the June 2\textsuperscript{nd} high ozone event.

### Table 3.1.4. Summary of Model performance in capturing O\textsubscript{3} at Chicago and Zion sites.

<table>
<thead>
<tr>
<th>Chicago</th>
<th>Hourly O\textsubscript{3} (ppbv)</th>
<th>8hr peak O\textsubscript{3} (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>R2</td>
</tr>
<tr>
<td>0.72NO\textsubscript{x} (base)</td>
<td>466</td>
<td>0.56</td>
</tr>
<tr>
<td>0.22NO\textsubscript{x}</td>
<td>72</td>
<td>0.76</td>
</tr>
<tr>
<td>0.5NO\textsubscript{x} 5HC</td>
<td>72</td>
<td>0.78</td>
</tr>
<tr>
<td>0.72NO\textsubscript{x} 5HC</td>
<td>466</td>
<td>0.57</td>
</tr>
<tr>
<td>0.72NO\textsubscript{x} 10HC</td>
<td>96</td>
<td>0.64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zion</th>
<th>Hourly O\textsubscript{3} (ppbv)</th>
<th>8hr peak O\textsubscript{3} (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>R2</td>
</tr>
<tr>
<td>0.72NO\textsubscript{x} (base)</td>
<td>467</td>
<td>0.35</td>
</tr>
<tr>
<td>0.22NO\textsubscript{x}</td>
<td>72</td>
<td>0.76</td>
</tr>
<tr>
<td>0.5NO\textsubscript{x} 5HC</td>
<td>75</td>
<td>0.79</td>
</tr>
<tr>
<td>0.72NO\textsubscript{x} 5HC</td>
<td>467</td>
<td>0.44</td>
</tr>
<tr>
<td>0.72NO\textsubscript{x} 10HC</td>
<td>99</td>
<td>0.72</td>
</tr>
</tbody>
</table>
Figure 3.1.5 shows the average vertical profiles from the WRF-Chem model base run (0.72 NEI 2011 NO\textsubscript{x}) vs. Scientific Aviation profiles for over the land and over the lake spirals. In other words, the offshore and onshore spirals (see Figure 2.5.1) measured during the campaign are separated and the corresponding model values are extracted. Additional vertical profile plots of model vs. observation can be found in the appendix. Key results from Figure 3.1.5 are that: (i) model captures the vertical variation in both O\textsubscript{3} and NO\textsubscript{2} profiles very well; (ii) ozone is underpredicted within the boundary layer sampled by Scientific Aviation; (iii) underprediction of ozone is most pronounced at the lowest layers, i.e. in the lake boundary layer; (iv) NO\textsubscript{2} is overpredicted at elevations below about 1 km with higher biases over the lake.

![Figure 3.1.5. Scientific Aviation vertical profiles (black) vs. paired WRF-Chem simulation results (red) for O\textsubscript{3} (top row) and NO\textsubscript{2} (bottom row) over land and over lake spirals. Elevations are meters above sea level. The lake surface is at 176m above sea level.](image)

### 3.1.4. Soil NO Emissions

One internal reviewer mentioned the potential importance of soil NO emissions in the region. Given the overlap in the early summer ozone period, and some fertilizer application timings, agricultural soil NO emissions may be an important part of the regional oxidant burden. This is an excellent point,
but one where the study design, which focused on lake-land breezes and anthropogenic plumes, may not be able to address.

A literature review indicates that (now that regional anthropogenic NO\textsubscript{x} is decreasing), biogenic NO, particularly from fertilized soils, may be a significant contribution. For example in Vinken et al. (Fig. 3c) indicates that the soil NO contribution to column NO\textsubscript{2} in the upper Midwest in June may be \(~0.6\times10^{15}\) molec/cm\textsuperscript{2}. This compares to NO\textsubscript{2} measurements from Pandora during LMOS of 5-15x10\textsuperscript{15} molec/cm\textsuperscript{2} at Sheboygan. Vinken et al. (Fig. 7) puts total June soil NO emissions from a large group of North Central Midwest agricultural states at 0.01 Tg N. Comparing this to Wisconsin emissions of NO\textsubscript{x} (247,000 short tons per year in 2014 NEI), the Wisconsin emission, when converted to Tg N per month, is 0.009 Tg N. So again, we see a possibility of a significant contribution from soil NO\textsubscript{x}. The spatial patterns and temporal allocation of the soil NO\textsubscript{x} from OMI indicate it is mainly from fertilizer application, which has improved spatial and temporal allocations recently, such as (Balasubramanian et al., 2015) and follow-on publications from the same group. Similarly, cropland NO is reported as significant and underestimated in traditional inventories in the San Joaquin Valley of California (Almaraz et al., 2018). They report that cropland NO may contribute 20-51\% of California NO emissions. Hudman et al. report Midwestern cropland emissions of 3-14 kg N/ha. Multiplying this by Illinois cropland acreage and assuming 1/6 of the emissions in a single growing season month (such as June) is equivalent to 0.006-0.026 Tg N soil NO\textsubscript{x} from Illinois cropland alone (Hudman et al., 2012).

