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Impacts of lake breeze meteorology on ozone gradient observations along Lake Michigan shorelines in Wisconsin

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ABSTRACT

Daytime onshore lake breezes are a critical factor controlling ozone abundance at coastal sites around Lake Michigan. Coastal counties along the western shore of Lake Michigan have historically observed high ozone episodes dating to the 1970s. We classified ozone episode days based on the extent or absence of the lake breeze (i.e., "inland", "near-shore" or "no" lake breeze) to establish a climatology of these events. This work demonstrated variable gradients in ozone abundances based on these different types of meteorology, with the sharpest ozone concentration gradients on days with a near-shore lake breeze. On 76–82% of days in which ozone reached 70 ppb for at least 1 h, a lake breeze was present. Evidence of ozone gradients from multiple observation platforms during the 2017 Lake Michigan Ozone Study (LMOS 2017) are shown for two days with different depths of lake breezes.

1. Introduction

The air quality in communities surrounding Lake Michigan has been of interest and concern for over 40 years (Lyons and Cole, 1976; Lennartson and Schwartz, 1999; Dye et al., 1995; Foley et al., 2011; Cleary et al., 2015). The lake breeze mesoscale meteorology driven by the presence of Lake Michigan influences the transport of pollutants emitted from urban areas along the lakeshore and farther upwind. Monitors around Lake Michigan consistently measure ozone concentrations that are among the highest observed in the eastern U.S. Accordingly, many counties surrounding Lake Michigan have long histories of being in nonattainment of federal ozone standards, and a number of counties around the lake are currently designated nonattainment of the 2008 and 2015 standards (Fig. 1). To develop effective strategies to reduce ozone pollution in this region, the complex interactions between lake breeze circulation, urban emissions and ozone concentrations must be resolved. It is particularly important to understand how ozone-rich air is distributed in this area in association with lake breeze meteorology.

Human exposure to ground-level ozone pollution has a wide range of serious health impacts, including inflammation of the airways and aggravation of lung diseases such as asthma (Bell et al., 2004, 2006; Wang et al., 1990). Exposure to high levels of ozone may also contribute to increased mortality. It is therefore important to understand how ozone pollution is distributed in the environment in order to know

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where people may be experiencing health impacts from ozone pollution. While ozone is considered a regional pollutant that may be well-mixed over dozens or hundreds of kilometers, its concentrations can change dramatically within a few kilometers in some environments. Wisconsin's Lake Michigan lakeshore is one such location.

Previous studies have demonstrated that elevated ozone concentrations can develop over the lake (Dye et al., 1995; Foley et al., 2011; Cleary et al., 2015; Hanna and Chang, 1995; Lennartson and Schwartz, 2002), where precursors emitted from shoreline urban areas (namely Milwaukee and Chicago) flow over the lake and react to form ozone. Onshore lake breezes can advect this high-ozone air onshore (Lyons and Cole, 1976; Dye et al., 1995; Lennartson and Schwartz, 2002). Dye et al. (1995) demonstrated from that an inversion over Lake Michigan confines urban pollution over the lake; other emissions, particularly those from inland and elevated point sources, may be located within or on top of this inversion, but with limited mixing. Lake breeze circulation patterns have also been investigated at other sites in the Great Lakes and other regions which are known to have an impact on air quality (Hanna and Chang, 1995; Lennartson and Schwartz, 2002; Curry et al., 2015;; Hayden et al., 2011; Levy et al., 2010; Sills et al., 2011; Blaylock et al., 2017; Lyons and Olsson, 1973). Photochemical models have difficulty predicting off-shore or near-shore ozone concentrations (Cleary et al., 2015), and improvements to models have focused on refining meteorological factors (McNider et al., 2018; Odman et al., 2019), model resolution (Abdi-Oskouei et al., 2020), and emissions inventories (Qin et al., 2019). Numerous studies have linked downwind precursor emissions to shoreline ozone concentrations during the lake breeze circulation (Lyons and Cole, 1976; Dye et al., 1995; Foley et al., 2011; Lyons and Olsson, 1973; Vermeuel et al., 2019; Keen and Lyons, 1978; Fast and Heilman, 2005). High resolution modeling and high-density air quality measurements have demonstrated the complex distribution of ozone exposure on neighborhood exposure scales in other parts of the US. (Basagana et al., 2012; Eeftens et al., 2019; Solomon et al., 2020) However, until recently, there were no long-term monitors in the right

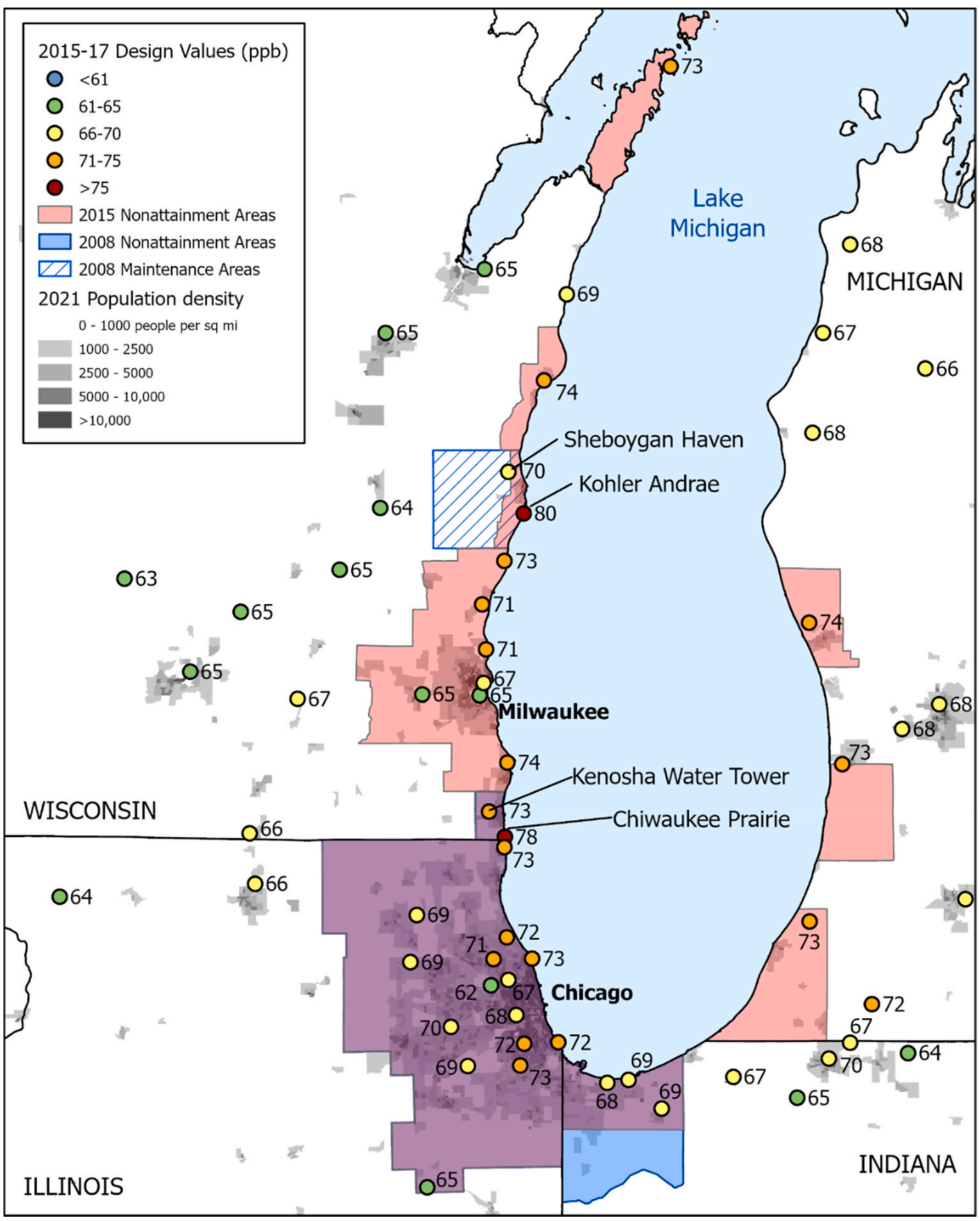

Fig. 1. Ozone design values for the years 2015–2015 for the Lake Michigan region (right), along with nonattainment and maintenance areas for the 2008 and 2015 ozone NAAQS. The purple shading in the Chicago area shows areas where the 2008 and 2015 ozone nonattainment areas overlap. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

positions to observe how ozone concentrations change with distance from the Lake Michigan lakeshore. Understanding shoreline ozone gradients along Lake Michigan will allow for better understanding of the impact to populations in this area, where population centers are concentrated near the lakeshore.

While the movement or presence of the lake breeze has been associated with higher ozone concentrations or higher particulate matter concentrations (Harris and Kotamarthi, 2005) the gradients of ozone perpendicular to the shoreline and their relationship to lake breezes have not been systematically characterized. We want to better understand the variability in how lake breezes impact the coastline and how the different types of meteorological patterns affect the distribution of ozone-rich air onshore. In doing so, these constraints on ozone extent can inform improved ozone modeling strategies, delineating between regional and local attributions to O_3 concentrations. Several processes lead to ozone concentration decreases as distance from the lake increases, but their relative impact, variability from episode to episode, and variability at different locations along the coast are not well quantified. The known processes are: (1) dilution of ozone from growth of the thermal internal boundary layer and subsequent entrainment of lower ozone air from aloft; (2) net chemical loss of ozone, dominated by the ozone titration reaction O_3+NO; (3) deposition of ozone to surfaces; and (4) frontal boundaries between air masses, with lower ozone air masses inland, and higher ozone airmasses toward the lake (Sills et al., 2011; Lyons and Olsson, 1973; Abdi-Oskouei et al., 2020). The analysis presented here attempts to focus on process (4) by analyzing for lake breeze extent, although dilution (1) and surface deposition (3) will occur as the lake breeze penetrates inland, linking processes 1, 2, and 4.

The Wisconsin Department of Natural Resources (WI DNR) began operating two ozone monitors located a few kilometers inland from shoreline monitors in 2013 and 2014. The continuous records available from these monitors allows the first investigation of ozone gradients in these locations over many years and a wide variety of conditions. A shorter-term, intensive study of ozone in the region, t The 2017 Lake Michigan Ozone Study, (LMOS 2017), took place from May 22-June 22, 2017 and was a collaborative effort between multiple universities and agencies to provide a suite of measurements to constrain ozone formation and dynamics in this complex environment (Doak et al., 2021). The team engaged aircraft, automobile-based measurements, ship-based measurements, ground monitoring measurements and satellite data in pursuit of a comprehensive look at ozone concentrations, ozone precursors, particulate matter, and meteorology (Stanier et al., 2021; Doak et al., 2021). LMOS 2017 was motivated by the gaps in current understanding of Lake Michigan ozone. Studies from LMOS 2017 have addressed ozone production sensitivity over water (Vermeuel et al., 2019), ozone modeling (Abdi-Oskouei et al., 2020), and lake breeze meterology (Wagner et al., 2021). However, no study has yet addressed the relationship between coastal ozone and lake breeze meteorology as measured during the LMOS 2017 campaign.

This investigation seeks to identify the localized gradients in ozone with respect to inland penetration of the lake breeze using many years of ground-based measurements. We further investigate the ozone distribution and coincident meteorology on selected days using higher resolution measurements taken during LMOS 2017.

