

White Paper: Lake Michigan Ozone Study 2017 (LMOS 2017)

Steering Group: Brad Pierce¹, Rob Kaleel², Angela Dickens³, Tim Bertram⁴, and Charles Stanier⁵, Donna Kenski²

¹NOAA NESDIS Center for Satellite Applications and Research (STAR), Cooperative Institute for Meteorological Satellite Studies, Madison, WI 53706

²Lake Michigan Air Directors Consortium (LADCO), Rosemont, IL 60018

³Wisconsin Department of Natural Resources, Madison, WI 53707

⁴University of Wisconsin-Madison, Department of Chemistry, Madison, WI 53706

⁵University of Iowa, Department of Chemical and Biochemical Engineering, Iowa City, IA 52242

Abstract

To address persistent violations of the ozone National Ambient Air Quality Standard in the coastal communities around Lake Michigan, we propose a joint aircraft and ground-based campaign to significantly expand observations of ozone and its precursors over Lake Michigan during the summer of 2017. The campaign will be 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 NO_x and VOC emissions and emissions sources on ozone production rates along Lake Michigan?
- 2) To what extent do lake breeze circulations effect ozone production?
- 3) What is the spatio-temporal distribution of ozone and its precursors over Lake Michigan?
- 4) How can remote sensing products (e.g., measurements of NO₂ and HCHO) be used to constrain ozone predictions?
- 5) How well do regional models capture ozone production chemistry as assessed through evaluation of critical measurement indicators (e.g., H₂O₂:HNO₃ ratio, HCHO:NO_x ratio, NO_y and VOC lifetime and partitioning).

To address these questions we propose a multicomponent field campaign utilizing both remote sensing instruments aboard research aircraft for high spatial coverage of ozone and its precursors (NO₂ and VOCs) and a ground-based sampling site equipped with high precision, high temporal resolution *in situ* trace gas instrumentation for the characterization of ozone production chemistry. Aircraft operations will be supported by the existing network of ground-based monitoring sites operated by the states in eastern Wisconsin, northeastern Illinois, northwestern Indiana, and western Michigan that provide continuous measurements of ozone, wind speed and wind direction. Additional monitoring sites provide enhanced monitoring of ozone precursors, including NO_x and select non-methane hydrocarbons (NMHC), and provide a comprehensive background for assessing ozone production rates and sensitivities to NO_x and VOC concentrations.

Introduction

In the eastern U.S., the most persistent ozone pollution problems are in coastal areas. Recent modeling by U.S. EPA¹ projected that 12 counties in the eastern U.S. will not attain the 2015 ozone NAAQS by 2025. Of those 12 counties 9 are located on coastlines, including two counties in Texas, six in the northeast (Connecticut, New York and Maryland) and one along Lake Michigan (Wisconsin). Ozone concentrations along coastlines can be enhanced significantly when urban emissions react within the shallow, stable, marine boundary layer. This high-ozone air can be advected back onshore either by prevailing winds or by diurnal sea, lake or bay breeze circulations leading to abnormally high ozone. This phenomenon was first documented for Lake Michigan (Lyons and Cole, 1976; Dye et al, 1995; Lyons et al. 1995) and has since been documented for the Gulf of Mexico/Houston (Banta et al, 2011), the Chesapeake Bay/Maryland (Loughner et al, 2014, Stauffer et al, 2015), and Lake Erie/southwestern Ontario (Brook et al., 2013).

Airborne measurement campaigns have played a significant role in improving our understanding of these coastal influences. The NOAA New England Air Quality Study (NEAQS) in 2002 and the 2004 New England Air Quality Study - Intercontinental Transport and Chemical Transformation (NEAQS – ITCT) provided measurements to characterize the processes responsible for ozone production and air quality of the New England coast (Angevine et al, 2004, Warneke et al, 2004). The recently completed NASA Earth Venture Mission “Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality” (DISCOVER-AQ) conducted field missions in the Baltimore/Washington DC area in 2011 and Houston, TX in 2013 which have provided insight into the role of bay breeze circulations in ozone exceedances in these areas (Loughner et al, 2014). Several field campaigns have also been conducted to study ozone over Lake Michigan, most notably the Lake Michigan Ozone Study (LMOS) in 1991 (Koerber et al. 1991) and the Lake Michigan Air Directors Consortium (LADCO) Airplane Project from 1994-2003 (Foley et al, 2011). While these Lake Michigan campaigns significantly expanded understanding about the drivers of ozone chemistry in this region, they did not fully constrain the physics and chemistry of ozone formation in this area. In addition, ozone precursor emissions have decreased significantly over the last decade. Consequently, ozone chemistry is likely to be in a different photochemical regime than when these field campaigns were conducted. Furthermore, new ground-based, airborne and satellite-based remote sensing capabilities have been developed since these earlier Lake Michigan campaigns and now provide unprecedented opportunities to map the distribution of ozone precursors and ozone production over the lake.

¹ <http://www3.epa.gov/ozonepollution/maps.html>

Scientific Rationale

The proposed Lake Michigan Ozone Study 2017 would extend the success of the DISCOVER-AQ mission in engaging local air quality management in the use of NASA satellite and sub-orbital measurements for air quality assessment activities. This project would pull together a wide range of partners from different government federal and state agencies (including U.S. EPA, NOAA, USGS, the Forest Service, and the State of Wisconsin), LADCO, and academic institutions to use NASA measurements to address air quality issues over Lake Michigan. The results of this study would help advance understanding of similar conditions in other coastal regions. The scientific rationale for a ground-based and airborne mission focusing on ozone production and transport over the Lake Michigan is summarized below.

I. Considerable previous research into ozone chemistry and meteorology around Lake Michigan provides an excellent baseline for further studies.

The LMOS campaign was conducted during the summer of 1991 and made the first systematic measurements over Lake Michigan. LMOS included measurements from surface monitoring networks, aircraft, and ships (Koerber et al. 1991). LMOS measurements showed that the highest ozone concentrations over Lake Michigan occurred when local sources added to ozone pollution from regional sources with southerly winds from stagnant high pressure systems centered to the southeast of the region. High levels of ozone were found in a shallow cool layer just above the surface of Lake Michigan, and this ozone-rich air was transported inland along the shorelines of Wisconsin and Michigan (Dye et al, 1995). Sillman et al. (1993) showed that suppressed vertical mixing and deposition were needed to produce high ozone concentrations over Lake Michigan. Ozone production rates over the lake are highly sensitive to lake temperature, with 5°C changes in lake temperatures leading to changes in ozone mixing ratios of as much as 50 ppb (Fast and Heilman, 2003). Local lake breeze circulations can cause transport of high ozone air inland from the lake (Lyons et al. 1995). Lake breezes have been shown to contribute to roughly 80% of high ozone episodes in eastern Wisconsin (Lennartson and Schwartz 2002). LADCO conducted an extended (1994-2003) Lake Michigan study, referred to as the LADCO Aircraft Project (LAP), to better constrain and understand ozone formation over Lake Michigan and test the conceptual model developed by Dye et al. (1995). Results from LAP have been summarized in Foley et al. (2011).

Figure 1 illustrates the diurnal cycle of the lake breeze circulation, which is particularly important for enhanced ozone production over Lake Michigan during summertime stagnation events when synoptic high-pressure systems centered to the southeast lead to large-scale subsidence, low-level inversions, and transport of emissions from upwind urban areas northward over the lake. During the evening through early morning, positive land/lake temperature gradients lead to off-shore flow within the shallow inversion layer (referred to as “land breeze”) that can transport local emissions, particularly from the morning rush hour, out over the lake. During the daytime, solar heating leads to a negative land/lake temperature gradients with on-

shore flow within the shallow inversion layer (referred to as the “lake breeze”) that can bring the local emissions back on shore and enhance daytime ozone production. While this conceptual model describes the basic process that leads to enhanced ozone production along the Lake Michigan shoreline, the unique meteorology and ozone chemistry of Lake Michigan are still only partially understood, as is the relative role of basin scale and long-range transport of ozone and ozone precursors in this region.