3.1.5. Future directions

The higher temperatures that occurred during the last two weeks of LMOS 2017 may have resulted in increased biogenic emissions. A future modeling experiment will explore this trend and assess how updating the Leaf Area Index (LAI) in the biogenic emissions model with MODIS LAI will impact the biogenic emissions estimates and the subsequent impact on modeled ozone. The WRF-Chem simulations performed to date all used the default WRF-Chem lake surface temperatures. A future modeling experiment will update the model defaults with lake temperature observations from the Great Lakes Surface Environmental Analysis (GLSEA) data (Schwab et al, 1999) for Lake Michigan. NO\textsubscript{x} emissions from lightning were not considered in any of the WRF-Chem simulations. An additional simulation will include lightning NO\textsubscript{x} emissions to assess the impact of these emissions on ozone formation. Finally, additional LMOS 2017 observational data, such as in-situ observation from Scientific Aviation aircraft, GeoTASO NO\textsubscript{2} columns, and HC observation at the Zion site (WAS and PTR-QiTOF), will be used to evaluate the skill of the WRF-Chem simulations.

3.2. NAM-CMAQ Model

Operational air quality forecasts from the National Weather Service (NWS) National Air Quality Forecasting Capability (NAQFC, Stajner et al., 2012 Chai, et al., 2013) were used to support daily flight planning activities during LMOS 2017. The NAQFC uses the NWS North American Model (NAM) Nonhydrostatic Multiscale Model with Arakawa B-grid staggering (NMMB) (Janjic and Gall, 2012) and the Environmental Protection Agency’s (EPA) Community Multiscale Air Quality Model (CMAQ; Appel et
al., 2017) to perform twice daily forecasts of air quality over the continental US (http://airquality.weather.gov/). The NMMB is run on a 12km grid over North America using the Rapid Radiative Transfer Model (RRTM) radiation scheme (Mlawer et al., 1997) for both shortwave and longwave, Ferrier's microphysics scheme (Ferrier et al, 2002), Betts-Miller-Janjic convection (Betts 1986; Betts and Miller 1986; Janjic’ 1994), Mellor-Yamada-Janjic PBL and surface layer schemes (Mellor and Yamada, 1982; Janjic 1990, 1994, 2001), and the NOAH land surface scheme (Ek et al., 2003). NAQFC uses CMAQ 5.0.2 with CB05 gas phase chemistry (Yarwood et al., 2005) and the 6th generation CMAQ aerosol chemistry (AERO6). The 2017 NAM-CMAQ point source emissions are based on 2015 Continuous Emissions Monitoring System (CEM), 2017 DoE Energy Outlook, Canada 2011 Environment Canada Emission Inventory (ECEI), and Mexico inventory (MI) 2012 version2.2. Area source emissions use NEI2011 (US), ECEI 2006 (Canada) and MI 2012 (Mexico). Mobile source emissions are based on Cross State Air Pollution Rule (CSAPR) 2011 Emission Data. Wildfire aerosol emissions use NESDIS Hazard Mapping System (HMS) fire detection and emissions from the US Forest Service (USFS) BlueSky v3.5.1 framework (O’Neill et al, 2008). Biogenic emissions are estimated inline in CMAQ with the Biogenic Emissions Inventory System (BEIS3) v3.14 (Pouliot, 2008; Pouliot and Pierce, 2009). NAM-CMAQ 48 hr forecasts are initialized every 6 hours. The 06Z NAM-CMAQ forecasts were used in the following comparisons.