1.1. Role of synoptic scale meteorology on high ozone

Ozone episodes in this area are generally associated with high pressure systems over the eastern United States that transport pollutants and the primary ozone precursors, volatile organic compounds (VOCs) and nitrogen oxides ($NO_x = NO + NO_2$) from the south and east into the Lake Michigan region.[3 9] These systems are typified by hazy, sunny, skies with generally weak, anticyclonic (clockwise) synoptic wind patterns, relatively shallow boundary layer depths, and reduced vertical mixing such that near-surface pollution concentrations are not as diluted as with other meteorological conditions. Dye et al.(Dye et al., 1995) estimated that 50 percent of Wisconsin's ozone exceedance days from 1980 to 1988 under the 1-h ozone NAAQS occurred when the center of a high pressure system was situated southeast of the area (i.e., Ohio and east thereof). Under these circumstances, high ozone concentrations in the Lake Michigan region may result when polluted air from high emissions regions, such as the Ohio River Valley, is transported northward along the western side of a high pressure system (Dye et al., 1995). In addition, while emissions from the heavily industrialized portions of the Lake Michigan region have decreased dramatically in recent decades, sources in large metropolitan areas along the lakeshore still generate ozone precursor emissions. Pollution from sources in these areas can add to regional upwind background of ozone and ozone precursors transported into the Lake Michigan region (Hanna and Chang, 1995). During lake breeze transport episodes, peak ozone concentrations usually move northward over the course of the day, carried by southerly winds. For example, on June 19, 2016, ozone peaked at Wisconsin's southern Chiwaukee Prairie monitor between 11 a.m. and 1 p.m. local time, at the Sheboygan Kohler Andrae (KA) monitor midway up the coast between 2 p.m. and 4 p.m., and at the northern Newport monitor between 4 p.m. and 6 p.m. (See Fig. S10 for site locations). However, high ozone events are episode-specific and synoptic winds and frontal movements can affect the transport of ozone precursors or concentration of ozone-rich air to various regions surrounding Lake Michigan (Dye et al., 1995).

1.2. Role of mesoscale meteorology on high ozone

Synoptic meteorological conditions often work in combination with lake-induced mesoscale meteorological features to produce the highest ozone concentrations along the western shore of Lake Michigan. With a surface area of approximately 58,000 km^2, Lake Michigan acts as a large heat sink during the warm months. The strong daytime temperature contrast between the warm land and lake-cooled air can lead to the formation of a thermally-driven circulation cell called the lake breeze, which will contribute an easterly component to the wind vector along the western Lake Michigan shoreline (Laird et al., 2001). Laird et al. described an analysis of 15 years of meteorological conditions surrounding the Lake Michigan lake breeze and concluded that the average difference in air-lake temperatures for lake breeze events were $\leq 12\ ^{\circ}C$ (Laird et al., 2001). The lake breeze is generally preceded by an early morning land breeze, driven by relatively warm temperatures over the lake (Dye et al., 1995). The land breeze can carry ozone precursors emitted from urban areas, primarily Chicago and Milwaukee, out over the lake, where they can react to form ozone (Lyons and Cole, 1976; Lyons and Olsson, 1973; Keen and Lyons, 1978). The onshore flow of the lake breeze circulation then transports elevated ozone from over the lake into coastal areas (Lyons and Cole, 1976; Lennartson and Schwartz, 2002; Levy et al., 2010; Lyons and Olsson, 1973). In this analysis, we connect the lake breeze meteorology with ground-based ozone observations to better understand the relationship to high ozone events.

1.3. Presence of gradients in ozone concentrations along the lakeshore

As a result of the synoptic southerly winds and the lake breeze circulation patterns, the highest ozone concentrations in the region typically occur along Wisconsin's and Michigan's lakeshores from May–September, well downwind of major pollution sources (Lennartson and Schwartz, 2002). As per the Clean Air Act, the US EPA must designate as nonattainment, any area that does not meet (or that contributes to ambient air quality in a nearby area that does not meet) the federal standard. . Fig. 1 shows the ozone design values for the years 2015 through 2017 for the region and non-attainment areas. The ozone design values (the three-year average of the annual fourth-highest maximum daily 8-h average concentrations for ozone) in Wisconsin's Kenosha County decreased by 5 ppb within a few km of the lakeshore, and design values in Wisconsin's Sheboygan County decreased by 10 ppb within a similar distance. Gradients were less steep in Michigan and in the urban regions around Chicago. The design values in Fig. 1 distill three years of ozone concentrations down to one value representative of the high end of ozone concentrations. However, the gradients in the years-long average design values resulted from variations in ozone concentrations on individual high-ozone days.

This study aims to determine how different inland penetration depths of lake breezes affect the distribution of ozone concentrations along Wisconsin's Lake Michigan lakeshore. We begin by defining the concentration differences along the lakeshore and a few km inland using data from paired nearshore and inland regulatory monitors in two Wisconsin lakeshore counties. We then connect the observed concentration gradients with the characteristics of the lake breeze meteorology on individual ozone episode days to better understand the origins of these gradients. Finally, we use the extensive measurement suite available from the LMOS 2017 campaign to examine the meteorology and ozone gradients in greater detail on two days with differing types of lake breeze classifications.

2. Methods

2.1. Classifying lake breeze phenomenon and high ozone

Hourly average measurements of ground-based ozone and meteorology (temperature, wind direction and wind speed) for regulatory monitors in Sheboygan (Kohler Andrae and Haven) and Kenosha (Chiwaukee Prairie and Water Tower) counties were downloaded from EPA's Air Quality System (https://aqs.epa.gov/aqs/). High-ozone days were defined as days where at least one site measured 1-h ozone concentrations exceeding 70 ppb at either the inland or the shoreline monitor. Note that this lies below the regulatory threshold of 8-h averaged ozone at 70 ppb used for assessing non-attainment. Lake breeze event types were classified for high-ozone days using wind direction data from the ground-based monitors in combination with radar and satellite images and model winds. This approach was modified from that described in Sills et al. (2011) (Sills et al., 2011). Radar images were accessed from the website https://weather.us/radar-us using data from both the Green Bay and Milwaukee radar stations at many times during the afternoon. Visible bands from the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite images were accessed from the website https://ge.ssec.wisc.edu/modis-today/index.php. The MODIS satellite passes over the Lake Michigan region around 2:30 p.m. CDT daily and collects multispectral images at resolutions varying from 250 m to 1 km depending on wavelength. Model synoptic scale winds (from the National Weather Service Global Forecast System model) were viewed from the website https://earth.nullschool.net/. All high-ozone days with measurements at both the inland and lakeshore monitors were examined.; For Kenosha County, this included 146 days during the years 2013–2019. For Sheboygan County, this included 106 days during the years 2014–2019. Table S1 lists the days examined and their classifications.

High-ozone days were classified into one of three categories according to the presence/absence of the lake breeze and how far it penetrated inland if present. On "inland" lake breeze days, the lake breeze affected both the lakeshore (i.e., Chiwaukee Prairie in Kenosha County or Kohler Andrae in Sheboygan County) and inland (i.e., Kenosha Water Tower or Sheboygan Haven) monitors. On "near-shore" lake breeze days, the lake breeze affected the lakeshore but not the inland monitor. On days classified as "no lake breeze", there was no apparent wind direction shift or lake breeze front at the monitors in Kenosha or Sheboygan counties. Unlike the "inland" and "near-shore" lake breeze categories, the "no lake breeze" category includes days with a wide range of meteorological conditions, as shown in Fig. S8 A small number of days were placed in a fourth category of unclassifiable days due to unclear or contradictory information, and several days had a lake breeze from an unusual wind direction (usually northeast at Kenosha and southeast at Sheboygan).

The criteria used to identify lake breezes were observations from surface meteorological monitors, satellite, radar and model winds (Table 1). In general, lake breezes were identified based on the occurrence of shifts in wind direction from prevailing winds to onshore flow accompanied by the presence of a lake breeze front evident from some combination of satellite (showing cumulus cloud lines), radar (showing lines of higher reflectance) and model winds (showing divergence over the lake and a convergence front over land). The primary criterion for distinguishing between inland and near-shore lake breezes was the occurrence of wind direction shifts at only the lakeshore monitor (for near-shore lake breezes) or at both lakeshore and inland monitors (for inland lake breezes).The lake breeze may occur for anywhere from a few

Table 1
Criteria used to identify lake breezes based on different observation platforms.

Platform	Indications of a lake breeze	Indications of no lake breeze	Ambiguous observations
Surface meteorological observations (hourly)	- Rapid shift in wind direction, usually from the southwest 1 h to onshore winds (from the SSW for Sheboygan and SE for Kenosha) the next hour	- No onshore winds	- Onshore winds without an abrupt wind direction shift
	- A drop in temperature accompanying the wind shift - Onshore winds sustained for ≥3 h -Inland lake breezes had wind shifts at lakeshore and inland monitors	- Onshore winds from an unusual direction*	
Satellite observations (daily, ~2:30 p.m. CDT)	- Sharp line parallel to the shoreline separating cumulus clouds inland and clear skies toward the lake	- Extensive, thick cloud cover	- No clouds visible
	- Near-shore lake breezes often had this line right near the shoreline		- Thin high- or mid-level clouds that obscure observations of cumulus clouds
Radar observations (~every 10 min)	- Fine line or sharp gradient in reflectivity roughly parallel to the shoreline - Gradual inland penetration or steady position of the line/gradient	- Persistent precipitation over the region	- No clear lines or gradients
Model winds (every 3 h)	- Divergence of winds over Lake Michigan	- No divergence over the lake	- Divergence over the lake with a convergence front located offshore
	- Convergence front (with synoptic winds) over land - Inland penetration or steady position of the convergence front over time	- Synoptic winds impact the sites all day	- Divergence over the lake interrupted by passage of a front

*These days were categorized as "lake breeze-unusual" if other platforms indicated the presence of a lake breeze.

minutes to 15 or more hours, but for classification purposes we only counted lake breezes that were sustained for 3 or more hours. Fig. S10 shows the evidence from these different platforms on example episode days. Mean hourly wind directions, ozone concentrations and other meteorological parameters, for three main classes of days are shown in Figs. S6 and S7.

2.2. 2017 LMOS measurement platforms

The 2017 Lake Michigan Ozone Study incorporated many different measurements of primary and secondary pollutants and meteorological variables via ground, mobile, ship and aircraft platforms (Stanier et al., 2021; Doak et al., 2021). The Scientific Aviation aircraft deployed regularly throughout the field campaign to measure ozone, NO_2, CO_2, CH_4 and meteorological parameters. At Spaceport Sheboygan supersite, an EPA research trailer contained instruments that measured in situ O_3, formaldeyde, NO_2, NO_x and NO_y. Three distributed 2B Personal Ozone Monitors (2B POM) were placed at 3 locations in Sheboygan: the Sheboygan Chamber of Commerce (SCC) site was 0.6 km from the lakeshore, the Sheboygan Fire Department Station (SFD) was 2.8 km inland, and the Kohler Water Plant (KWP) was 5.7 km from the lakeshore (See SI Fig. S8). The POMs did not always log data simultaneously because of data storage limitations. Published POM detection limit is 4.9 ppb with 1.5 ppb precision (Andersen et al., 2010). The distributed POMs measured ozone with 5-min averaging. Each POM in the network was logging to internal storage and the data were not downloaded regularly enough to prevent over-writing logged data, so the data is not continuous. The POMs were not at the same height above ground level, as they were positioned atop different buildings. The NOAA Research Vessel carried monitors for O_3 and NO_2, measured at 1-min intervals. Interception of the engine emissions on the ship was identified and removed from the data. The UWEC Mobile ozone (2B POM) measurements were conducted by stopping at regular positions at or between routine monitoring stations for a minimum of 5 min. The UWEC 2B POM instrument was calibrated before or after each day of measurements. The U.S. EPA's GMAP (Geospatial Measurement of Air Pollution) mobile van measured O_3 concentrations along with vehicle speed, wind direction and wind speed (Stanier et al., 2021). The Zion supersite housed a wide variety of instruments including an Illinois Environmental Protection Agency (IEPA) ozone monitor (AQS ID 17-097-1007). Data from the WDNR shoreline monitoring sites were provided at 1-min intervals for all times that the monitors were operating. The WDNR and IEPA sites all comply with EPA regulatory procedures for calibration and maintenance for 1-h averaged data. A comprehensive list of instruments and platforms can be found as a supplement to Stanier et al. (2021) (Stanier et al., 2021). The data repository is available at https://www-air.larc.nasa.gov/cgi-bin/ArcView/lmos.