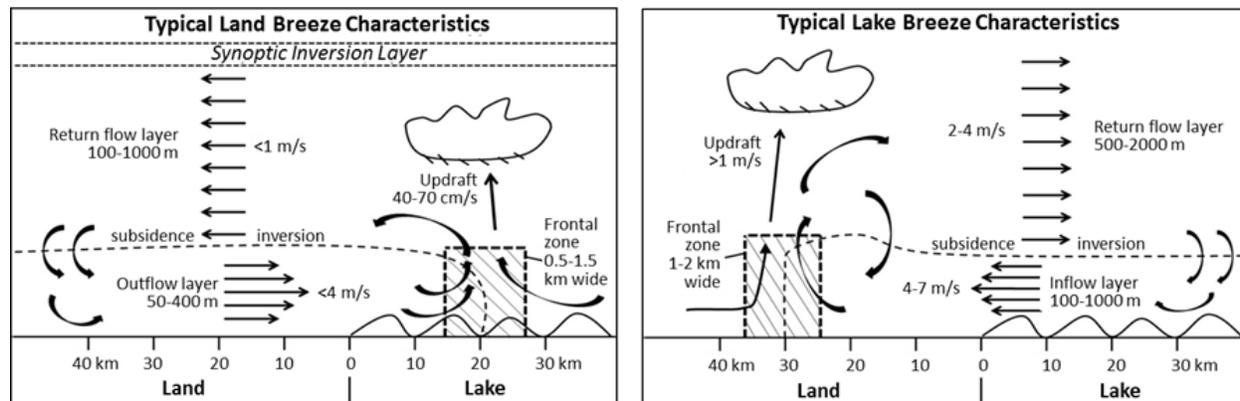


Figure 1: Conceptual model of land/lake breeze circulations responsible for enhanced ozone production along the shores of Lake Michigan (modified from Foley et al., 2011)

While the lake breeze is understood to be a major driver of ozone concentrations along the lakeshore, photochemical models have historically been unable to reproduce lake breeze circulation. This has made it difficult for states and LADCO to accurately predict ozone concentrations along the Lake Michigan lakeshore. One challenge to improving these models has been the limited number of observations of ozone and ozone precursor concentrations, along with meteorological parameters, that have been made over Lake Michigan in recent years. In particular, no major field campaigns have been conducted since the implementation of a number of significant regulatory programs to reduce emissions of ozone precursors.

II. The location of the worst ozone pollution issues in rural areas of Wisconsin and Michigan, far downwind of urban source regions, makes Lake Michigan an ideal area to study the development and evolution of urban plumes and the role of coastal meteorology in ozone pollution.

As a result of regulatory programs, emissions of NO_x and VOCs have decreased substantially during the last decade and are continuing to decline in the Lake Michigan region and across the country (Figure 2). These reductions have been concentrated in certain sectors that are easier to control (e.g., power plants and highway vehicles). This has increased the relative importance of emissions from harder-to-control sources such as off-highway vehicles, which includes everything from lawnmowers and forklifts to commercial marine vessels.

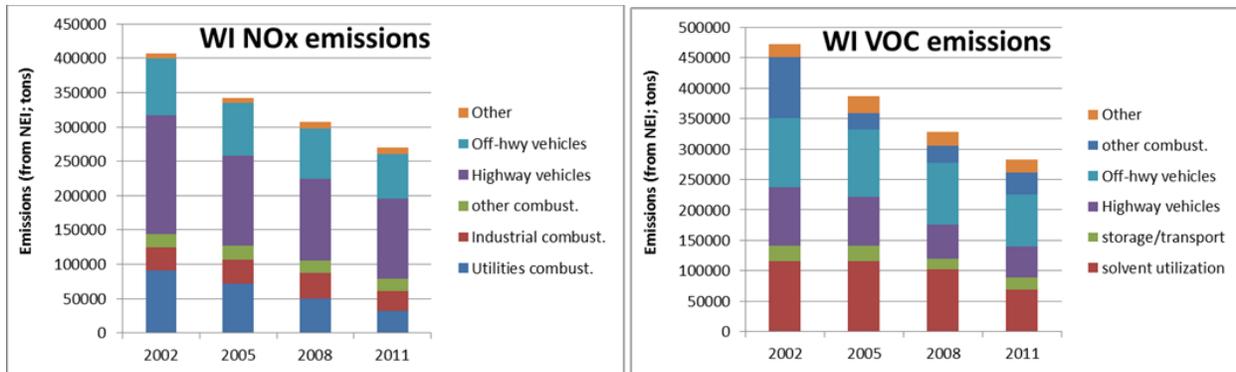


Figure 2: Wisconsin NO_x (left) and VOC (right) emissions (tons) by sector for 2002-2011 based on data reported to the National Emissions Inventory (NEI; <http://www.epa.gov/air-emissions-inventories>).

Despite dramatic reductions in ozone precursor emissions, many areas bordering Lake Michigan continue to violate federal air quality standards for ozone. These problems have persisted for decades and are some of the most challenging air quality issues in the eastern U.S. The highest ozone concentrations in the Midwest are concentrated along the coastlines of the Great Lakes. Lake Michigan in particular, due to emissions from upwind urban areas, combined with the unique meteorology of the Great Lakes region, has an unusually high number of sites whose ozone “design values” exceed the 2015 ozone NAAQS (Figure 3). Persistent exposure to ozone mixing ratios as low as 60ppbv can cause ozone injury to forests. This can have significant implications for the ecology of the Great Lakes region. The Huron-Manistee National Forest in Lower Michigan has ozone levels which can damage vegetation (Smith et al., 2012). Observing the transport processes responsible for these elevated ozone concentrations would help improve our understanding of these ecological impacts.

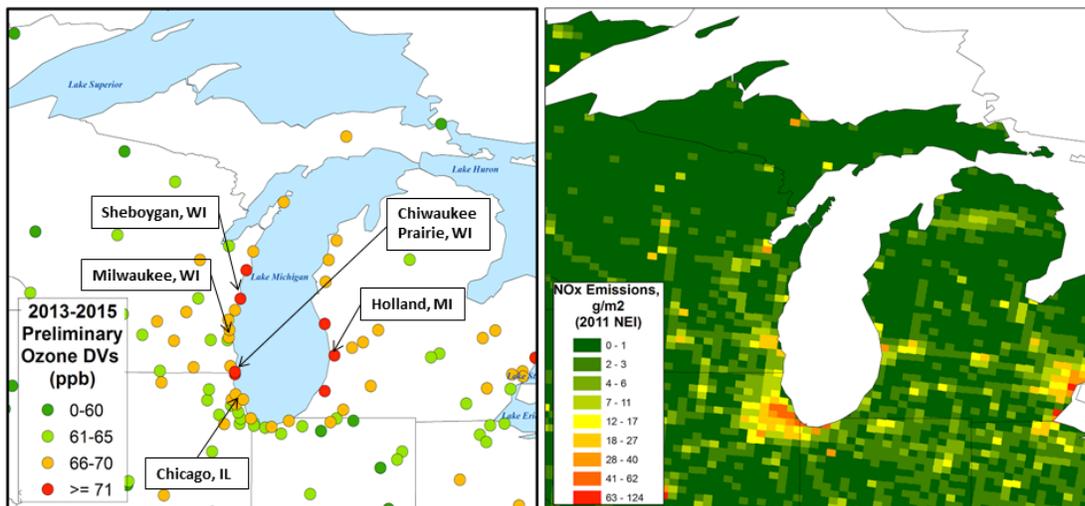


Figure 3: Preliminary 2013-2015 ozone Design Values (DV) in ppb (left) and NEI 2011 NO_x area emissions in g/m² (right). DVs greater than or equal to 71ppbv (red) exceed the 2015 NAAQS for ozone.

In Wisconsin, Sheboygan and Kenosha counties have recently monitored ozone concentrations violating the 2008 ozone standard, and both counties will be subject to reclassification to a more severe nonattainment classification by U.S. EPA. Sheboygan County² is a mostly rural county located on the western shore of Lake Michigan about 60 miles north of Milwaukee and 140 miles north of Chicago. According to the EPA NEI 2011 emission inventory³, Sheboygan County's total annual NO_x emissions account for just 2% of the total NO_x emissions within Wisconsin with the largest source being coal-fired electrical power generation at the Edgewater Generating Station. Sheboygan County has been designated “nonattainment” with every ozone standard, beginning with the 1979 one-hour NAAQS. Despite significant reductions in ozone concentrations at this site, a nonattainment designation is expected with the new 2015 ozone standard.

Michigan counties bordering Lake Michigan have similar ozone pollution challenges. Allegan County, Michigan⁴, which includes Holland, MI, is even less urbanized than Sheboygan County. Allegan County's total annual NO_x emissions account for only 1% of the total NO_x emissions within Michigan with the largest source being light-duty onroad vehicles. Figure 4 shows a record of ozone concentrations in Sheboygan, WI, and Holland, MI. These two coastal sites, located on opposite sides of Lake Michigan, show persistently high and highly correlated annual ozone NAAQS that have routinely exceeded each NAAQS standard in spite of their rural locations.