Comparison with WI DNR Coastal Ground Monitors

Figure 3.2.1 and 3.2.2 show observed and NAM-CMAQ wind speed and ozone wind roses for the Chiwaukee and Sheboygan KA WDNR coastal monitors during LMOS 2017 (May 22-June 22). NAM-CMAQ captured the prevailing southwesterly wind direction at Chiwaukee but underestimated the frequency of the prevailing southerly winds and overestimated the frequency of westerly winds at Sheboygan KA. The NAM-CMAQ forecasts consistently overestimated wind speed at both monitors, with a factor of 2 underestimate in the frequency of winds less than 3 m/s and a factor of 2-10 overestimate in the frequency of winds greater than 6 m/s. The overestimate in the frequency of winds greater than 6 m/s was most pronounced at the Sheboygan KA monitor where they accounted for less than 2% of the observations and nearly 24% of the NAM-CMAQ wind speeds. NAM-CMAQ forecasts consistently underestimated ozone mixing ratios at both monitors, with nearly 68% and 88% of the NAM-CMAQ ozone forecasts predicting less than 40 ppbv at Chiwaukee and Sheboygan KA, respectively. This result is significantly higher than the percentages of ozone less than 40 ppbv observed at these two sites, which are 40% and 45%, respectively. During southerly flow, ozone greater than 60 ppbv was observed at both monitors for 12% of the LMOS 2017 period. In contrast, NAM-CMAQ forecasts predicted that only 6% and 1% of the ozone during LMOS 2017 was greater than 60 ppbv at the Chiwaukee and Sheboygan KA monitors, respectively.
Figure 3.2.1. Wind Speed (m/s, upper) and Ozone (ppbv, lower) wind roses for 1-minute WDNR observations (left) and hourly NAM-CMAQ (right) at the Chiwaukee, WI monitor during the period from May 22 through June 22, 2017. The overall percentage of wind directions are indicated by the length of the wind rose in 20° bins. The percentage of wind speeds (in 3 m/s bins) and ozone (in 20 ppbv bins) are indicated by colors for each wind direction. The overall percentage of observed and modeled wind speed and ozone at Chiwaukee during LMOS are indicated underneath the color bars.
Figure 3.2.2. Wind Speed (m/s, upper) and Ozone (ppbv, lower) wind roses for 1-minute WDNR observations (left) and hourly NAM-CMAQ (right) at the Sheboygan KA monitor during the period from May 22 through June 22, 2017. The overall percentage of wind directions are indicated by the length of the wind rose in 20° bins. The percent age of wind speeds (in 3 m/s bins) and ozone (in 20 ppbv bins) are indicated by colors for each wind direction. The overall percentage of observed and modeled wind speed and ozone at Chiwaukee during LMOS are indicated underneath the color bars.
Comparison with Scientific Aviation profiles

Figure 3.2.3 shows statistical comparisons between Scientific Aviation (SA) and NAM-CMAQ vertical profiles of wind direction, temperature, ozone and NO$_2$ for all flight legs over Lake Michigan during LMOS 2017. The observed and predicted median profiles are indicated by the solid and dotted lines, respectively. The observed and predicted middle 50$^{th}$ percentiles (i.e., 25$^{th}$ to 75$^{th}$ percentile values) of the distributions in 250 m altitude bins are shown by the yellow and red bars, respectively. The “whiskers” show the middle 90$^{th}$ percentiles of the distributions in each 250 m altitude bin. The NAM-CMAQ over-water wind direction predictions captured the observed transition from prevailing southerly winds over the surface of the lake to prevailing westerly winds above 2 km. The model tended to overestimate the frequency of westerly winds in the lowest 250 m and overestimate the frequency of southerly winds between 1-1.5 km above the lake. NAM-CMAQ temperature predictions were systematically about 2 degrees colder than observed but captured the median strength of the low level inversion associated with the marine boundary layer. The NAM-CMAQ simulation captured the overall variance in the observed temperatures throughout the profiles. Median ozone mixing ratio predictions systematically underestimated observed values by 12-15 ppbv throughout the column and the observed variance was underestimated below 1 km. Median NO$_2$ predictions overestimated observed values by a factor of 2 in the lowest 250 m and underestimated observed values by a factor of 2-10 above 1 km.