3. Results and discussion

3.1. Analysis of historical WI DNR data set (2013–2019)

3.1.1. Inland-lakeshore ozone concentration differences

Analysis of data from WI DNR monitors operating inland and along the lakeshore provides insight into the spatial distribution of ozone concentrations along Wisconsin's Lake Michigan shoreline. Consistent with well-established patterns of ozone titration by fresh NO in urban areas, and the time required for net ozone formation to lead to accumulation of high ozone (Fast and Heilman, 2003, 2005), ozone concentrations on ozone episode days are lower in the regions with the highest emissions (in central Chicago and central Milwaukee) and higher in less densely populated locations (smaller cities and rural areas in Racine, Kenosha, Sheboygan, Ozaukee and Door Counties, WI) (Fig. 1). Proximity to the lake shore is also an important factor in concentration. The two monitors that generally measure the highest ozone concentrations in Wisconsin (Sheboygan County's Kohler Andrae monitor and Kenosha County's Chiwaukee Prairie monitor), are both located within a few hundred meters of the Lake Michigan shoreline.

Since 2013 or 2014, WI-DNR has operated additional monitors located a few km inland from these highest ozone monitors. Comparison of ozone concentrations and meteorology at the inland and lakeshore monitors can help define the occurrence, frequency and meteorological drivers of ozone gradients in this area. The Kenosha Water Tower monitor began operating in 2013 and is located 11.7 km northwest of the Chiwaukee Prairie monitor and 5.9 km inland from Lake Michigan. In Kenosha County, the annual fourth highest maximum daily 8-h average (MDA8) values were 3–7 ppb lower at the inland Kenosha Water Tower monitor when compared to the Chiwaukee Prairie lakeshore monitor through 2017 (Table S1 in the Supplemental Information). The annual fourth highest MDA8 values at these two Kenosha County sites were almost identical in 2018 and 2019.

The Sheboygan Haven inland monitor began operating in 2014 and is located 17.7 km north-northwest of the Kohler Andrae monitor and 5.1 km from the lakeshore. In Sheboygan County, the fourth highest MDA8 values at the inland monitor were 4–14 ppb lower than those at the lakeshore monitor every year since 2014. These differences are also reflected in the three-year average design values at these monitors (see Fig. 1). This confirms the steep drop-off of ozone concentrations with increasing distance from the lakeshore on high ozone days (annual fourth highest MDA8 values).

Examination of the hourly ozone concentrations within Sheboygan County provides insights into the patterns of ozone concentrations near the lakeshore on a finer timescale. Fig. 2 shows the 1-h average ozone concentrations for the Kohler Andrae and Sheboygan Haven monitors over the course of an example 5-day ozone episode in 2014. Three days in this episode resulted in MDA8 values over 70 ppb at the Kohler Andrae monitor and one day resulted in an MDA8 value over 70 ppb at the Sheboygan Haven monitor. This ozone episode is typical of the episodes that affect the lakeshore and offers an excellent example of how ozone concentrations compare at the two monitors located in Sheboygan County.

Hourly ozone concentrations generally changed at both sites in parallel (Fig. 2). However, 1-h concentrations at the lakeshore Kohler Andrae monitor were almost always higher than those at the inland Haven monitor. Peak concentrations were also consistently higher at the lakeshore monitor: as much as 20 ppb higher on July 19 and 22. Overall,

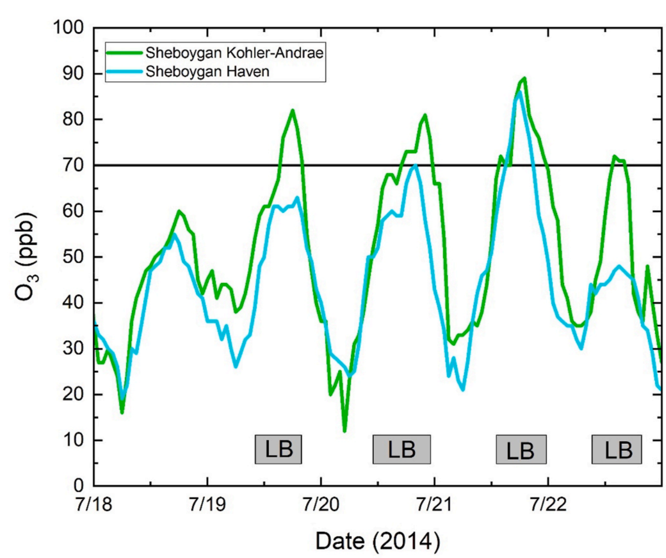

Fig. 2. Hourly ozone concentrations at the Sheboygan County lakeshore (Kohler Andrae) and inland (Sheboygan Haven) monitors for an episode from July 18–22, 2014. Grey blocks designate days specified as influenced by a lake breeze.

this episode shows systematic differences between inland and lakeshore ozone concentrations, with generally higher concentrations at the lakeshore. These offsets are consistent with the differences observed in fourth high MDA8 and design values. The episode also demonstrates considerable variability from day to day in the concentration differences with distance inland. The differences in observed ozone at the two sites show the day-to-day variability due to several drivers: increased chemical and depositional losses over land, increased precursor concentrations within a plume, differences in dilution and different air mass trajectories due to positioning of the lake breeze over land. The goal of this analysis is to analyze for the frontal boundary positioning of the lake breeze.

The relationships between ozone concentrations at these inland and lakeshore monitors for all monitored hours from 2014 to 2019 (Sheboygan) or 2013–2019 (Kenosha) are depicted in Fig. 3. The median 1-h ozone concentrations at both inland monitors were consistently lower than those monitored at the lakeshore for coastal ozone concentrations greater than 30 ppb (the median inland concentration is below the blue 1:1 line in Fig. 3). Inland-lakeshore concentration differences tend to be greater in Sheboygan County relative to Kenosha County, particularly for coastal ozone concentrations greater than 50 ppb. The same trends are found with MDA8 values (not shown). The hourly O_3 concentration

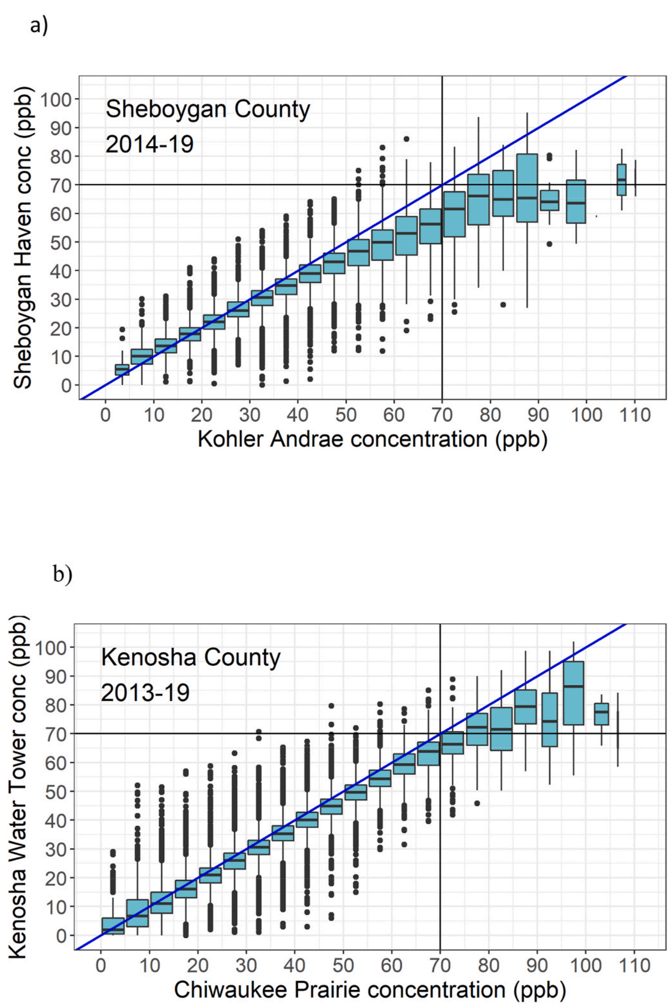

Fig. 3. Boxplots of 1-h ozone concentrations comparing inland monitors (y-axes) to lakeshore monitors (x-axes) in a) Sheboygan and b) Kenosha counties. The blue lines show the 1:1 line. Boxplots show the median (line) and range (box is 25th to the 75th percentile; whiskers are highest or lowest within 1.5 x interquartile mean) of concentrations observed. The points are outliers that fall beyond the whiskers. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

data also shows that the concentration differences between lakeshore and inland monitors were greatest when lakeshore ozone concentrations were at their highest (Fig. 3). During hours when lakeshore ozone was above 70 ppb, inland median concentrations were consistently much lower. For example, during periods when lakeshore ozone concentrations were between 90 and 95 ppb in Sheboygan County, the median inland concentration was only 66 ppb. These findings demonstrate that the highest ozone concentrations are generally confined to the lakeshore monitors and ozone concentrations are reduced at sites just a few km inland. The reason for this discrepancy between monitors is explored further below, by investigating only high ozone days and inspecting the role of lake breeze front position on the ozone concentrations observed.

3.1.2. Distribution of lake breeze days on high ozone days

High-ozone days in Kenosha ant Sheboygan counties were classified into three categories according to the presence or absence of the lake breeze and the penetration distance of the lake breeze, if present, relative to the inland monitor. The distribution of lake breeze event types on high ozone days in Kenosha and Sheboygan counties show a high occurrence of inland lake breezes associated with high ozone (Table 2). A majority of the high ozone days occurred during an inland lake breeze for both sites, with these inland lake breezes being somewhat more frequent in Sheboygan (65% of events) than in Kenosha (55% of events). Near-shore and no lake breeze events were less common during high ozone days but still important at both sites, and the two types of events occurred with similar frequencies. High ozone events were observed from as early as April to as late as September (See SI Table 1). The presence of a lake breeze appears to be almost necessary for high ozone, with only 15–19% of high ozone days without a lake breeze, although a lake breeze in itself is not sufficient to create high ozone; downwind precursor emissions, high temperatures and other conducive meteorological conditions are also necessary.

The meteorology of the different types of high ozone events at the Kenosha and Sheboygan sites are shown in Figs. S8 and S9. Inland and near-shore lake breezes have characteristic and distinct meteorological patterns at the different monitors, as evident from the wind directions, westerly wind component speeds and temperatures at different points of the day. Lake breeze winds came from a narrow band of directions at each site, and the onset of these winds varied between the lakeshore and inland monitors. In addition, on near-shore lake breeze days, stronger westerly winds likely prevented the lake breeze from penetrating far inland, as has been shown in other analyses of lake breezes near the Great Lakes (e.g., Sills et al., 2011 (Sills et al., 2011)). A wide range of meteorology was observed on days with no lake breeze. In general, the prevailing winds were more southerly on days without a lake breeze and didn't shift as much from the overnight to afternoon hours (See SI Section 2.2).

The different types of lake breeze events (inland, near-shore and no lake breeze) show a differential impact on maximum 1-h ozone at inland and lake shore monitors for high ozone days (Fig. 4). While median peak ozone concentrations at the lakeshore were similar across all event types, median peak concentrations at inland monitors varied between the different types of events. Median ozone concentrations were lower at inland monitors relative to lakeshore monitors for all types. However, the inland lakeshore concentration differences were especially large during near-shore lake breeze events, with median offsets of more than 23 ppb in Sheboygan and more than 15 ppb in Kenosha. During these events, the lake breeze carried ozone-rich air to the lakeshore monitors but did not reach the inland monitors, resulting in the large concentration gradients observed. Even during inland lake breeze events that reached the inland monitor, median concentrations inland were 5 ppb lower than at the lakeshore monitor in Sheboygan and 3 ppb lower in Kenosha.

Overall, this analysis demonstrates that, while lake breezes usually reach the inland monitors located 5.2–5.6 km from the lakeshore, the ozone concentrations carried by these lake breezes decrease by an

Table 2
Distribution of the occurrence of different types of lake breeze events during high ozone days at the Sheboygan and Kenosha County monitors. The table lists the number of days in each event type and the percentage of the classifiable events (which excludes "unclear" events) in each category in parentheses. The total days in the ozone season from April–September used to generate this data set is also given. High ozone days are days with 1-h average ozone that reached 71 ppb or higher.