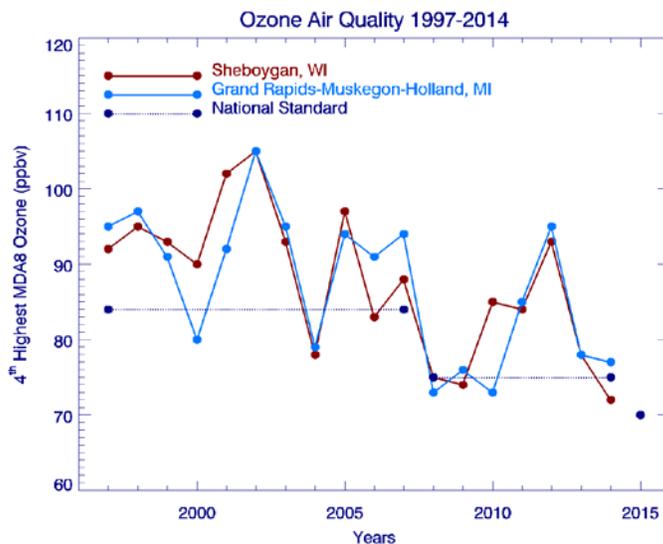


Figure 4: 4th Highest annual maximum daily average 8-hr (MDA8) ozone (ppbv) for Sheboygan, WI, and Holland, MI, and the level of the NAAQS for 1997-2015.

² <http://www.census.gov/quickfacts/table/PST045215/55117,00>

³ <http://www3.epa.gov/ttnchie1/net/2011inventory.html>

⁴ <http://www.census.gov/quickfacts/table/PST045215/26005,00>

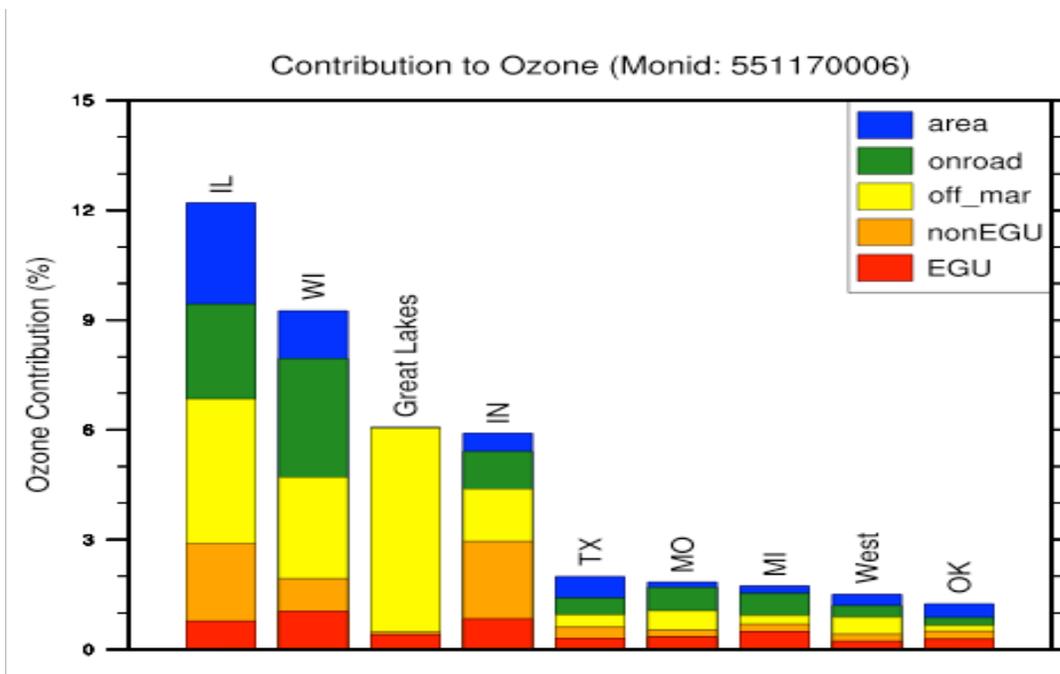


Figure 5: Source Attribution for Sheboygan, WI (Monitor ID: 551170006) showing the percentage contribution by region (bars) and emission sector (colors).

LADCO source apportionment modeling studies suggest that Wisconsin contributes to less than 10% of the ozone at Sheboygan (Figure 5), significantly limiting the state’s options to reduce ozone concentrations at this site. Upwind states (primarily Illinois and Indiana) and emissions from commercial shipping on the Great Lakes contribute 2-3 times as much as Wisconsin. Commercial shipping on the Great Lakes is an important source of air pollutants including sulfur dioxide (SO₂), nitrogen oxides (NO_x) and particulate matter (PM). Commercial marine vessels typically burn diesel fuel and operate in three modes: cruising, hoteling, and maneuvering. Cruising operations occur between ports, maneuvering occurs as ships move into or out of the ports, and hoteling covers the operational activities of the vessel during the period it is docked at a port. Fuel consumption is greatest while ships are cruising between ports; although the resulting emissions are dispersed spatially along the primary vessel tracks (see Figure 6). Emissions during maneuvering and hoteling are still significant, and are more concentrated at or near the ports. Chicago and Milwaukee are the largest ports on Lake Michigan, especially for large cargo vessels. Most of the cities on the Lake Michigan shoreline, however, experience some commercial marine traffic from smaller commercial passenger or pleasure craft, fishing boats, etc. The proximity of these emission sources to critical receptors on the Lake Michigan shoreline, and their location in the shallow marine boundary layer, adds to the significance of this emission category on lakeshore ozone concentrations.

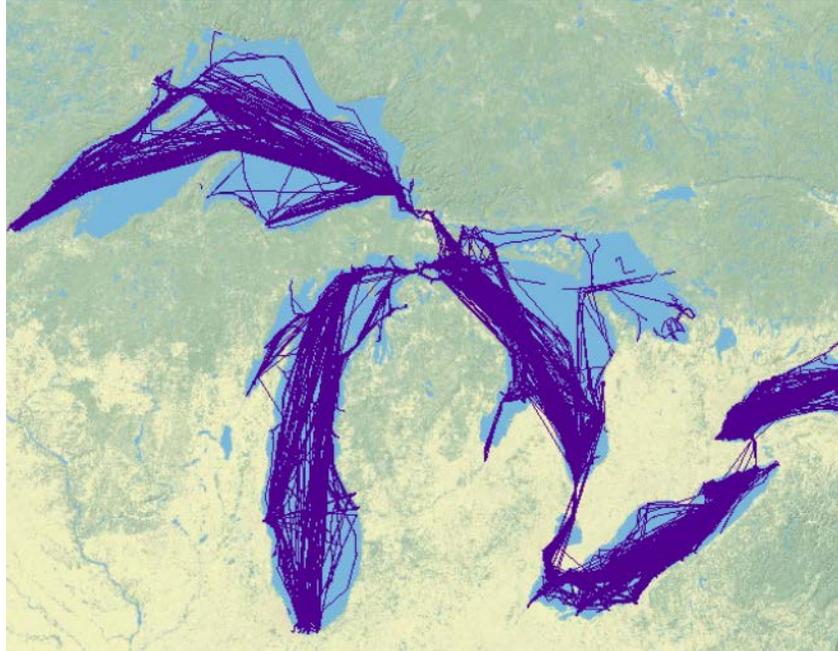


Figure 6: Vessel Tracks in the Great Lakes. (From “Emission Inventory Assistance for Commercial Marine Vessels on the Great Lakes and Major Midwest Rivers”, Report to LADCO by ENERCON Services Inc., September 2015.)

III. Current and future NASA and European satellite and airborne measurements can make a significant contribution to understanding the development and evolution of urban plumes and the role of coastal meteorology in enhanced ozone production over the Great Lakes.

Currently available satellite-based measurements of tropospheric column NO_2 (Bucsela et al, 2006) and HCHO (Abad et al, 2015) from the NASA Aura Ozone Monitoring Instrument (OMI) instrument provide opportunities to map the spatial distribution of ozone precursors on a daily basis and can be used to assess the relative sensitivity of ozone production to NO_x and VOC amounts over the Great Lakes (Duncan et al, 2010). Figure 7 shows comparisons between tropospheric NO_2 and HCHO columns from OMI and from LADCO CAMx simulations for July 2011. CAMx estimates of tropospheric NO_2 and HCHO columns over Chicago are both higher than OMI measurements. In contrast, over rural areas CAMx models lower tropospheric NO_2 columns and higher HCHO columns than measured by OMI. As a result, CAMx shows higher than observed formaldehyde-to- NO_2 ratios (FNR) for rural regions and lower than observed FNR over Chicago, suggesting that CAMx may be underestimating ozone NO_x sensitivity in the Chicago metropolitan area. The proposed Lake Michigan Ozone Study 2017 would provide an opportunity to understand the reasons for these discrepancies between model predictions and satellite measurements.