Figure 3.2.4 shows statistical comparisons between SA and NAM-CMAQ vertical profiles of wind direction, temperature, ozone and NO$_2$ for all flight legs over Lake Michigan on June 2 and 11. The median predicted wind direction profile showed less directional shear in the lowest 1.5 km and the median predicted temperature profile was more stable than observed below 500 m. Median ozone mixing ratio was systematically underestimated by NAM-CMAQ by over 20 ppbv throughout most of the column. The largest underestimates in median ozone on these high ozone days occurred in the lowest 250 m where the median observed ozone mixing ratio was 90 ppbv and the median predicted ozone was slightly larger than 65 ppbv. These large underestimates in median ozone were associated with a factor of 10 overestimate in median NO$_2$ mixing ratio in the lowest 250 m during the high ozone events.
Figure 3.2.3. Statistical comparison between Scientific Aviation (SA, yellow bars/solid line) and NAM-CMAQ (red bars/dotted line) vertical profiles of wind direction (Degrees, upper left), temperature (K, upper right), ozone (ppbv, lower left), and NO$_2$ (ppbv, lower right) over Lake Michigan during LMOS. The solid and dotted lines show the median observed and predicted median profiles, respectively. The yellow and red “bars” show the 50th percentiles of the observed and predicted distributions within each 250 m layer, respectively. The “whiskers” show the 90th percentiles within each 250 m layer.
Figure 3.2.4. Statistical comparison between Scientific Aviation (SA, yellow bars/solid line) and NAM-CMAQ (red bars/dotted line) vertical profiles of Wind Direction (Degrees, upper left), Temperature (K, upper right), Ozone (ppbv, lower left), and NO2 (ppbv, lower right) over Lake Michigan on June 02 and June 11, 2017. The solid and dotted lines show the median observed and predicted median profiles, respectively. The yellow and red “bars” show the 50th percentiles of the observed and predicted distributions within each 250 m layer, respectively. The “whiskers” show the 90th percentiles within each 250 m layer.
3.3. WRF-Met Modeling

The suite of in situ meteorological observations made during LMOS 2017 are being used to test and inform future modeling of weather within the region, the results of which will also be used in modeling air quality. The current EPA meteorological modeling platform uses the Weather Research and Forecasting (WRF) model (Skamarock and Klemp, 2008), configured with Morrison microphysics (Morrison et al, 2009), Kain-Fritsch cumulus parameterization (Kain, 2004), ACM2 boundary layer physics (Pleim, 2007), and Pleim-Xiu surface physics (Xiu and Pleim, 2001). This WRF configuration will be referred to here as the “EPA baseline”. Beyond the parameterizations used for solving key physics in the meteorological model, the use of data assimilation for initial conditions, boundary conditions, lake temperature, soil moisture and other variables has been explored by the LMOS 2017 team and reported herein.

Figure 3.3.1. Modeling domains used in the first round of meteorological parameterization sensitivity studies. The outer domain has a horizontal resolution of 12 km by 12 km; the inner domain has a horizontal resolution of 4 km by 4 km.

Nested model simulations were performed with WRF (Figure 3.3.1) for the period May 21-June 3 2017. This period was selected for modeling because it included a notable lake breeze and ozone exceedences on June 2. The outer domain has a horizontal resolution of 12 km by 12 km and covers the continental U.S., the inner domain has a horizontal resolution of 4 km by 4 km. With one-way nesting, both 12 km resolution results, and 4-km resolution results are available for in inner domain. This enables comparison of the effect of finer resolution. Though fairly well correlated with observations of temperature and wind, the EPA baseline WRF configuration was seen to overestimate daytime high temperatures, underestimate nighttime low temperatures, and underestimate wind speed. Figure 3.3.2 and Table 3.3.1 show these biases for the Chiwaukee monitor and averaged across several coastal sites, respectively. The EPA-baseline configuration also does not capture the timing of the lake breeze in
Chiwaukee (Figure 3.3.2, middle panel), nor mixed layer heights observed at Zion, which were underestimated at night and overestimated during the daytime (Figure 3.3.3).

![Temperature, Wind Direction, and Wind Speed](image)

**Figure 3.3.2.** Temperature (top), wind direction (middle), and wind speed (bottom) as observed (black lines) and modeled (red lines) at Chiwaukee.

**Table 3.3.1.** Statistical comparison of WRF (EPA baseline configuration) with observed meteorology at near-lakeshore sites. Average statistics across all near-lakeshore sites (Sheboygan KA, Sheboygan Haven, Newport, Milwaukee SER, Manitowoc, and Chiwaukee) and Lake Geneva, for the period May 23-June 3 2017. Note: biases are calculated as observation-model, a low model bias is positive.