Location (Years)	Inland lake breeze	Near-shore lake breeze	No lake breeze	Inland unusual*	Unclear	Total high O_3 days **(total days)**	Average high O_3 days/year
Sheboygan (2014–19)	69 (65%)	17 (16%)	15 (14%)	1 (1%)	4	106 (1098)	17.7
Kenosha (2013–19)	81 (55%)	32 (22%)	28 (19%)	3 (2%)	2	146 (1281)	20.9

*Unusual wind direction.

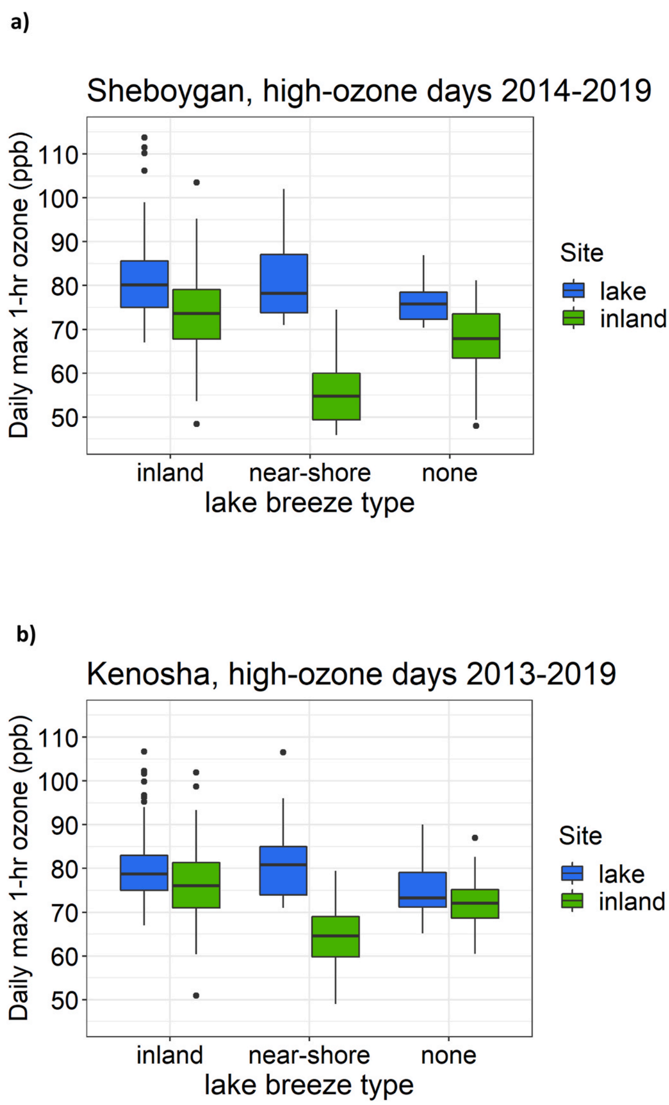

Fig. 4. Boxplots for Sheboygan and Kenosha counties showing the median and range of daily maximum 1-h average ozone concentrations for ozone episodes with inland, near-shore, and no lake breeze. Data are shown for the lakeshore and inland monitors in each county. Boxplots show the median (line) and range (box is 25th to the 75th percentile; whiskers are highest or lowest within 1.5 x interquartile mean) of concentrations observed. The points are outliers that fall beyond the whiskers.

average of 3–5 ppb as they move inland across this distance (Fig. 4) from the lakeshore. A number of mechanisms can account for these inland decreases in ozone concentrations, as stated above: 1) dilution, 2) chemical loss, 3) dry deposition and 4) frontal boundaries. The observed reductions in ozone as the lake breeze moves inland helps explain the differences observed in the 8-h ozone design values at these monitors. Similar reductions in ozone concentrations with distance inland were observed on days without a lake breeze, presumably due to similar mechanisms. In addition, this analysis shows that some lake breeze events don't reach the inland monitors at all. The concentration gradients during these near-shore lake breeze events are even more pronounced, 25 ppb in just 5 km in Sheboygan and 15 ppb in 5.5 km in Kenosha. While these events are less frequent, they lead to extremely sharp concentration gradients along the lakeshore based on how far inland the lake breeze reaches.

Taken together, the gradients in ozone design values apparent in Fig. 1 result from a combination of two primary factors. The first factor reduces ozone concentrations within an air mass as it moves inland on a lake breeze or during non-lake breeze transport. This factor occurs most frequently and results in intermediate reductions in ozone concentrations inland. The second factor occurs when ozone-rich air from the lake breeze fails to reach inland monitors because the lake breeze remains near-shore. These events result in sharp gradients in ozone concentrations but occur less frequently. Fast and Heilman modeled ozone exposures at nearshore sites as the highest in their study area, but the grid-scale of their model could not capture steeper gradients (Fast and Heilman, 2003). Dye et al. (Dye et al., 1995) observed highest surface ozone within 15–20 km of the Lake Michigan shoreline on July 18, 1991, which they attributed to an internal boundary layer expansion as the lake breeze moves inland. Lyons and Cole (1976) also asserted that ozone is fumigated within an internal boundary layer as the marine air flowed onshore. Here, we specify that the internal boundary layer fumigation could only apply for 55–65% of high ozone events, when a lake breeze front moves well inland.

3.2. Lake breeze and high ozone events during LMOS 2017

Data from ground based and airborne platforms collected during the LMOS 2017 field campaign were examined in greater depth on two days representative of either an inland or a near-shore lake breeze. These data sources show features of the lake breeze with more detail than available from routine observations. General summaries of the 2017 LMOS have been described elsewhere (Stanier et al., 2021;Doak et al., 2021). Our focus here is on mobile platforms or other measurements that highlight the lake breeze depth and shoreline gradients in ozone in the context of lake breeze classifications above. Table 3 shows the Lake Breeze classifications for days during 2017 LMOS as determined through the methods described above. All 32 days of the campaign were classified regardless of their ozone concentrations, which differs from the method used above for the historical data sets which were only investigated for lake breeze during high ozone events. Days with a lake breeze, either inland or near-shore, are a higher percentage of high O_3 days, than during the historical record. The distribution of inland, near-shore and non-lake breezes during high ozone events are similar to those found in the long-term record depicted in Table 1, in which inland lake breezes are the majority of high ozone events. As with Table 1, the near-shore lake breeze high ozone days have roughly the same % of total days as the no lake breeze high ozone % of total days. This does appear

Table 3
Lake breeze classifications for the LMOS 2017 campaign (May 22, 2017–June 22, 2017). High ozone days had peak 1-h ozone over 70 ppb.

Location	Inland lake breeze		Near-shore lake breeze		No lake breeze		Total High Ozone days
	High O_3 (% high days)	**All days (% all days)**	**High O_3 (% high days)**	**All Days (% all days)**	**High O_3 (% high days)**	**All days (% all days)**	**32 total days (% total days)**
Sheboygan	4 (67%)	11 (34%)	1 (17%)	3 (9%)	1 (17%)	18 (56%)	6 (19%)
Kenosha	4 (40%)	8 (25%)	3 (30%)	5 (16%)	3 (30%)	19 (59%)	10 (34%)

coincidental, as the near-shore lake breezes make up a fewer percent of total days, but a larger percent of high ozone events, whereas no lake breeze is the meteorological condition for a majority of all days and is a small subsection of high ozone days. This analysis points to how modeling studies could be conducted to investigate how high ozone occurs at these sites with no lake breeze, but that is outside the scope of this study.

This analysis identifies more days as lake breeze days than Wagner et al. (2021), which used a different methodology for identification. All lake breeze days identified by Wagner et al. are identified by our methods (June 2, 8, 11,12, 16, 17 at Kenosha/Zion area and June 2, 8, 11, 12, 15, 16 at Sheboygan), however we identify 7 or 8 additional days with lake breezes at Kenosha/Zion and Sheboygan respectively. Wagner et al. applied more conservative approach to lake breeze identification (requiring an abrupt negative temperature change at the sites) and the one presented in this analysis as more inclusive. Other studies have also found differing percentages of lake breeze day identifications depending on the type of analysis applied. For example, Sills, et al.(Sills et al., 2011) and Wentworth et al. (Wentworth et al., 2015) identified more lake breeze days when using a manual inspection of satellite and radar imagery along with meteorological observations from ground stations, similar to the methods used here. Lennartson and Schwartz (2002) report lake breeze meteorology coinciding with 85% of high ozone days at the Lake Michigan shoreline. Our findings align with the observations from Lennartson and Schwartz, but deomonstrate that some lake breezes are situated close to the shoreline and occur at times of the day when a temperature drop is not always an identifying feature of the circulation pattern.

Below, we examine the distribution of ozone concentrations on evidence on two days during LMOS 2017: one day with an inland lake breeze (June 2, 2017), and one day with a near-shore lake breeze (June 12, 2017).

3.3. Individual days as examples of lake breeze classifications during 2017 LMOS

Two days during the 2017 LMOS campaign had high coverage by various platforms that captured many features of these regional ozone events. Table 4 lists the dates that exemplify different lake breeze classifications, along with the measurement platforms and wind conditions for those specific days. Each day will be described in detail below. The maximum 1-h ozone trend follows those observed for the historic data sets, where the larger ozone gradient is observed between the shoreline and inland monitors at the Kenosha and Sheboygan county sites on these two select days from 2017 LMOS (Fig. 5). Note that the daily 1-h maximum ozone exceeds 75 ppb for both days at the shoreline sites and does not exceed 75 ppb for the inland sites for the near-shore lake breeze day, June 12, 2017. Detailed descriptions for each day are expanded upon in the following sections. See also SI Section 5.

Table 4
Examples of individual lake breeze classification days from 2017 LMOS.

Date	Lake Breeze Classification	Ground Level Winds	2017 LMOS Platforms* (in addition to monitoring network)
June 2, 2017	Inland	SW to SE (Kenosha) W to S/SSE (Sheboygan)	Zion supersite, Spaceport supersite, UWEC mobile, NOAA RV Ship, Scientific Aviation, SCC POM, KPW POM
June 12, 2017	Near-Shore	SSW to SSE (Kenosha) SSW or SW (Sheboygan)	Zion supersite, Spaceport supersite, NOAA RV Ship, EPA GMAP, Scientific Aviation, KPW POM

*See Section 2.2 for descriptions of the different platforms.

3.3.1. Inland lake breeze: June 2, 2017

June 2, 2017 was a classic high ozone day along the western shore of Lake Michigan with an inland lake breeze. There was a high pressure system located to the southeast of the region that created southwesterly synoptic winds in the morning. Temperatures reached 27.2 °C at Milwaukee's Mitchell Airport, with mostly sunny skies and some clouds later in the afternoon (See SI S.11). Fig. 6 depicts the ozone concentrations throughout the day with coincident wind direction data at select sites. Ground site O_3 observations were averaged to 30-min averages to get closer to the time resolution for mobile platform operations. A lake breeze began to form in the morning with a wind shift observed at Chiwaukee Prairie at 9:00 CDT and at Sheboygan Kohler Andrae around 10:00 CDT (Fig. 6-f and 6-h). The lake breeze reached farther inland sites (Milwaukee SER, Grafton and Sheboygan Haven) a few hours later, around 12:00 CDT (Fig. 6-f,g). This classic inland lake breeze was evident from radar images (see SI S.5) on this day.

The 8-h ozone concentrations for Wisconsin lakeshore sites as far north as Manitowoc exceeded 70 ppb, including at inland sites Sheboygan Haven and Kenosha Water Tower (see SI: Table S.2). Hourly ozone concentrations reached 93 ppb at the Chiwaukee Prairie monitor (Fig. 6-d). The POM located at SCC recorded a 5-min concentration of 99 ppb. The UWEC mobile platform measured ozone concentrations at and between the monitoring sites that showed relatively similar concentrations but more variability (See SI, Fig. S12).