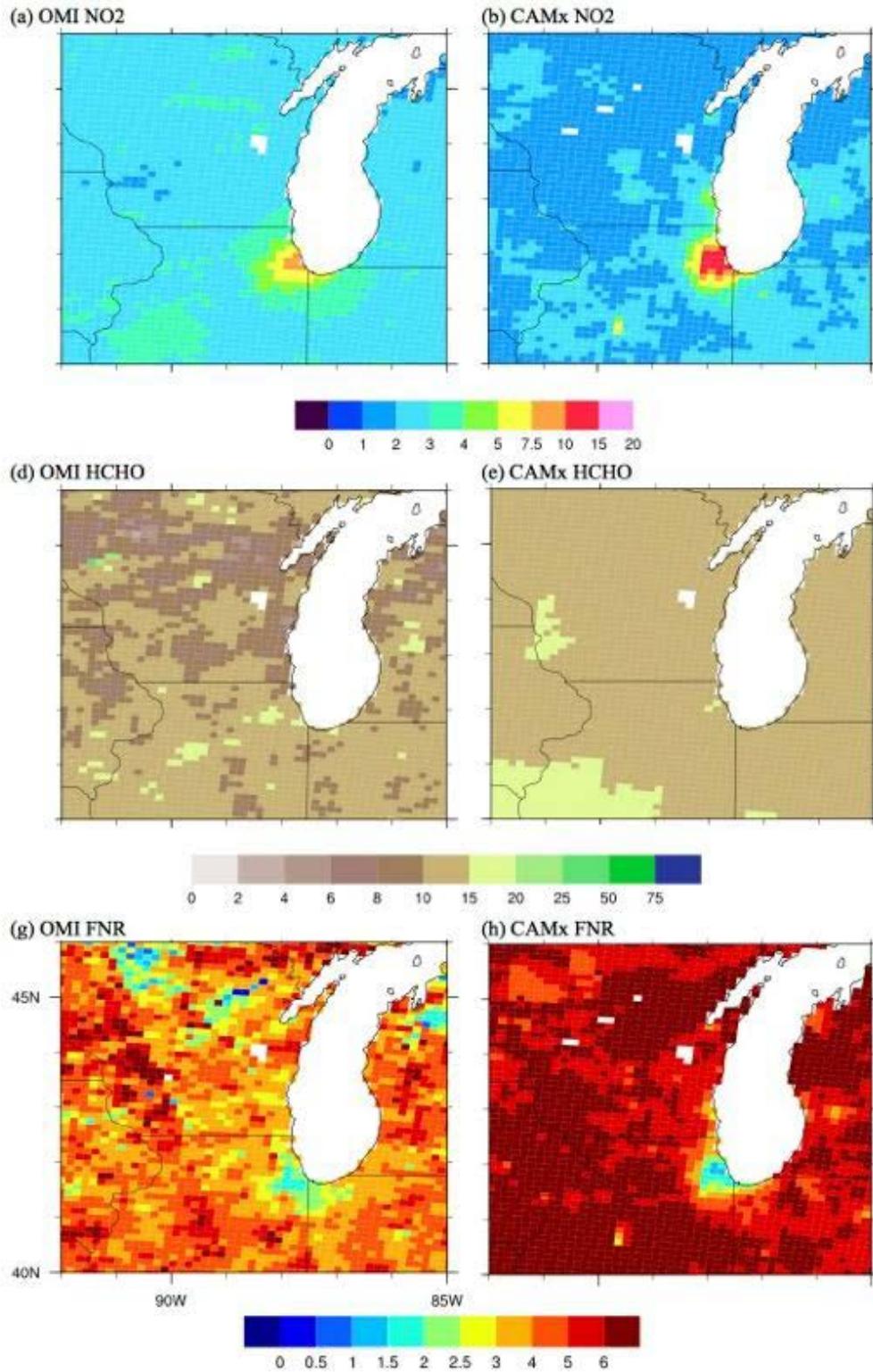


Figure 7: OMI (left panels) and CAMx (right panels) tropospheric NO_2 columns (upper panels), HCHO columns (middle panels) and formaldehyde to NO_2 ratios (FNR, lower panels) for July 2011. (Harkey et al., unpublished results). The CAMx model was run using 2011 emissions data from NEI.

The proposed Lake Michigan Ozone Study 2017 would provide an opportunity to conduct ground-based and airborne validation measurements for the TROPospheric Monitoring Instrument (TROPOMI⁵), which will be launched in 2016 on board the European Sentinel-5 Precursor satellite. TROPOMI will measure total and tropospheric O₃ columns and profiles, NO₂ total and tropospheric columns, as well as total HCHO, SO₂, CO, and CH₄ columns at a high spatial resolution of 7x7 km² providing nearly 6 times the spatial resolution as OMI. The proposed field study would also provide an opportunity to validate aerosol and cloud retrievals from the NOAA GOES-R Advanced Baseline Imager (ABI⁶), which will be launched in October 2016 and will provide MODIS quality aerosol optical depth and cloud retrievals from geostationary orbit.

IV. Existing Lake Michigan air quality monitoring networks and enhanced supersites will provide additional support for this study.

Aircraft operations will be supported by the existing network of ground-based monitoring sites operated by the states around Lake Michigan (Fig. 8). An extensive network of monitoring sites within the study region provides continuous measurements of ozone, wind speed, wind direction and temperature. In addition, state air agencies conduct enhanced monitoring of ozone precursors at a number of sites (Table 1 & Fig. 8) on timeframes ranging from hourly to once every 12 days. This monitoring data provides a comprehensive background for assessing O₃ production rates and sensitivities to NO_x and VOC concentrations. Monitored VOCs include carbonyls (formaldehyde, acetone, etc.), speciated hydrocarbons (benzene, propene, etc.), and nitrogen compounds include NO_x components and total NO_y⁷.

Measurements have been conducted at these sites for years to decades so that comparison with this monitoring data can provide historical context for campaign measurements and determine representativeness of conditions during the study period. Similarly, the broad spatial coverage of the state monitoring locations will, in combination with satellite measurements, help put airborne measurements in context. In addition, having access to an extended ground-based monitoring network can help with interpretation of the satellite information. For example, the Wisconsin DNR recently began operating ozone monitors 3-4 miles inland of the long-term monitors on the lakeshore in Sheboygan and Kenosha County. Ozone concentrations at these monitors are 10-20 ppb lower than those at the lakeshore monitors on average for high-ozone days, confirming that

⁵ <http://www.tropomi.eu/>

⁶ <http://www.goes-r.gov/>

⁷ Some of this monitoring is conducted as part of the Photochemical Assessment Monitoring Stations (PAMS) network. EPA is in the process of redesigning this network, which puts ozone precursor measurements at one site (marked "*" in Table 1) at risk of being discontinued in 2017. We are working with state air agencies to track this situation.

the high-ozone air in this area is largely confined to a very narrow strip of land to the east of the lake breeze front along the lakeshore. Comparison with meteorological data collected at these monitors further indicates that very specific wind conditions lead to peak ozone concentrations at these locations. Combining this kind of long-term monitoring data with short-term but intensive observations from airborne and enhanced ground-based studies would provide powerful insight into ozone formation and evolution in this region.