<table>
<thead>
<tr>
<th></th>
<th>Mean Bias</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12 km</td>
<td>4 km</td>
</tr>
<tr>
<td>temperature</td>
<td>0.740 K</td>
<td>0.289 K</td>
</tr>
<tr>
<td>wind speed</td>
<td>-1.415 m/s</td>
<td>-1.390 m/s</td>
</tr>
<tr>
<td>wind direction</td>
<td>7.466 °</td>
<td>6.832 °</td>
</tr>
</tbody>
</table>
Three other WRF configurations were tested, as detailed in Table 3.3.2. The first of the alternate configurations is referred to by the name MYJ-NOAH.\textsuperscript{1} The second of the alternate configurations is referred to as YSU-NOAH.\textsuperscript{2} By comparing the EPA baseline, MYJ-NOAH, and YSU-NOAH results, the sensitivity of the modeled meteorology to surface and boundary layer physics can be assessed. A fourth configuration, referred to as YSU-NOAH-Thompson, was used to isolate the impact of cloud and precipitation (i.e. microphysics) parameterization from the YSU-NOAH sensitivity test. Overall, these sensitivity experiments were all well-correlated with observed temperatures, but had a low bias in temperature. The sensitivity runs were well-correlated for wind direction and speed, but wind speed had an overall high bias compared to observations. Example summary statistics are provided for all lakeshore sites in Tables 3.3.3 (temperature), 3.3.4 (wind direction), and 3.3.5 (wind speed). All sensitivity experiments underestimated mixing layer heights at Zion, and the sensitivity to microphysics parameterization was small. The sensitivity experiments also showed improved correlation with a higher horizontal resolution.

\textsuperscript{1} MYJ refers to the Mellor-Yamada-Janjic Planetary Boundary Layer (PBL) Physics Scheme, while NOAH refers to the selection of the surface (land) physics option.

\textsuperscript{2} YSU refers to the Yonsei University scheme for PBL physics.
Table 3.3.2. WRF sensitivity experiments relative to the EPA baseline.

<table>
<thead>
<tr>
<th>configuration</th>
<th>microphysics</th>
<th>cumulus parameterization</th>
<th>boundary layer</th>
<th>surface layer physics</th>
<th>surface physics</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA baseline</td>
<td>Morrison</td>
<td>Kain-Fritsch</td>
<td>ACM2</td>
<td>Pleim</td>
<td>Pleim-Xu</td>
</tr>
<tr>
<td>MYJ-NOAH</td>
<td>Morrison</td>
<td>Kain-Fritsch</td>
<td>MYJ Eta Operational</td>
<td>Monin-Obukov</td>
<td>NOAH</td>
</tr>
<tr>
<td>YSU-NOAH</td>
<td>Morrison</td>
<td>Kain-Fritsch</td>
<td>YSU</td>
<td>Monin-Obukov</td>
<td>NOAH</td>
</tr>
<tr>
<td>YSU-NOAH-Thompson</td>
<td>Thompson</td>
<td>Kain-Fritsch</td>
<td>YSU</td>
<td>Monin-Obukov</td>
<td>NOAH</td>
</tr>
</tbody>
</table>

Table 3.3.3. Statistical comparison (temperature) of WRF (alternate configurations) with observed meteorology at near-lakeshore sites. Statistics for three sensitivity experiments’ temperature averaged across all near-lakeshore sites (Sheboygan KA, Sheboygan Haven, Newport, Milwaukee SER, Manitowoc, and Chiwaukee) and Lake Geneva, for the period May 23-June 3 2017. Note: biases are calculated as observation-model, a low model bias is positive.

<table>
<thead>
<tr>
<th></th>
<th>Mean Bias</th>
<th>Correlation</th>
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<tbody>
<tr>
<td></td>
<td>12 km</td>
<td>4 km</td>
</tr>
<tr>
<td>MYJ-NOAH</td>
<td>0.384 K</td>
<td>0.591 K</td>
</tr>
<tr>
<td>YSU-NOAH</td>
<td>0.110 K</td>
<td>0.426 K</td>
</tr>
<tr>
<td>YSU-NOAH-Thompson</td>
<td>-0.157 K</td>
<td>0.131 K</td>
</tr>
</tbody>
</table>

Table 3.3.4. Statistical comparison (wind direction) of WRF (alternate configurations) with observed meteorology at near-lakeshore sites. Statistics for three sensitivity experiments’ wind direction averaged across all near-lakeshore sites (Sheboygan KA, Sheboygan Haven, Newport, Milwaukee SER, Manitowoc, Lake Geneva, and Chiwaukee) for the period May 23-June 3 2017. Note: biases are calculated as observation-model, a low model bias is positive.