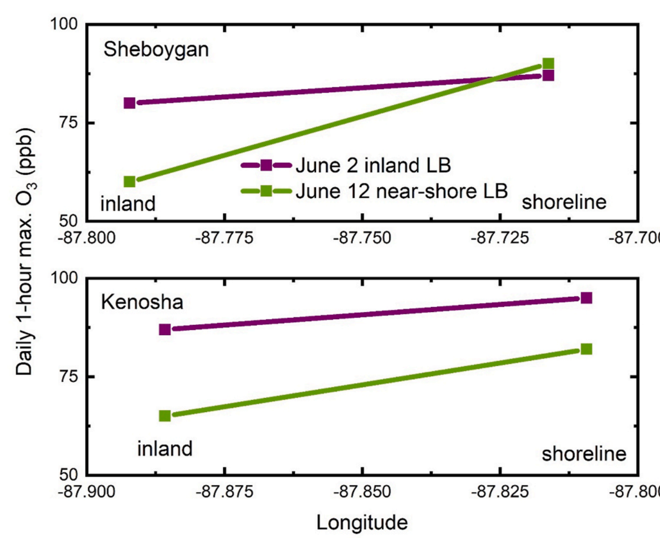

Fig. 5. Maximum daily 1-h ozone concentrations for June 2, 2017 (inland lake breeze) and June 12, 2017 (near-shore lake breeze) at the Kenosha County and Sheboygan County monitoring sites as a function of longitude. The shoreline sites are Chiwaukee Prairie in Kenosha County and Sheboygan Kohler Andrae in Sheboygan County. The inland sites are Kenosha Water Tower in Kenosha County and Sheboygan Haven in Sheboygan County.

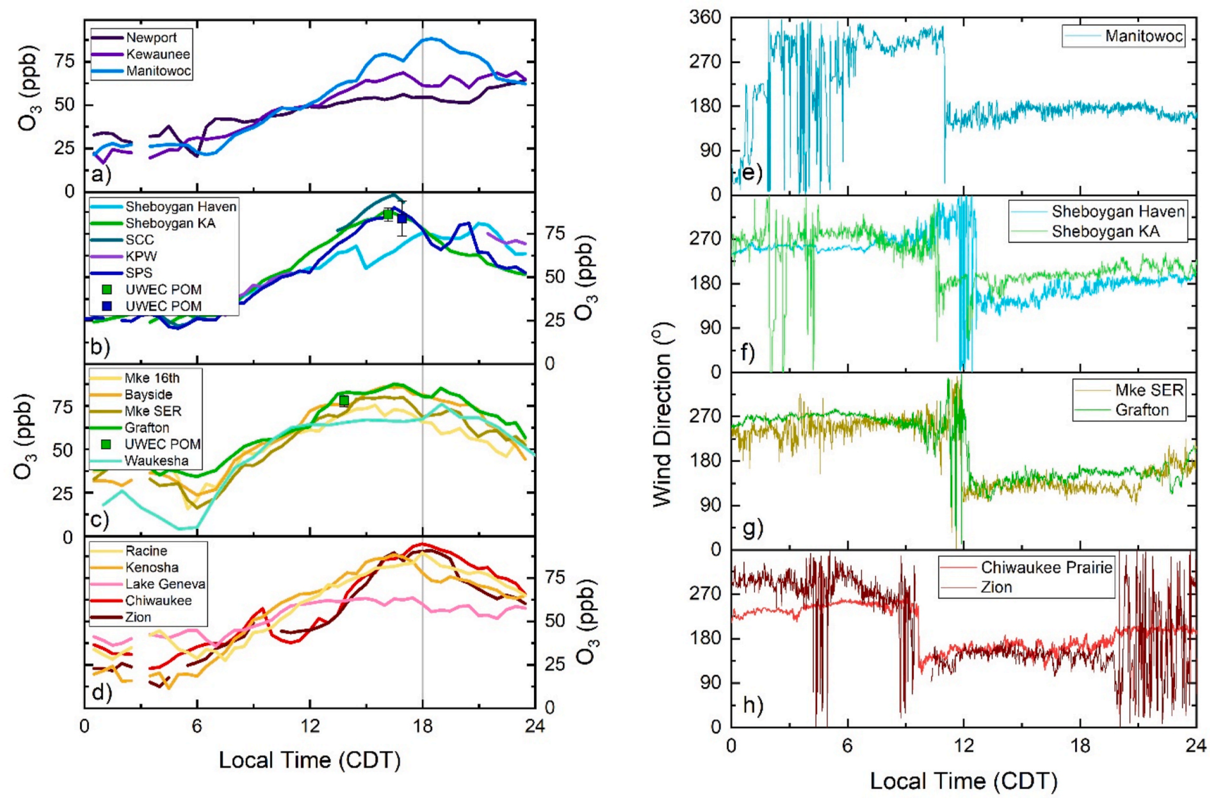

Fig. 6. O_3 measurements at ground (30 min average) and mobile (5 min average) sites June 2, 2017 (panels a–d), wind direction measurements (1 min average) in e) Sheboygan Haven and Kohler Andrae, f) Grafton, g) Milwaukee SER, and h) Chiwaukee Prairie, WI. Sites are arranged based on their location, from the south (bottom) to the north (top). The grey bar indicates the time for data used in the map in Fig. 7.

A map of 1-h ozone concentrations at monitoring sites at 6:00 p.m. CDT from June 2 (Fig. 7) shows the spatial distribution of ozone concentrations measured across several platforms on this day, including measurements from WI DNR regulatory sites, the Zion and Sheboygan supersites, and ship measurements over the lake (where 1 min data are shown for the 1-h time window). Measurements of ozone are consistently elevated at monitors reaching several km inland in eastern Wisconsin, however, the high ozone concentrations do not reach inland counties dozens of km away from the lakeshore. Ozone observations from the ship are lower than measurements at the coastal sites.

Aircraft measurements were used to better understand the dimensions of the ozone-rich marine layer on June 2. The Scientific Aviation aircraft flew in the afternoon from 14:03 to 18:48 CDT on June 2, 2017 (Fig. 8). The aircraft left the Sheboygan airport to completed onshore and off-shore spirals at Sheboygan, flew to offshore Zion with low level ascents and descents in transit, then completed offshore and onshore spirals at Zion, flew north to Milwaukee and completed an offshore spiral at Milwaukee, then flew northward at low altitude toward the shoreline, and then completed a second set of offshore and onshore spirals near Sheboygan before landing at 18:48 CDT. The highest ozone concentrations measured during these flights is over water offshore of Milwaukee at altitudes below 200 m above lake level.

As an illustration of the ozone rich marine layer, a segment of the Scientific Aviation flight is depicted in Fig. 9. An altitude versus longitude plot (referred to as an apron plot) was constructed using ground station and aircraft spiral data in the later afternoon at Milwaukee (9-a) (42.9 N–43.2 N). In Fig. 9-a, the aircraft did not fly over land. The lower ozone concentrations on land during that plot depict conditions for urban monitors which are impacted by local NOx emissions, reducing overall O_3 concentrations. The aircraft was able to fly lower in altitude over water than over land (see Fig. 9a-bb). Ozone concentrations are higher during the low-level aircraft legs over the lake than ground measurements, with ozone-rich air dominating altitudes below 500 m agl, with some layers of depleted ozone. The observation of a depleted ozone layer above the marine layer over Lake Michigan was also noted by Dye et al. (1995) which they attributed the a difference in air parcel origin and limited convective mixing above the conduction layer. Foley et al. (2011) did not describe any layers of low ozone above the conduction layer, but did analyze trends in NO_y and O_3 above and below 200 m agl over water. Foley et al. described a low altitude haze observed by flight crews, which could pertain to possible high NO_x plumes or aerosols stratified over the lake. High over-water ozone was also observed by Hastie et al. (1999) over Lake Ontario by manned aircraft observations, with ozone over 100 ppb at 400 m AGL.

An altitude versus temperature plots overlaid with ozone concentrations is given in Fig. 9 b for the same spiral near Milwaukee in Fig. 9-a. Here, we refer to sections of aircraft vertical temperature profiles within 10% of the dry adiabatic lapse rate (9.76 K per km) as neutral, and sections of temperature profiles with slopes below 8.78 K per km as stable, and sections of temperature profiles that increase with height as inverted. This graph shows a distinct break from a linear altitude-temperature relationship, close to a dry adiabatic lapse rate, above 500 m agl to a stable atmosphere below 500 m agl. The region near 200 m agl shows lower concentrations of ozone in a band of this stable atmosphere. Fig. 9b shows that ozone is enhanced within the colder air nearer to the surface within the inversion. There were coincident NO_2 measurements on the Scientific Aviation aircraft that do not explain this low O_3 region as merely from titration with NO to conserve O_x ($O_x = O_3 + NO_2$). Fresh NO can titrate O_3 through the following reaction.

$$NO + O_3 \rightarrow NO_2 \quad (1)$$

Ship plumes were investigated as a source of over-water ozone depletion events by Gronhoff et al. (Gronoff et al., 2019) during the OWLETS campaign at Chesapeake Bay where column NO_2 observations

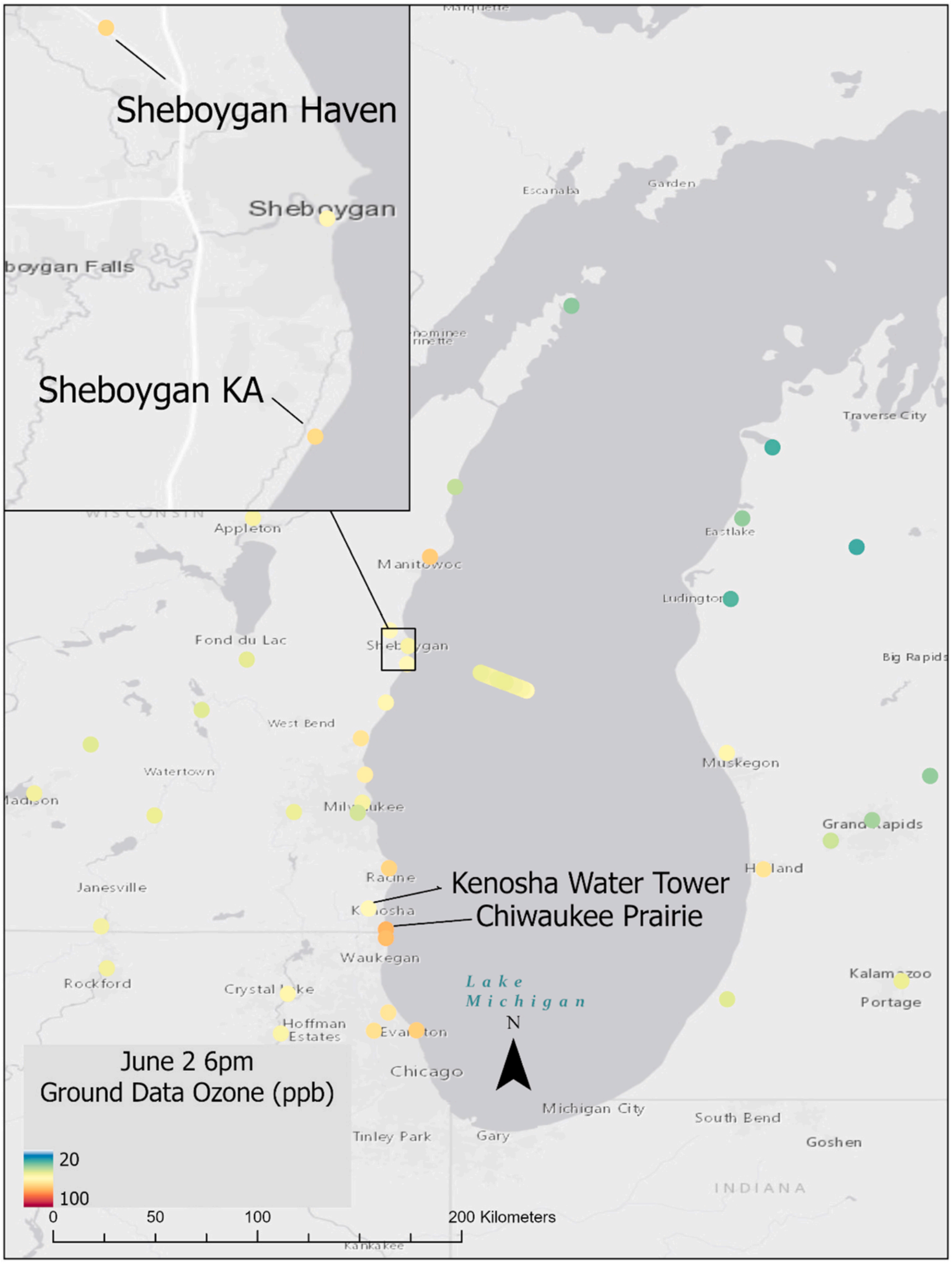

Fig. 7. Map of ground and ship-based ozone measurements at WDNR sites, EPA Sheboygan Spaceport site, Zion and ship measurements at 18:00 CDT June 2, 2017. Ground measurements are 30 min averages centered at 18:00 CDT, ship measurements are 1-min average in the time window of 17:45–18:15 CDT.