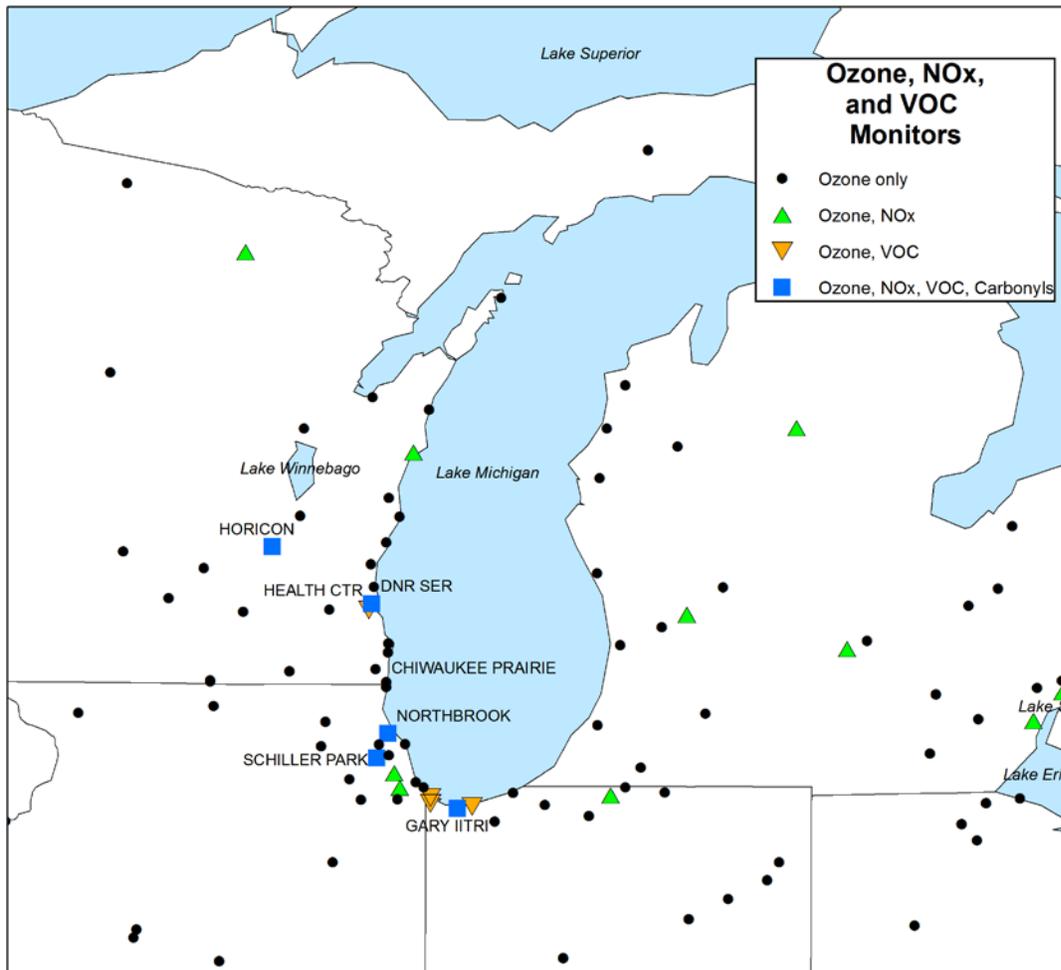


Figure 8: Locations of existing state monitors throughout the study area.

Table 1. Existing monitoring network for ozone precursors.

Parameter	Inland				WI Lakeshore			IL Lakeshore				IN Lakeshore				
	Potawatomi, WI	Horicon, WI	South Bend, IN	Grand Rapids, MI	Manitowoc	Milw. DNR SER*	Milw. Health Ctr	Northbrook	Schiller Park	Cicero	Com Ed	Whiting	Hammond 141 st St	East Chicago Marina	Gary IITRI	Ogden Dunes
Ozone	X	X	X	X	X	X	X	X	X	X	X		X		X	X
VOCs (carbonyls)		1/6				1/6	1/12	1/6	1/6						1/6	
VOCs (speciated hydrocarbons)		1/6				1/6	1/12	1/6				1/6	1/6	1/6	X	1/6
CO		X		X				X								
NOx	X	NO	X		X	X		X	X	X	X				X	
NOy		X		X	X	X		X								
Ammonia		X														
SO ₂	X	X		X		X		X			X		X		X	
PM _{2.5} (filter-based)	1/6	1/3	1/3	1/3		1/6	1/3	1/3	1/3	1/6	1/6				1/3	1/3
PM _{2.5} (continuous)	X	X	X	X		X	X	X		X	X				X	X
Speciated PM _{2.5}		1/3		1/3		1/3		1/3			1/3				X	
PM ₁₀		X		1/6		X	1/12	1/6						1/6	1/1	
PM coarse		X		1/6		X										
Toxic metals (TSP or PM ₁₀)		1/6		1/6			1/12	1/6					1/6	1/6		
Mercury	X	X				X	X									
Wind Speed/Direction & Temp.	X	X	X	X	X	X	X	X	X		X		X		X	

Note that there is additional monitoring for PM_{2.5} and SO₂ that is not shown in this table. Wisconsin and Illinois also operate additional monitors for NO₂ and CO in urban near-road locations, but these are focused on local emissions. Ammonia is also monitored at Hoxeyville, MI, and CO is measured at East Chicago, IN.

X indicates continuous measurement, * indicates a PAMS monitor that is at risk of being discontinued, and 1/# indicates how frequently samples are collected. For example, 1/3 indicates that samples are collected every third day.

Campaign Study Period

The timing of the Lake Michigan Ozone Study 2017 needs to consider the seasonal climatology of ozone exceedances along the shoreline as well as water temperatures since the lake breeze is driven by diurnal heating over land coupled with relatively cool water temperatures. Figure 9 shows a comparison between the frequency of daily 8-hr maximum values in excess of 70 ppbv and the mean Lake Michigan surface temperatures during April- October⁸. The frequency of values above 70 ppbv shows a sharp increase in late May, peaks in late June, and remains high through early September. Lake Michigan surface temperatures begin below 5°C in early April and show a gradual warming through early May. Lake temperatures frequently show rapid warming from mid-May through early June with lake temperatures ranging from 8-17 °C in mid-June. The LMOS 2017 campaign will target mid-May to mid-June based on this climatological data. This time period has adequate sunlight to drive the photochemical reactions and cool enough lake temperatures and warm enough land temperatures to create strong lake breeze circulations. These conditions have led to near-peak production of ozone in this time period (Figure 9), making this an optimal time period for this study.

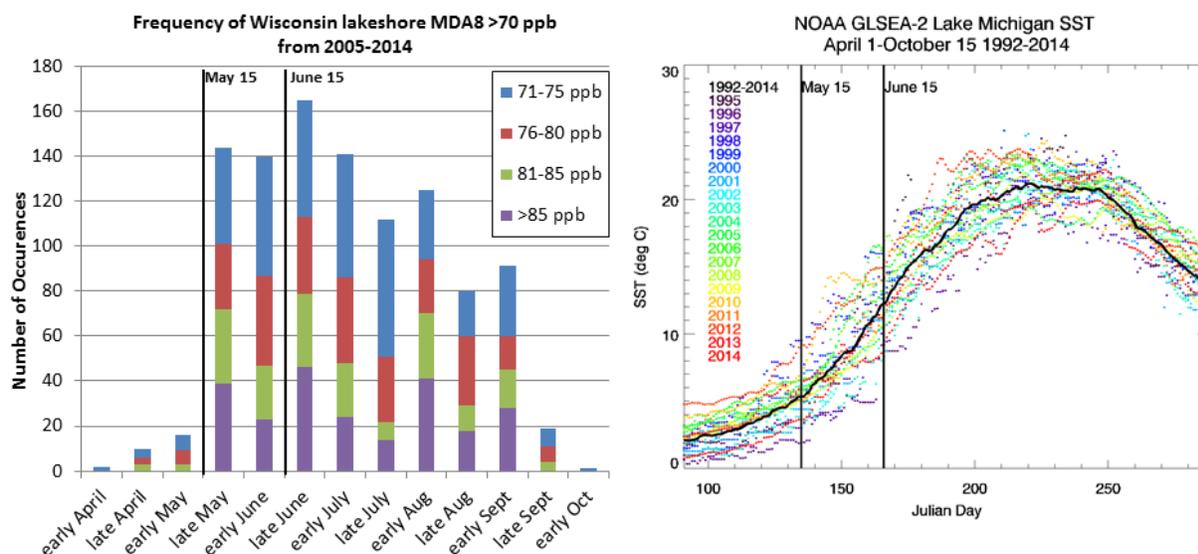


Figure 9: Seasonality of (left) high maximum daily 8-hour average ozone concentrations (MDA8) at Wisconsin Lakeshore monitors and (right) mean Lake Michigan surface temperature (SST) from April 1 through October 15. MDA8 values are shown for the years 2005-2014 and SST for 1992-2014.

⁸ Surface temperature analyses were obtained from the Great Lakes Surface Environmental Analysis (GLSEA2) produced by the NOAA Great Lakes Environmental Research Laboratory (GLERL) (<http://coastwatch.glerl.noaa.gov/glsea/doc/>).