<table>
<thead>
<tr>
<th></th>
<th>Mean Bias</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12 km</td>
<td>4 km</td>
</tr>
<tr>
<td>MYJ-NOAH</td>
<td>6.916 °</td>
<td>9.207 °</td>
</tr>
<tr>
<td>YSU-NOAH</td>
<td>3.129 °</td>
<td>4.711 °</td>
</tr>
<tr>
<td>YSU-NOAH-Thompson</td>
<td>5.473 °</td>
<td>6.101 °</td>
</tr>
</tbody>
</table>

Table 3.3.5. Statistical comparison (wind speed) of WRF (alternate configurations) with observed meteorology at near-lakeshore sites. Statistics for three sensitivity experiments’ wind speed averaged across all near-lakeshore sites (Sheboygan KA, Sheboygan Haven, Newport, Milwaukee SER, Manitowoc, Lake Geneva, and Chiwaukee) and Lake Geneva, for the period May 23-June 3 2017. Note: biases are calculated as observation-model, a low model bias is positive.

<table>
<thead>
<tr>
<th></th>
<th>Mean Bias</th>
<th>Correlation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>12 km</td>
<td>4 km</td>
</tr>
<tr>
<td>MYJ-NOAH</td>
<td>-2.419 m/s</td>
<td>-2.588 m/s</td>
</tr>
<tr>
<td>YSU-NOAH</td>
<td>-1.809 m/s</td>
<td>-1.874 m/s</td>
</tr>
<tr>
<td>YSU-NOAH-Thompson</td>
<td>-1.862 m/s</td>
<td>-1.913 m/s</td>
</tr>
</tbody>
</table>
The EPA-baseline and sensitivity experiments all assumed a constant surface temperature for Lake Michigan, reflecting default sea surface temperature (SST) settings in WRF. As shown in Figure 3.3.4, the assumption of constant SST (top row) in WRF is not consistent with data from the Great Lakes Surface Environmental Analysis (GLSEA, bottom row). Since SST impacts the timing and extent of lake breeze circulations in the model, future LMOS 2017 WRF modeling will include the high-resolution satellite-based SST observations from GLSEA. Future work will also include investigating the impact of both vertical and horizontal resolution on model performance. Based on discussions with stakeholders and researchers, all future sensitivity simulations will employ an expanded 4-km domain to cover all LADCO states and a 1.3 km by 1.3 km domain focused on Lake Michigan, as shown in Figure 3.3.5.

Figure 3.3.4. SST values output from WRF using EPA baseline configuration (top), and from gridded analysis from the GLSEA dataset (bottom).
Figure 3.3.5. Modeling domains used for ongoing meteorological parameterization sensitivity studies. The outer domain has a horizontal resolution of 12 km by 12 km; the inner domain covering LADCO partner states has a horizontal resolution of 4 km by 4 km; the domain covering Lake Michigan has a horizontal resolution of 1.3 km by 1.3 km.

Figure 3.3.6 illustrates the sensitivity of the simulated lake breeze circulation to the land surface model (LSM) formulations for May 27, 2017. This result is from the University of Wisconsin WRF modeling effort, using the 1.3-km resolution domain. The VIIRS true color image (center panel) shows a sharp transition from clear to fair weather cumulus along the eastern and western shores of Lake Michigan, clear evidence of a strong lake breeze circulation with fairly deep inland penetration on both sides of the lake. The EPA Baseline configuration uses the Pleim-Xiu LSM (see Table 3.3.2). The predicted boundary layer depth from the EPA baseline (left panel) shows only slight penetration of the shallow marine boundary layer air onshore while the WRF sensitivity experiment using the Noah LSM shows much more inland penetration, which is in better agreement with the lake breeze penetration inferred from the VIIRS image. The University of Iowa WRF-Chem sensitivity experiments have also independently shown improved meteorological skill with the NOAH land surface model.
Use of satellite and surface observations to constrain the land surface (soil moisture, soil temperature, leaf area index) and water surface (sea and lake surface temperatures) is an important contributor to meteorological modeling skill. Options for improving lake surface temperatures, soil moisture, and vegetation fraction, are explored below.