aided in identifying titration events over water by the reaction of NO with O_3. Concentrations of NO_2 from the Scientific Aviation aircraft on June 2, 2017 are mostly below 2 ppb in the altitudes between 100 and 250 m agl with only two distinct titration events where NO_2 concentrations rose up to 16 ppb are observable in confined spatial areas within this low-level layer. There are 3 titration events with lower O_3 and higher NO_2 below 100 m AGL off-shore of Milwaukee on June 2. A feature of ozone on June 2 is persistent high concentrations (>70 ppb) at altitudes up to and approaching the continental boundary layer height (~2500 m AGL, as seen by the capping inversion near 2500 m AGL). Conditions for high ozone are favorable within the marine layer and aloft up to the boundary layer height except for where cleaner air masses are confined to limited mixing over the marine layer.

The ship was in a transect across Lake Michigan headed west toward Sheboygan on June 2, 2017. At 18:00, ozone concentrations observed in the middle of the lake offshore from Sheboygan were up to 76 ppb, indicating the horizontal extent of the ozone-rich airmass within the marine boundary layer at this time. These concentrations were high, but still much lower than those measured at the same time farther south by the Scientific Aviation aircraft (see Fig. 7). Within 3 h (18:00–20:30 CDT) the ship transected Lake Michigan and reached Sheboygan Harbor, and during that time, ozone concentrations between Spaceport Sheboygan and the ship were similar. At (20:06–20:29 CDT), ozone concentrations were uniformly around 80–84 ppb. This suggests that the ship was intercepting air similar in composition to that at Spaceport Sheboygan, but which differed from air sampled at Sheboygan Kohler Andrae to the southwest, with some evidence for a localized Sheboygan plume (see SI: Fig. S13).

Overall, analysis on this day showed that high ozone concentrations extended from the middle of Lake Michigan to many kilometers inland,

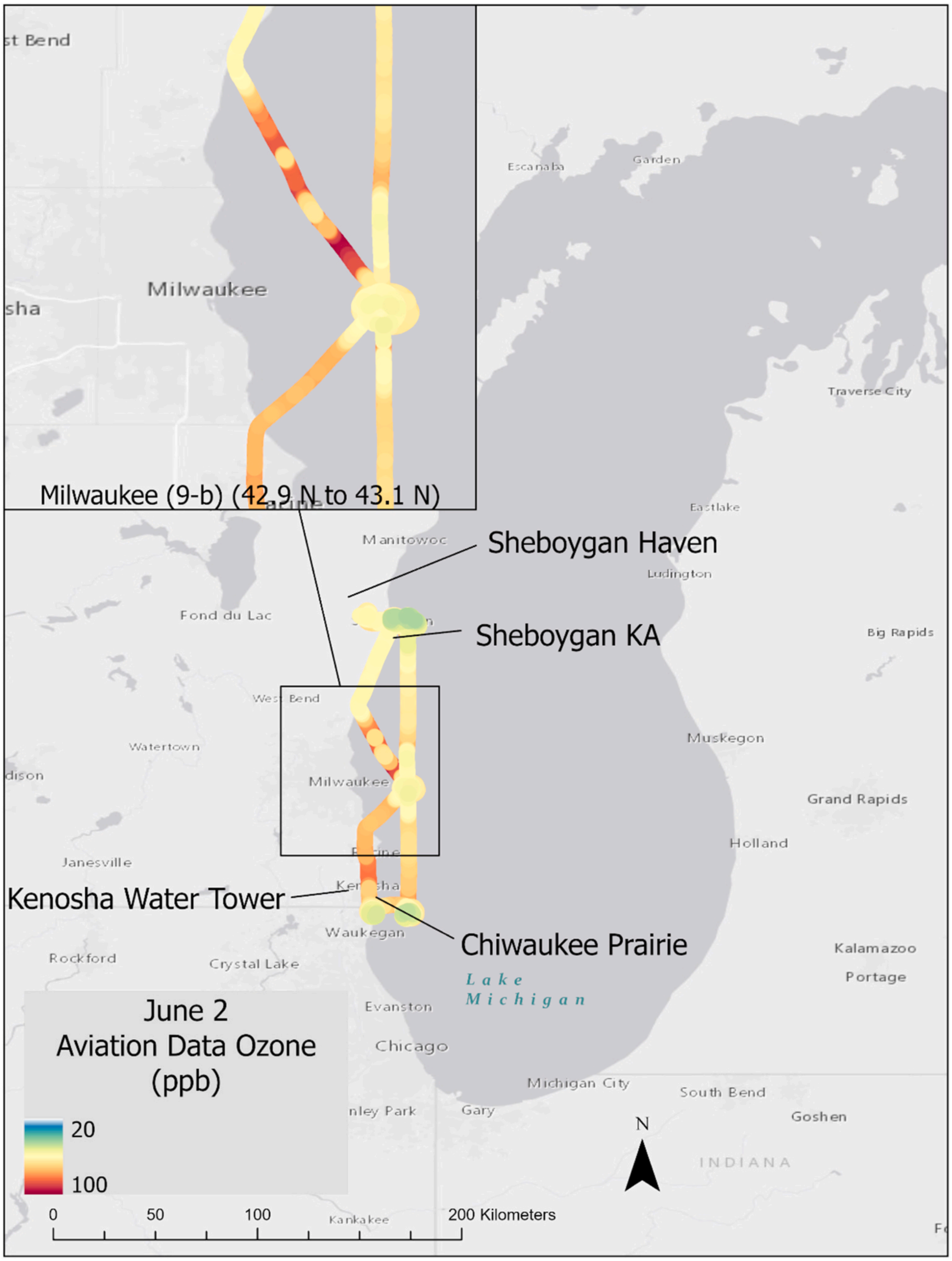

Fig. 8. Scientific Aviation flight on June 2, 2017. The aircraft departed from Sheboygan Airport at 14:03 CDT, completed two spirals near Sheboygan, flew southward over water to offshore Zion, completed two spirals near Zion, flew northward to complete one spiral offshore of Milwaukee and completed one more spiral near Sheboygan before landing at the Sheboygan airport at 18:48 CDT.

with the highest concentrations measured at very low altitudes (dozens of meters) over the lake, offshore of Milwaukee.

3.3.2. *Near-shore lake breeze: June 12, 2017*

The day of June 12, 2017 was deemed a near-shore lake breeze in both Kenosha (southern) and Sheboygan (northern) counties. There was a high pressure system to the southeast of the region that created strong southwesterly winds, which opposed the easterly lake breeze circulation. There was also a cold front that crossed Wisconsin, beginning north of the study region and bringing thunderstorms to the lakeshore in the late afternoon and evening. Temperatures reached 93 °F at Milwaukee's Mitchell Airport, and skies were clear in the morning with more cloud cover in the afternoon. The strength and westerly component of the synoptic winds prevented the lake breeze from penetrating far inland.

The inland and lakeshore Kenosha County monitors differed in their ozone readings and meteorological measurements. In the time series of the ground data on June 12, 2017, shown in Fig. 10, winds and ozone concentrations demonstrate shifts attributable to a lake breeze at locations near to the shoreline of Lake Michigan. The clearest example of the difference of inland and lakeshore sites is Fig. 10-h where Chiwaukee Prairie shows a change in wind direction at 12:00 CDT with a corresponding drop in temperature, whereas the inland Kenosha Water Tower site shows similar winds and temperatures before that time with no evidence of lake breeze afterwards. Ozone concentrations start to increase at southern sites (Racine, Chiwaukee, Zion) at noontime (Fig. 10-d), at Milwaukee area sites (Bayside, Milwaukee SER, Grafton, Harrington Beach) nearer to 14:00 CDT where wind and temperature shifts for Grafton precedes the Milwaukee SER site by almost 3 h (Fig. 10-g).

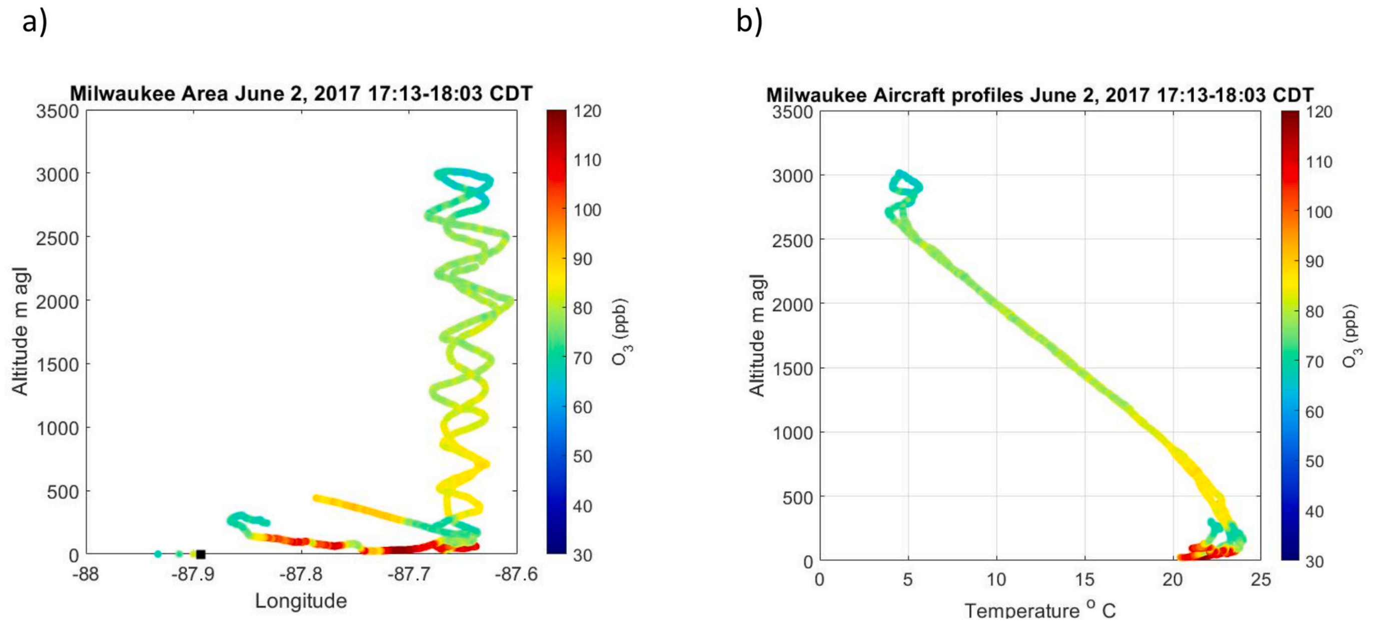

Fig. 9. Aircraft, ship and ground measurements of O_3 near Milwaukee and on June 2, 2017. a) 1 min aircraft data and ground measurements at Milwaukee SER, Milwaukeee 16th St and Bayside at their elevations above lake level. Temperature, altitude, ozone plot is given for the aircraft data near Milwaukee in b). Altitudes are given as m agl, which is set to 0 at lake level. Lake level is at 176 m asl. Black square indicates the location of the shoreline in a).