Measurement Requirements

Airborne Remote Sensing: High spatial and temporal resolution tropospheric NO₂ and HCHO column measurements from the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO; Nowlan et al, 2015) or the GEOstationary Coastal and Air Pollution Events (GEOCAPE) Airborne Simulator (GCAS; Kowalewski and Janz, 2014) airborne remote sensing instruments would allow for detailed spatial mapping of the Chicago and Milwaukee urban plumes over Lake Michigan. These airborne measurements, combined with airborne Differential Absorption Lidar (DIAL) ozone profiles (Browell et al 1989) and boundary layer depth retrievals from airborne High Spectral Resolution Lidar (HSRL) aerosol backscatter profiles (Hair et al, 2008) would provide an unprecedented opportunity to quantify the ozone production from urban emissions within the shallow marine boundary layer over Lake Michigan. Airborne aerosol and cloud extinction profiles could also be used to support GOES-R ABI validation science objectives.

Nominal airborne flight plans would include transects along the western shore of Lake Michigan and across Lake Michigan (Milwaukee to Holland), urban emission mapping in Chicago and Milwaukee, upwind and downwind sampling of urban emissions, as well as mapping of emissions plumes from commercial marine vessels on the lake. Figure 10 shows possible bases of operations for the aircraft, including Madison, WI (MSN), Milwaukee, WI (MKE), or Gary IN (KGGY). Each of these locations is well within 200 nautical miles (nm) of Southern and Central Lake Michigan (50% range for local flights of the NASA King Air).

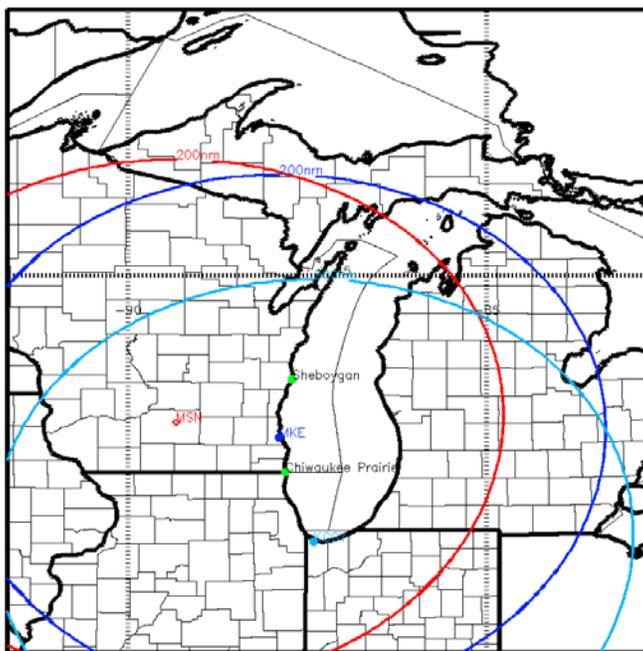


Figure 10: Potential locations of aircraft operations with 200 nautical miles (nm) range rings and proposed locations of the ground-based remote sensing site and the ground-based in situ supersite.

Ground-based remote sensing: As part of LMOS 2017, we propose to supplement the ongoing ground-based ozone monitoring with high vertical and temporal resolution measurements of temperature and water vapor from the Atmospheric Emitted Radiance Interferometer (AERI) (Knuteson et al. 2004a,b). This instrument would provide continuous measurements of boundary layer thermodynamics associated with the lake breeze circulation. Aerosol backscatter measurements from High Spectral Resolution LIDAR (HSRL) (Shipley et al, 1983) and Doppler Lidar wind measurements would provide continuous measurements of boundary layer depths and transport associated with the lake breeze circulations. Ground-based aerosol and cloud extinction profiles will also be used to support GOES-R ABI validation science objectives.

Ideally, we would also like to deploy an ozone lidar capable of providing profiles of boundary layer ozone such as the Tunable Optical Profiler for Aerosol and oZone (TOPAZ) lidar (Langford et al, 2015). This instrument would allow continuous measurements of ozone profiles in order to estimate ozone fluxes associated with the lake breeze circulation.

We propose to locate the ground-based remote sensing instrumentation at Sheboygan, WI, the location of Wisconsin's highest ozone concentrations, dependent on siting approvals. Nearby Manitowoc, WI, will be a backup location.

Ground-based in situ supersite: As part of the Lake Michigan Ozone Study 2017 we propose to supplement the ground-based ozone sampling with a single "supersite" where high precision chemical instrumentation will be deployed to provide unique insight on ozone photochemistry, oxidant (OH, HO₂, and RO₂) production and loss rates, NO_x lifetime, and observation-based indicators of NO_x/VOC ozone sensitivity. The enhanced supersite gas-phase measurements are designed to provide quantitative constraints for regional chemical transport models and 0-D chemical box models (e.g., Master Chemical Mechanism (MCM)). Of specific interest to the regional scale modeling efforts is the utility of ratios such as the H₂O₂/HNO₃ ratio as a mechanistic indicator of HO_x lifetime and radical termination mechanisms (Sillman and West, 2008; Song et al., 2010; Tonnesen and Dennis, 2000) and the sensitivity of ozone production to NO_x and VOC. In parallel, speciated VOC measurements will be utilized within a MCM framework to provide constraints on instantaneous ozone production rates, the contribution of various VOC precursors to radical formation (e.g., O₁D + H₂O, carbonyl photolysis), and the primary compounds that control OH reactivity. The most important VOC compound class to sample is isoprene plus its oxidation products, which has been shown to contribute over half of the OH reactivity in summer in the eastern U.S. (Millet et al. 2005). Also important for OH reactivity are OVOCs (21%), followed by CO (6%), and C₃-C₆ alkenes + alkynes at 5% (Propene, trans-2-butene, 1-butene, 2-methylpropene, cis-2-butene, cyclopentene, propyne, 3-methyl-1-butene, trans-2-pentene, 2-methyl-1-butene). Percentages are the percent contribution to OH reactivity measured by Millet et al. (2005).

Potential in situ supersite Location: We propose to locate the ground-based supersite at the Chiwaukee Prairie monitoring site in Kenosha County, WI, pending siting approvals. This site measures the second-highest ozone concentrations in the state and is part of the Chicago ozone nonattainment area under the 2008 ozone NAAQS. This location is in the Chiwaukee Prairie State Natural Area on the Lake Michigan shoreline near the WI/IL border and would provide good opportunities to sample fresh urban plumes along the western shore of Lake Michigan.

Gas-phase Measurements: Table 2 lists candidate in situ supersite gas phase and photochemical measurements ranked by importance. Measurements are needed for characterization of the photochemical state of the atmosphere, for model evaluation, for emission inventory evaluation, for observation-based NO_x/VOC sensitivity methods, and for source apportionment.

Table 2. Gas-phase measurement prioritization for the ground-based supersite.

Measurement	Instrument	Priority
Ozone*	UV absorption	1
NO, NO ₂ *	Chemiluminescence	1
Total NO _y		1.5
Photolysis Rates (JNO ₂ , JO ₃) †	Radiometer	1
Boundary Layer Height †	Ceilometer	1
CO, CO ₂ , CH ₄ †	CRDS	1
NMHC (speciated)*	GC-MS, PAMS	1
oVOC (alcohols, aldehydes)	PTR-MS, LIP	1
Alkyl Nitrates (RONO ₂)	CIMS (I)	1
Peroxy Nitrates (RO ₂ NO ₂)	CIMS (I)	1
Nitric Acid (HNO ₃) †	CIMS (I)	1
H ₂ O ₂ , organic peroxides	Derivatization or CIMS	1
N ₂ O ₅ , ClNO ₂	CIMS (I)	2
HONO	CIMS (I)	2
OH, HO ₂ , OH Reactivity	LIF	3
NH ₃ †	CIMS or CRDS	3
Hg †		††

*Measurements that are listed on the PAMS website as required measurements (3 hour time resolution during ozone season).

†Measurements that are not PAMS target compounds, but may be measured at some routine monitoring sites in the region.

††Depends on interest from collaborating agencies interested in Hg fate and transport

Aerosol Measurements: Table 3 lists candidate in situ supersite aerosol variables ranked by importance. Aerosol composition and characteristics, in conjunction with back trajectories and gas concentrations, are useful in characterization of air mass source region and source apportionment (Fomba et al. 2014; Kulmala et al. 2000; Browell et al. 2003). Aerosol composition measurements will also be valuable for GOES-R ABI validation science.