*High resolution 1.8-km resolution GLESA daily SST analyses*

Figure 3.3.7 compares the NCEP Global Data Assimilation System (GDAS) 1/12th degree SST analysis used in the EPA baseline configuration with the high-resolution SST analyses from the NOAA Great Lakes Environmental Research Laboratory (GLERL) Great Lakes Surface Environmental Analysis (GLSEA) (Schwab et al, 1999) for 27 May 2017. The GLSEA SST analysis shows much colder lake temperatures along the northwestern shore of Lake Michigan. Improving the resolution of pockets of colder lake temperatures will lead to better depictions of atmospheric stability within the Lake Michigan boundary layer. More stable layers due to cold SSTs would lead to shallower boundary layer depths and more concentrated ozone precursors. Stronger land/water thermal gradients associated with these colder lake temperatures would strengthen the lake breeze circulation and could play an important role in ozone predictions along the lakeshore by leading to more extensive transport of pollutants onshore, and potentially greater inland lake breeze penetration.
Figure 3.3.7. 1/12th degree GDAS (left) and 1.8km GLSEA (right) Lake Michigan SST (°C) analyses on May 27, 2017.

**NASA SPoRT-LIS Soil Moisture, Soil Temperature, and Green Vegetation Fraction/Leaf Area Index Analyses**

Accurate constraints on soil moisture are necessary to capture the depth of the planetary boundary layer and near surface temperatures through the impact on surface sensible and latent heat fluxes. The frequency of MDA8 values greater than 70 ppbv rises sharply beginning in mid-May and peaks in late June (LADCO, 2016). The timing of the ozone peaks corresponds to the leaf-out period in the upper Midwest. Leaf-out is associated with enhanced evapotranspiration and leads to rapid reductions in the Bowen ratio, which in turn affects the boundary layer temperature and humidity profiles (Fitzjarrald et al, 2001). Weekly variations in vegetation distributions can play a major role in the accuracy of predicted isoprene emissions. Huang et al (2017) showed that use of NASA Soil Moisture Active Passive (SMAP) soil moisture retrievals assimilated into the NASA Short-term Prediction Research and Transition Center (SPoRT) Land Information System (SPoRT-LIS) analyses reduced biases in near-surface air temperatures and boundary layer heights over the Missouri Ozarks during the NASA SEAC4RS campaign, which, along with improved estimates of green vegetation fraction from the SPoRT-LIS.
analyses, had a significant impact on biogenic isoprene emissions in the region. Unique feedbacks
between crops and meteorology may exist due to heavy agricultural intensity in the region, with large
changes in crop leaf area during the early ozone season (Alter et al., 2018). Ability of these data
assimilation products at capturing meteorological effects of crops should be assessed.

WRF simulations in the LADCO region should use the SMAP soil moisture analyses to constrain
soil moisture and MODIS Green Vegetation Fraction (GVF) retrievals to constrain the Leaf Area Index
(LAI) to improve the overall performance of the LADCO meteorological modeling framework in
simulating land/lake-breeze circulations planetary boundary layer depths, and surface fluxes.

Section 4. Recommendations for Meteorological/Photochemical Modeling

4.1. Photochemical Modeling

The existing LMOS 2017 WRF-Chem simulations and NWS NAM-CMAQ operational forecast
underestimated the maximum ozone concentrations during high ozone episodes. One take away
message from the model and airborne in situ ozone comparison done to date using WRF-Chem and the
NWS NAM-CMAQ forecast is that the models underpredict ozone in the marine boundary layer during
high coastal ozone events, and consistently underpredict ozone up to the maximum altitude of the
airborne in situ profiles (~3 km). This is a change from recent reports of ozone overprediction such as
those in Cleary et al. (2015) and citations therein. Cleary’s work was based on measurements over the
lake and at shore monitors during summer 2009. Coastal ozone on days (summer 2011 with NEI 2011
emissions) with MDA8 ozone in excess of 60 ppbv are also biased high in the WRF-CMAQ5.2 modeling
by Georgia Tech, UAH, and EPRI (Qin et al., 2019). Recommended modifications to the model
configuration in Qin et al. (MEGAN biogenics, reduction in NOx by 30%) decrease the bias at coastal
sites, and result in underprediction at inland sites. We conclude that, while the reasons are not fully
understood, the overall evolution of these modeling systems seems to have shifted the typical error
from overprediction to underprediction of coastal ozone.