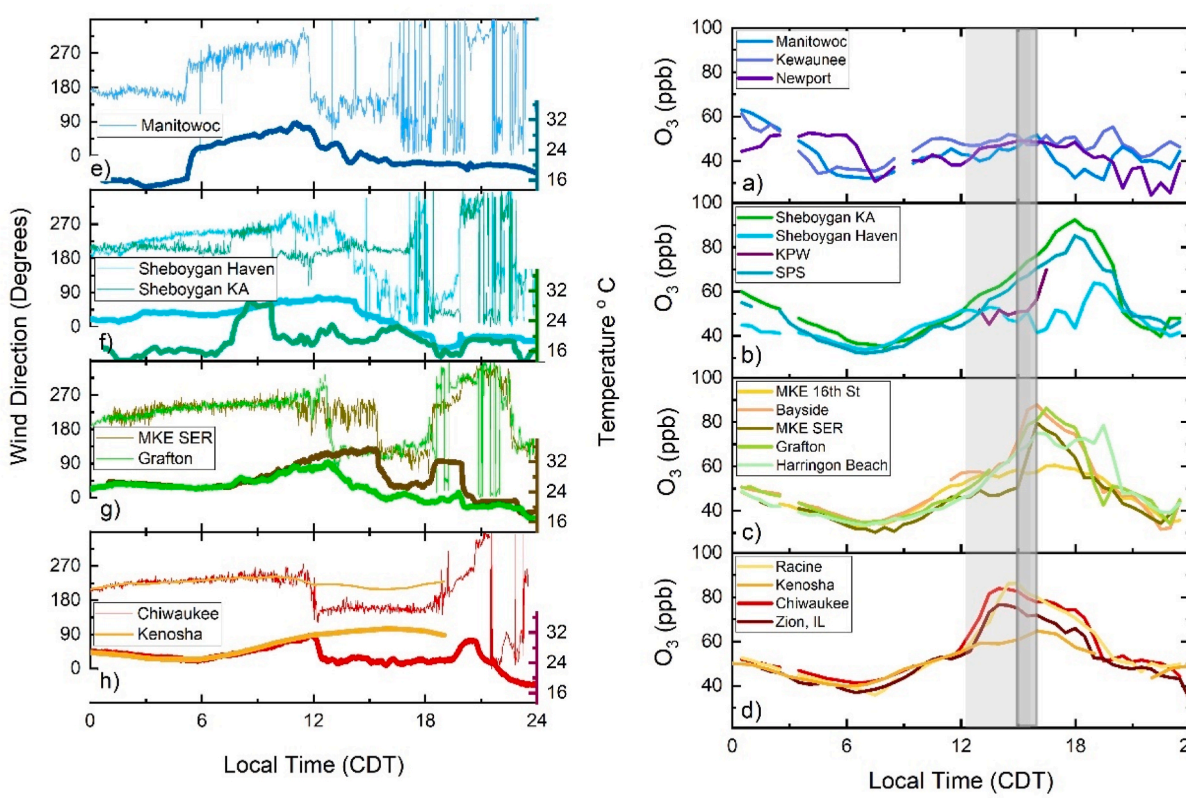

Fig. 10. a) Time series of O_3 on June 12, 2017 at Zion, Chiwaukee Prairie, Lake Geneva, Kenosha Water Tower, Racine, Milwaukee 16th St, Milwaukee Bayside, Milwaukee SER, Grafton, Harrington Beach, Sheboygan Haven, Sheboygan KA, Sheboygan Spaceport, POM at Kohler Power Works, Manitowoc, Kewaunee, Newport. Gray bar indicates time window when GMAP was sampling. B) Time series for wind direction (left axis, thin line) and temperatures (right axis, bold line) at Chiwaukee Prairie, Lake Geneva, Milwaukee SER, Grafton, Harrington Beach, Sheboygan Haven and Sheboygan Kohler Andrae. The light grey band is the time GMAP was in operation, the dark grey bar is the 1-h averaged time for the ground stations shown in Fig. 11.

The Sheboygan area and northern monitors have a more complicated relationship between ozone and meteorology, where the Sheboygan Haven, Manitowoc, Kewaunee and Newport monitors do not show significant increases in ozone (10-a, 10-b), but the shoreline ozone observations at Kohler-Andrae and Spaceport show elevated ozone. The Sheboygan Kohler-Andrae meteorology shows winds from a direction closely parallel to the shoreline ~190° with a brief period of winds arriving from the southwest between 8:00–10:00 CDT where temperatures were higher (10-f). Sheboygan Haven does not demonstrate a sharp wind direction shift during the day but a gradual shift from the W to the ENE between 13:00 CDT to 17:00 CDT. During that gradual temperature shift, temperatures gradually decrease, but without characteristic fast drops associated with a lake breeze front (Laird et al., 2001). Manitowoc shows a sharper wind shift at 12:00 CDT and gradual decrease in temperature, but with no increase in ozone. This demonstrates that the marine layer incursion is not ozone rich at that latitude.

The inland sites of Milwaukee 16th street, Kenosha Water Tower, Sheboygan Haven, and the northern sites of Kewaunee, Manitowoc and Newport either do no show a wind shift or if they do, not a large increase in ozone concentration. Fig. 11 depicts a map of ozone measurements at ground sites at 15:00–16:00 CDT, with continuous measurements depicted for GMAP from 14:40–16:00 and other ground measurements as 1-h averages in that time window. This illustrates more concentrated high ozone (>70 ppb) measurements near to the lake shore.

On this day, the GMAP mobile platform drove between the Zion supersite to Chiwaukee Prairie, Kenosha water tower, and Racine, while also driving along the lakeshore and along some east-west street transects. The highest ozone measured on land was near to the shoreline of Lake Michigan and decreased more than 20 ppb within 4 km of the

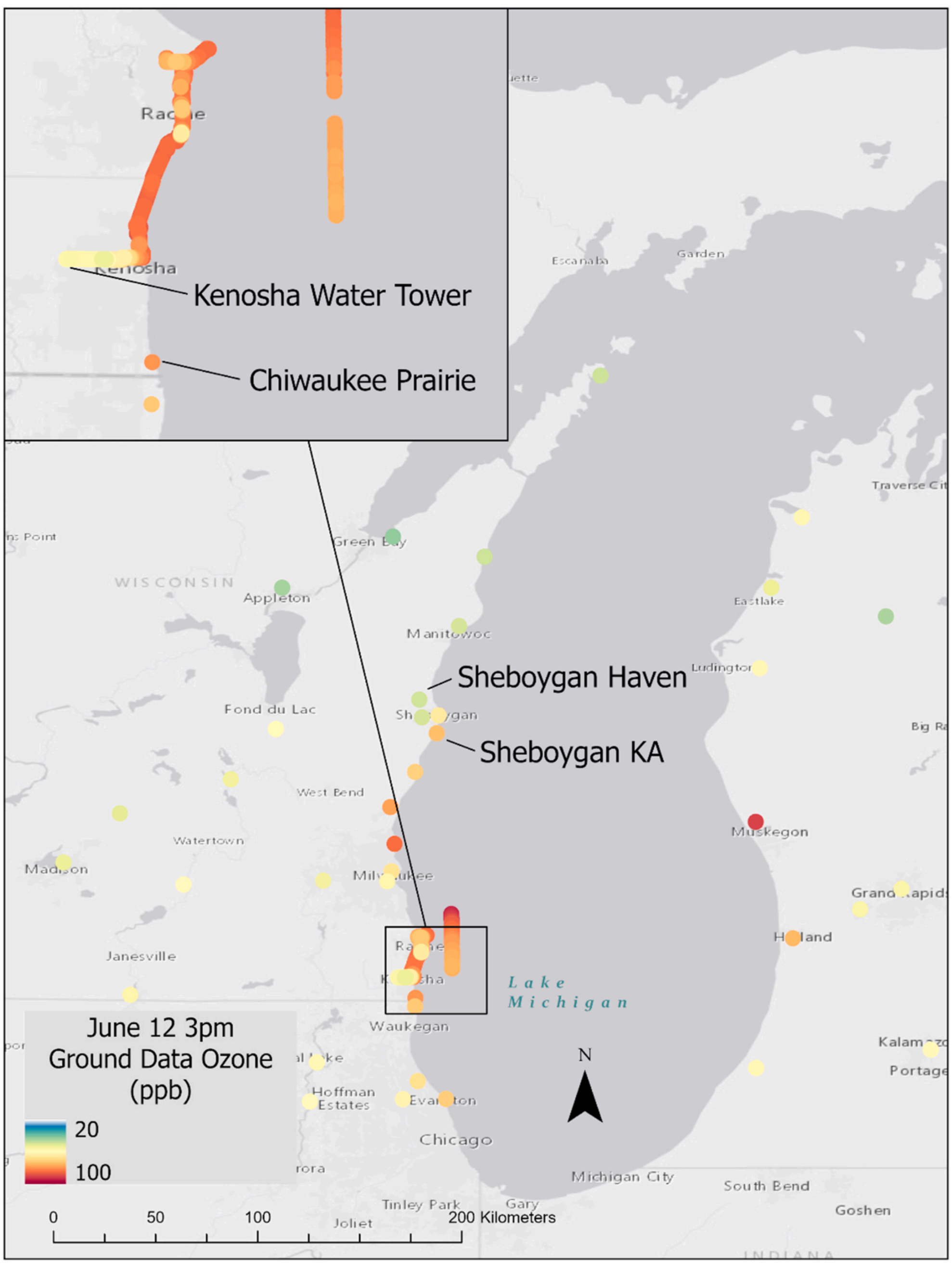

Fig. 11. Map of ground measurements from June 12, 2017 at 15:00 CDT. Ground station measurements are 1-h averages centered at 15:00 CDT and GMAP shows all measurements within the time window of 14:30–15:20 CDT, travelling from south to north.

shoreline (Figs. 11 and 13). (Stanier et al., 2021) The contrast between shoreline observations and inland observations during the E-W transects provides further evidence of steep gradients in ozone between inland and shoreline monitors on near-shore lake breeze days.

The Scientific Aviation aircraft also flew on June 12, 2017 from 11:07 to 15:08 CDT and collected measurements in spirals offshore of Zion and over the Zion ground site. GMAP was also deployed between 12:14–15:40 CDT starting at Zion, IL and ending in Racine County (Fig. 12). GMAP was in the vicinity of Zion during the Zion spirals of the aircraft (12:36 to 13:54 CDT). The GMAP and Scientific Aviation aircraft ozone measurements with respect to altitude and longitude with a latitude range from 42.46 N (Zion, IL) to 42.7 (Racine, WI) are given in Fig. 13. The GMAP mobile platform was not at the exact same latitude as the Scientific Aviation aircraft flights, representative of multiple east-west transects of GMAP on land during the time window the aircraft was overhead. Above 500 m AGL the ozone distributions above land and water are similar, but the aircraft was able to fly lower to the surface over water and captured higher ozone at 30 m agl. This shows a shallow vertical depth of high ozone over water, which extends to a limited extent over land. In comparison to Fig. 7, ozone above 70 ppb only extends to 600 m AGL in altitude, much lower in altitude than the observations from June 2, 2017. The continental boundary layer depth on June 12, 2017 is closer to 1700 m AGL, as referenced by HRRR.v1 stability data archives. The GMAP platform demonstrates that elevated ozone at the shoreline extends north-south at the shoreline.