Table 3. Aerosol Measurements Prioritization

Measurement	Instrument	Priority
Inorganic Ion (NO ₃ ⁻) [†]	Various options	1.5 (needed for total NO _y)
Size Distributions	SMPS	2
Inorganic Ions (NH ₄ ⁺ , SO ₄ ²⁻) [†]	Various options	2
OC/EC [†]	Various options	2
Speciated organics	Various options	3
Hg [†]		††
Metals [†]	Filter + ICPMS or XRF	3

^{††}Depends on interest from collaborating agencies interested in Hg fate and transport

Data Policy

Data management is necessary to maximize the scientific value of the airborne and ground-based observations collected during LMOS 2017. We will follow the NASA data management policy which defines three stages of data within the project lifecycle: field data, preliminary data, and final data. The field data is generated during the field deployment and is primarily used to measure progress in achieving the science goals. The preliminary data incorporates possible adjustments due to post-deployment instrument calibration/characterization, data synchronization, and the QA/QC process. The final data is intended to be publication-quality and open to the public. As required by NASA’s data policy, the final data will be archived at the Atmospheric Science Data Center at NASA Langley Research Center. Final data will be delivered to the Center and made publicly available within one year of completion of LMOS 2017.

Conclusion

The proposed LMOS 2017 field mission will provide valuable information on the ozone and ozone precursor distributions over Lake Michigan as well as a detailed description of the chemical processes that control ozone production and the meteorological factors that control the distribution of ozone and its precursors. This information is of critical importance to the LADCO states so that they can develop strategies to mitigate the harmful effects of ozone on public health and the ecology of the Great Lakes region. The proposed LMOS 2017 field campaign will also provide airborne measurements that can be used to validate new satellite trace gas and aerosol retrievals from TROPOMI and GOES-R ABI instruments. The LMOS 2017 mission will also provide airborne remote sensing measurements that can demonstrate the utility of future geostationary measurements of ozone and ozone precursors from the NASA Tropospheric Emissions: Monitoring Pollution (TEMPO) mission for addressing regional air quality issues and will help to engage regional air quality management in the use of satellite measurements for air quality management.

References:

- Abad, G. G., X. Liu, K. Chance, H. Wang, T. P. Kurosu, and R. Suleiman, 2015: Updated Smithsonian Astrophysical Observatory Ozone Monitoring Instrument (SAO OMI) formaldehyde retrieval, *Atmos. Meas. Tech.*, 8, 19-32.
- Angevine, W.M., C.J. Senff, A.B. White, E.J. Williams, J. Koerner, S.T.K. Miller, R. Talbot, P.E. Johnston, S.A. McKeen, and T. Downs, 2004: Coastal boundary layer influence on pollutant transport in New England. *J. Appl. Meteorol.*, 43, 1425-1437.
- Banta, R.M., C. J. Senff, R. J. Alvarez, A. O. Langford, D. D. Parrish, M. K., Trainer, L. S. Darby, R. M. Hardesty, B. Lambeth, J. A. Neuman, W. M., Angevine, J. Nielsen-Gammon, S. P. Sandberg, A. B. White, 2011: Dependence of daily peak O₃ concentrations near Houston, Texas on environmental factors: Wind speed, temperature, and boundary-layer depth. *Atmos. Environ.* 45, 162–173.
doi:10.1016/j.atmosenv.2010.09.030
- Bucsela, E. J., E. A. Celarier, M. O. Wenig, J. F. Gleason, J. P. Veefkind, K. F. Boersma, and E. J. Brinksma, 2006: Algorithm for NO₂ Vertical Column Retrieval From the Ozone Monitoring Instrument, *IEEE Transactions on Geoscience and Remote Sensing*, 44, 1245-1258.
- Bell, ML; Dominici, F; Samet, JM. (2005). A meta-analysis of time-series studies of ozone and mortality with comparison to the national morbidity, mortality, and air pollution study. *Epidemiology* 16: 436-445. <http://dx.doi.org/10.1097/01.ede.0000165817.40152.85>
- Browell, E. V., Differential absorption lidar sensing of ozone, *Proc. of the IEEE*, 77, 419-432, 1989.
- Browell, E V, M A Fenn, C F Butler, W B Grant, V G Brackett, J W Hair, M A Avery, et al. 2003. "Large-Scale Ozone and Aerosol Distributions, Air Mass Characteristics, and Ozone Fluxes over the Western Pacific Ocean in Late Winter/early Spring." *Journal Of Geophysical Research-Atmospheres* 108 (D20). <Go to ISI>://000185361800002.
- Crounse, John D., Karena a. McKinney, Alan J. Kwan, and Paul O. Wennberg. 2006. "Measurement of Gas-Phase Hydroperoxides by Chemical Ionization Mass Spectrometry." *Analytical Chemistry* 78 (19): 6726–32. doi:10.1021/ac0604235.
- Duncan, B. N., Y. Yoshida, J. R. Olson, S. Sillman, R. V. Martin, L. Lamsal, Y. Hug, K. E. Pickering, C. Retscher, D. J. Allen, J. H. Crawford, 2010: Application of OMI observations to a space-based indicator of NO_x and VOC controls on surface ozone formation, *Atmospheric Environment*, 44, 2213–2223.

- Dye, T. S., P. T. Roberts, and M. E. Korc, 1995: Observations of transport processes for ozone and ozone precursors during the 1991 Lake Michigan Ozone Study. *J. Appl. Meteor.*, 34, 1877–1889.
- Fast, J. D. and W. E. Heilman, 2003: The Effect of Lake Temperatures and Emissions on Ozone Exposure in the Western Great Lakes Region, *J. Appl. Meteor.*, 42, 1197-1217.
- Fischer, H., A. Pozzer, T. Schmitt, P. Jöckel, T. Klippel, D. Taraborrelli, and J. Lelieveld. 2015. “Hydrogen Peroxide in the Marine Boundary Layer over the Southern Atlantic during the OOMPH Cruise in March 2007.” *Atmospheric Chemistry and Physics* 15: 6971–80. doi:doi:10.5194/acp-15-6971-2015.
- Foley, T. , E. A. Betterton, P.E. R. Jacko, and J. Hillery, 2011: Lake Michigan air quality: The 1994-2003 LADCO Aircraft Project (LAP), *Atmos. Env.*, 45, 3192-3202.
- Fomba, K. W., K. Müller, D. Van Pinxteren, L. Poulain, M. Van Pinxteren, and H. Herrmann. 2014. “Long-Term Chemical Characterization of Tropical and Marine Aerosols at the Cape Verde Atmospheric Observatory (CVAO) from 2007 to 2011.” *Atmospheric Chemistry and Physics* 14 (17): 8883–8904. doi:10.5194/acp-14-8883-2014.
- Hair, J. W., C. A. Hostetler, A. L. Cook, D. B. Harper, R. A. Ferrare, T. L. Mack, W. Welch, L. R., Izquierdo, F. E. Hovis, 2008: Airborne High Spectral Resolution Lidar for Profiling Aerosol Optical Properties, *Applied Optics* , 47,doi: 10.1364/AO.47.006734
- Knuteson, R. O., F. A. Best, N. C. Ciganovich, R. G. Dedecker, T. P. Dirks, S. Ellington, W. F. Feltz, R. K. Garcia, R. A. Herbsleb, H. B. Howell, H. E. Revercomb, W. L. Smith, J. F. Short, 2004a: Atmospheric Emitted Radiance Interferometer (AERI): Part I: Instrument Design, *J. Atmos. Oceanic Technol.*,21, 1763-1776
- Knuteson, R. O., F. A. Best, N. C. Ciganovich, R. G. Dedecker, T. P. Dirks, S. Ellington, W. F. Feltz, R. K. Garcia, R. A. Herbsleb, H. B. Howell, H. E. Revercomb, W. L. Smith, J. F. Short, 2004b: Atmospheric Emitted Radiance Interferometer (AERI): Part II: Instrument Performance, *J. Atmos. Oceanic Technol.*,21, 1777-1789
- Kowalewski, M. G. and Janz, S. J.: Remote sensing capabilities of the GEO-CAPE airborne simulator, *Proc. SPIE*, 9218, 92181I–92181I–12, doi:10.1117/12.2062058, 2014. 13103, 13109
- Koerber, M., R. Kaleel, L. Pocalujka, and L. Bruss, 1991: An overview of the Lake Michigan Ozone Study. Preprints, Seventh Joint Conf. on Applications of Air Pollution Meteorology, New Orleans, LA, Amer. Meteor. Soc., 260–263.
- Kulmala, Markku, Üllar Rannik, Liisa Pirjola, Miikka Dal Maso, Janne Karimäki, Ari Asmi, Arto Jäppinen, et al. 2000. “Characterization of Atmospheric Trace Gas and Aerosol