Most sensitivity tests performed to date (RACM-ESRL vs. MOZART-GOCART chemical mechanism;
doubling of biogenic emissions) in the WRF-Chem system have had fairly limited leverage on these peak
ozone levels. One notable exception would be sensitivity testing using a 5 times multiplier for
anthropogenic hydrocarbon emissions shows increased ozone concentrations, especially in the Chicago
plume most influenced by those hydrocarbon emissions. This in turn improves WRF-Chem peak surface
ozone bias substantially for the June 2 episode. This result should not be interpreted as a conclusion that
the NEI 2011 hydrocarbon emissions are low by a factor of 5 (relative to actual emissions from summer
2017). It is likely that part of the observed sensitivity is compensation of other model errors (i.e.
meteorology, mixing, chemistry) through emissions. Much more extensive model-model
intercomparison, model-observation comparison, and model process studies would be needed to justify
broad changes in the emission inventory. An additional caveat is that our emissions have not been
verified against NEI emissions; while a VOC-specific error in translating NEI emissions to model-ready emissions is unlikely, we have not explicitly ruled it out.

The high sensitivity does indicate, however, that within the WRF-Chem system tested, a more reactive plume (with higher HO2 radical concentrations) downwind of Chicago helps the model performance for ozone. **These sensitivity studies are ongoing and specific modeling recommendations for air quality management agency modelers are not yet available.** A general focus on the evaluation of hydrocarbon emissions (including speciation and spatio-temporal release patterns) by regional air managers, and by LMOS 2017 scientists, seems warranted based on the information on sensitivity and bias that we have to date (McDonald et al., 2018).

Additional comparisons to column loadings from remote sensing (GeoTASA, OMI, and Pandora), to vertically resolved meteorological observations, to ship-borne observations, and to speciated hydrocarbons, as well as additional sensitivity studies (for meteorological and chemical factors) are continuing. Using an updated emission inventory (e.g. NEI-2014 and NEI-2017) should also be explored in future modeling simulations.

### 4.2. Meteorological Modeling

Simulations at 4 km horizontal resolution using standard WRF physics settings common to many air quality modeling applications successfully captured general meteorological features and some aspects of the lake breeze. These were completed with WRF-Chem v3.6.1 (University of Iowa) and WRF v3.8 (University of Wisconsin). However, some shortcomings in the meteorology produced in the initial WRF-Chem and WRF simulations can be improved with better settings, improved horizontal resolution, and use of more accurate lake and land surface conditions.

- Both the Iowa group and the Wisconsin group found decreased bias in temperature from using the NOAH LSM rather than the 5-layer thermal diffusion LSM used in the base case runs.
- Sensitivity to PBL model (MYJ and YSU were tested by Wisconsin; MYNN3 was used by Iowa) was relatively small. No single PBL model had across-the-board improvement in metrics of meteorological skill.
- Sensitivity to microphysics was relatively small. The University of Wisconsin compared Morrison and Thompson microphysics.

Tests are ongoing with respect to the use of improved initial and boundary conditions for atmospheric and surface variables. These improved initial and boundary conditions achieve improved accuracy due to extensive data assimilation of remote sensed and surface observations. The University of Iowa is testing the NOAA High-Resolution Rapid Refresh (HRRR) model as an initial and boundary condition for meteorology. The University of Wisconsin is testing influence of lake surface temperature (GLSEA vs. GDAS), and the NASA SPoRT-LIS soil moisture, soil temperature, green vegetation fraction, and leaf area index product. Improved accuracy of these model inputs is expected to improve meteorological model performance, but the quantitative assessment of that is ongoing.
Recommendations on vertical resolution are also under investigation and should be reported in future LMOS reports or publications.

While statistical metrics comparing 4 km and 12 km results for meteorology are mixed, LMOS stakeholders agree that 1.3 km horizontal resolution is necessary to resolve features of the lake breeze, and the interaction of fine meteorological features with concentrated sources of ozone precursors. The 1.3-km resolution nest is needed to resolve the large gradients in surface ozone concentrations that often occur along the Lake Michigan shoreline. The 1.3km domain is also needed to capture the inland penetration of the lake breeze circulation.
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