- Concentrations at Forest Sites in Southern and Northern Finland Using Back Trajectories.” *Boreal Env. Res.* 5 (July 1999): 315–36.
- Langford, A. O., et al. (2015), An overview of the 2013 Las Vegas Ozone Study (LVOS): Impact of stratospheric intrusions and long-range transport on surface air quality, *Atmospheric Environment*, 109, 305-322, doi:10.1016/J.Atmosenv.2014.08.040.
- Lazrus, Allan L., Gregory L. Kok, John A. Lind, Sonia N. Gitlin, Brian G. Heikes, and Richard E. Shetter. 1986. “Automated Fluorometric Method for Hydrogen Peroxide in Air.” *Analytical Chemistry* 58 (3). AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC 20036: 594–97. doi:10.1021/ac00294a024.
- Lee, M, BC Noone, D O’Sullivan, and BG Heikes. 1995. “Method for the Collection and HPLC Analysis of Hydrogen Peroxide and C-1 and C2 Hydroperoxides in the Atmosphere.” *Journal of Atmospheric and Oceanic Technology* 12 (5). Amer. Meteorological Soc., 45 Beacon St., Boston, MA 02108-3693: 1060–70. doi:10.1175/1520-0426(1995)0122.0.CO;2.
- Lennartson, G.J. and M.D. Schwartz. 2002. The Lake Breeze-Ground Level Ozone Connection in Eastern Wisconsin: A Climatological Perspective. *Int. J. Climatology*, 22, 1347-1364.
- Loughner, C. P., M. Tzortziou, M. Follette-Cook, K. E. Pickering, D. Goldberg, C. Satam, A. Weinheimer, J. H. Crawford, D. J. Knapp, D. D. Montzka, G. S. Diskin, and R. R. Dickerson, 2014: Impact of Bay-Breeze Circulations on Surface Air Quality and Boundary Layer Export. *J. Appl. Meteor. Climatol.*, 53, 1697–1713. doi: <http://dx.doi.org/10.1175/JAMC-D-13-0323.1>
- Lyons WA, Cole HS. 1976. Photochemical oxidant transport: mesoscale lake breeze and synoptic-scale aspects. *Journal of Applied Meteorology* 15 : 733 – 743.
- Lyons, W. A., C. J. Tremback, and R. A. Pielke, 1995: Applications of the Regional Atmospheric Modeling System (RAMS) to provide input to photochemical grid models for the Lake Michigan Ozone Study (LMOS). *J. Appl. Meteor.*, 34, 1762–1786.
- Mansfield, T. A., 1998: Stomata and plant water relations: does air pollution create problems? *Environmental Pollution*, 101, 1-11.
- Millet, D B, N M Donahue, S N Pandis, A Polidori, C O Stanier, B J Turpin, and A H Goldstein. 2005. “Atmospheric Volatile Organic Compound Measurements during the Pittsburgh Air Quality Study: Results, Interpretation, and Quantification of Primary and Secondary Contributions.” *Journal of Geophysical Research* 110 (D07S07). doi:doi:10.1029/2004JD004601.

- Morgan, R B, and A V Jackson. 2002. "Measurements of Gas-Phase Hydrogen Peroxide and Methyl Hydroperoxide in the Coastal Environment during the PARFORCE Project - Art. No. 8109." *Journal Of Geophysical Research-Atmospheres* 107 (D19): 8109.
- Nowlan, C. R., X. Liu, J. W. Leitch, K. Chance, G. González Abad, C. Liu, P. Zoogman, J. Cole, T. Delker, W. Good, F. Murcray, L. Ruppert, D. Soo, M. B. Follette-Cook, S. J. Janz, M. G. Kowalewski, C. P. Loughner, K. E. Pickering, J. R. Herman, M. R. Beaver, R. W. Long, J. J. Szykman, L. M. Judd, P. Kelley, W. T. Luke, X. Ren, and J. A. Al-Saadi, 2015: Nitrogen dioxide observations from the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) airborne instrument: retrieval algorithm and measurements during DISCOVER-AQ Texas 2013, *Atmos. Meas. Tech. Discuss.*, 8, 13099–13155, doi:10.5194/amtd-8-13099-2015
- Ryan M. Stauffer, R. M., A. M. Thompson, D. K. Martins, R. D. Clark, D. L. Goldberg, C. P. Loughner, R. Delgado, R. R. Dickerson, J. W. Stehr, and M. A. Tzortziou, 2015: Bay breeze influence on surface ozone at Edgewood, MD during July 2011, *J. Atmos. Chem.* 72, 335–353.
- Ren, Yu, Aijun Ding, Tao Wang, Xinhua Shen, Jia Guo, Jiamin Zhang, Yan Wang, et al. 2009. "Measurement of Gas-Phase Total Peroxides at the Summit of Mount Tai in China." *Atmospheric Environment* 43 (9). Elsevier Ltd: 1702–11. doi:10.1016/j.atmosenv.2008.12.020.
- Shipley, S.T., D.H. Tracy, E.W. Eloranta, J.T. Trauger, J.T. Sroga, F.L. Roesler and J.A. Weinman, "A High Spectral Resolution Lidar to measure optical scattering properties of atmospheric aerosols , Part I: Instrumentation and theory" *Applied Optics*, 23, 3716--3724, 1983.
- Sillman, S., & West, J. J. (2008). Reactive nitrogen in Mexico City and its relation to ozone-precursor sensitivity: results from photochemical models. *Atmospheric Chemistry and Physics Discussions*, 8(6), 20501–20536. <http://doi.org/10.5194/acpd-8-20501-2008>
- Song, J.; Lei, W.; Bei, N.; Zavala, M.; de Foy, B.; Volkamer, R.; Cardenas, B.; Zheng, J.; Zhang, R.; Molina, L. T. Ozone response to emission changes: a modeling study during the MCMA-2006/MILAGRO Campaign. *Atmos. Chem. Phys.* 10 (8), 3827–3846.
- Tonnesen, G. S.; Dennis, R. L. Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO_x : 1. Local indicators of instantaneous odd oxygen production sensitivity. *J. Geophys. Res.* 2000, 105 (D7), 9213. Snow, Julie A., Brian G. Heikes, Haiwei Shen, Daniel W. O’Sullivan, Alan Fried, and Jim Walega. 2007. "Hydrogen Peroxide, Methyl Hydroperoxide, and Formaldehyde over North America and the North Atlantic." *Journal of Geophysical Research* 112 (D12). AMER

GEOPHYSICAL UNION, 2000 FLORIDA AVE NW, WASHINGTON, DC 20009
USA: D12S07. doi:10.1029/2006JD007746.

Sillman, S, P. J. Samson, and J. M. Masters, 1993: Ozone production in urban plumes transported over water: Photochemical model and case studies in the northeastern and midwestern United States. *J. Geophys. Res.*, 98, 12 687–12 699.

Smith, G. C. Smith, R. S. Morin, G. L. McCaskill, 2012: Ozone Injury to Forests Across the Northeast and North Central United States, 1994 – 2010, United States Department of Agriculture Forest Service, Northern Research Station, General Technical Report NRS-103.

U.S. Environmental Protection Agency, 2007: Review of the National Ambient Air Quality Standards for ozone: policy assessment of scientific and technical information. OAQPS Staff Paper. Section 7.6.3.2. EPA 452/R-07-007. Office of Air Quality Planning and Standards. Research Triangle Park, NC.

Walker, S. J., M. J. Evans, a. V. Jackson, M. Steinbacher, C. Zellweger, and J. B. McQuaid. 2006. “Processes Controlling the Concentration of Hydroperoxides at Jungfraujoch Observatory, Switzerland.” *Atmospheric Chemistry and Physics Discussions* 6 (4): 7177–7205. doi:10.5194/acpd-6-7177-2006.

Warneke C., de Gouw J.A., Goldan P. D., Kuster W. C., Williams E. J., Lerner, B.M., Jakoubek R., Brown S. S., Stark H., Aldener M., Ravishankara A. R., Roberts J. M., Marchewka M., Bertman S., Sueper D. T., McKeen S.A., Meagher J. F., Fehsenfeld F. C. (2004), Comparison of daytime and nighttime oxidation of biogenic and anthropogenic VOCs along the New England coast in summer during New England Air Quality Study 2002, *J. Geophys. Res.*, 109, D10309, doi:10.1029/2003JD004424.

Wittig, A E, N Anderson, A Y Khlystov, S N Pandis, C Davidson, and A L Robinson. 2004. “Pittsburgh Air Quality Study Overview.” *Atmospheric Environment* 38 (20): 3107–25. <Go to ISI>://000221838500002.