An apron plot for the Zion, IL onshore and offshore aircraft spirals and the nearest east-west transect of GMAP is given in Fig. 13-a. The aircraft could fly lower in altitude over water and shows increased ozone concentration in altitudes lower than 300 m agl, with the highest ozone at the lowest altitudes over water. The observed maximum ozone aloft

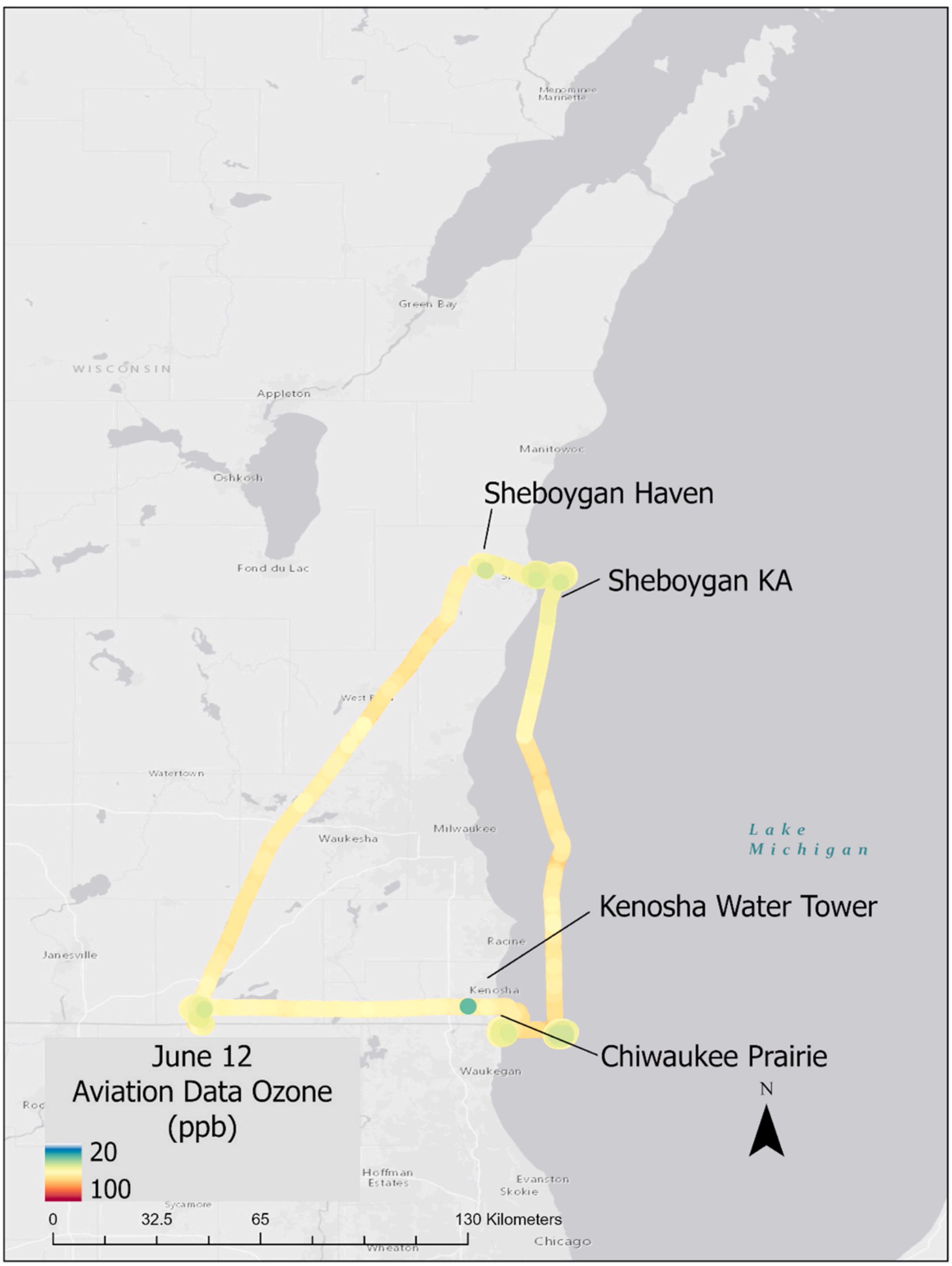

Fig. 12. Scientific Aviation flight June 12, 2017. The aircraft departed Sheboygan Airport at 11:07 CDT, completed two spirals near Sheboygan then flew over water to Zion completed an over water spiral, an over land spiral and then flew inland for a background over land spiral, returning to Sheboygan at 15:08 CDT.

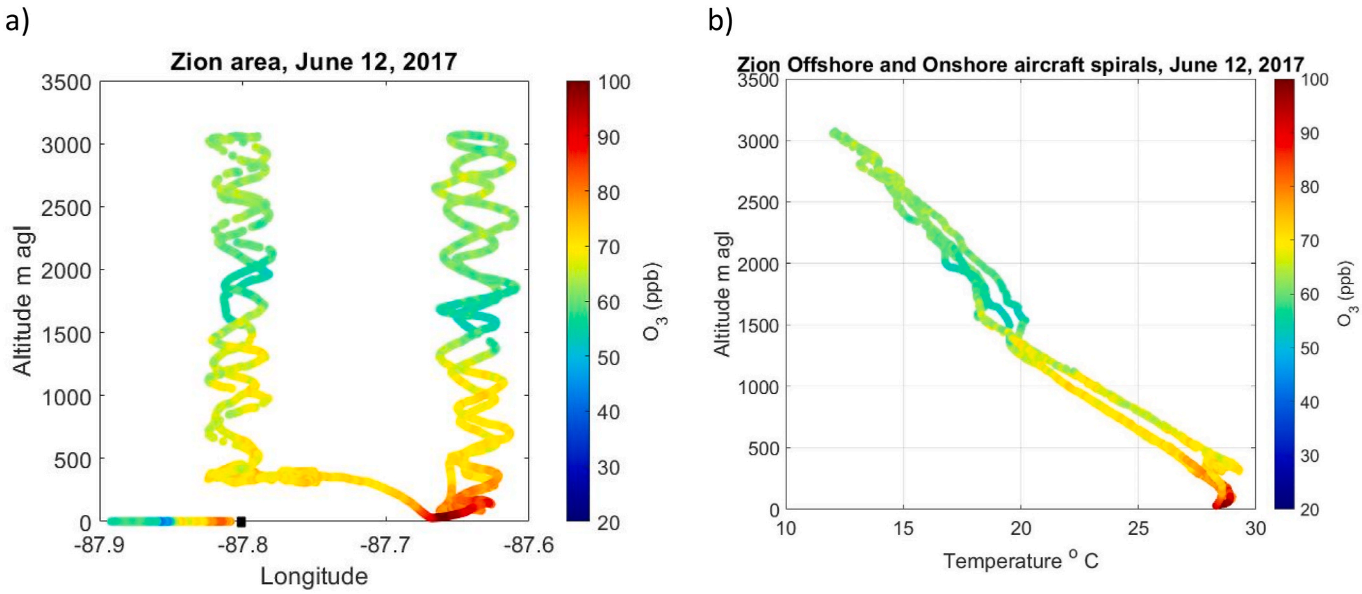

Fig. 13. a) GMAP and Scientific Aviation aircraft measurements of O_3 on June 12, 2017 near Zion, IL from 12:36 to 13:54 CDT. B) altitude, temperature and ozone observations from aircraft data depicted in a) GMAP observations are located at latitudes between 42.5 and 42.6 N. Scientific Aviation ranges from latitudes 42.45–42.53 N, where the vertical spirals are mostly between 42.45 and 42.49 N). Black square represents shoreline nearest GMAP measurements.

over water likely contributes to the high shoreline concentrations observed at ground monitors, if they relate to development of an internal boundary layer at the shoreline. These observations to not resolve the issue of how ozone concentrations observed on the ship are lower than high ground monitor shoreline ozone concentrations and low-altitude high ozone aloft over water. The temperature, altitude, ozone relationships for the aircraft spirals near Zion (Fig. 13-b), demonstrate a non-linear relationship between altitude and temperature below 150 m agl where the highest ozone was observed. The slope of the temperature, altitude relationship is different over land, which also indicates that the marine layer did not significantly impactover-land airmasses above 500 m agl. The aircraft measurements did not capture a low ozone layer over the marine layer as was seen on June 2.

The GMAP measurements clearly demonstrated that ozone-rich air from the over-lake plume impacted all ground-level near-shoreline locations in this area, with ozone concentrations over 80 ppb along the shoreline and reaching 89 ppb (Figs. 11 and 13). Ground-level ozone concentrations along the GMAP east-west transect were highest very close to the shoreline and decreased sharply with distance inland, reaching levels around 60 ppb a few miles inland. This presumably resulted from the GMAP driving from near-shore areas impacted by the lake breeze to inland areas unimpacted by lake breeze circulation.

On June 12, the ship was travelling offshore of Milwaukee and Zion. All afternoon (from 13:45–19:15 CDT), the ship platform ozone concentrations were above 70 ppb in a swath within about 20 km of shore offshore of Milwaukee to Zion. Concentrations peaked at around 14:40 at up to 95.7 ppb around 16 km offshore of South Milwaukee. These peak concentrations are similar to those in the marine layer off of Zion (from Scientific Aviation) a bit earlier and farther south and a bit higher than those seen by GMAP on land slightly later and farther south. Why ozone is not as high as measured by the ship at the same time as when GMAP was sampling at a shoreline site is not well resolved, although the observations differed by less than 6 ppb. It could be due to higher ozone following a near-shoreline path, or a difference in development of a thermal internal boundary layer at the shoreline interface. What is consistent on this day is that high ozone concentrations (>70 ppb) are observed within the marine layer via ship, aircraft and ground measurements, and that ozone concentrations drop off sharply to the west of the lake breeze front along the GMAP transect and at inland sites such as Kenosha Water Tower, Sheboygan Haven and Milwaukee 16th St. Understanding low altitude gradients in ozone over water and at shoreline environments is an area for further study which these observations do not resolve.

Overall, the analysis on this day suggests a widespread and long-lived high ozone event over the lake that moved northward over time. This ozone-rich air was advected onshore by a lake breeze that impacted only a narrow band at the shoreline.

4. Conclusions

Using historical ground-based ozone monitoring data sets, systematic gradients in ozone concentrations with distance inland from the Lake Michigan lakeshore were apparent in two different counties along the Wisconsin lakeshore. High-ozone events at these sites were classified based on the presence/absence and type of lake breezes. Lake breeze events accounted for over 80% of high ozone events in these areas, with most lake breeze events reaching at least several kilometers inland. The high-resolution data from the LMOS 2017 campaign highlight the gradients in ozone with respect to shoreline and over-water abundances of ozone on two example days. This analysis confirmed that the steep ozone gradients found along the lakeshore result from differences in lake breeze phenomenon. The steepness of the ozone concentration gradient depends on the type of lake breeze event, with larger discrepancies between shoreline and inland monitors during near-shore lake breezes, which occurred 15–19% of high ozone events.

The in-depth analysis presented here of ozone and meteorology from the air monitoring data sets and the two different types of days during 2017 LMOS provides insights into the origins of the patterns seen in the longer-term records. Measurements on both the inland and near-shore lake breeze days confirmed that the high ozone reaching the monitors originated from ozone enriched air over Lake Michigan. These over-lake enhanced ozone air masses were observed in the marine layer on both days, with the highest ozone concentrations at the lowest altitudes. The ship observed elevated ozone regions that were 7–20 km wide on the two days, with some smaller areas with the highest ozone concentrations. These two days of data from LMOS 2017 give concrete examples of differences in ozone concentrations across two different monitors within one county (Kenosha or Sheboygan County). Furthermore, the relative contribution of a main causal factor, the distance of penetration of the lake breeze, vary across the examples. Mobile, ship and aircraft platforms can successfully highlight the complex relationship between ozone and lake breeze along the shoreline of Lake Michigan. Highest observed ozone was measured on both example days aircraft over water. Spatial gradients at the ground or lake level as measured via ship are not resolved and future work could be done to understand the role of low-altitude high ozone air moving over land at shoreline environments.

During 2017 LMOS ground-based measurements show different inland penetration distances on the two example days with a lake breeze. On the inland lake breeze day, ozone-rich air reached at least 35 km inland to the Waukesha monitor, which had values of 76 ppb for 1 h at 19:00 CDT (Fig. 6). The monitors closer to the lakeshore were impacted by the high-ozone air for longer time periods. In contrast, on the near-shore lake breeze day, the ozone-rich air never reached the inland monitors 5–5.5 km inland in Sheboygan and Kenosha counties. GMAP measurements on this day demonstrated that ozone concentrations were high (>80 ppb) and consistent along much of the southern lakeshore. Ozone concentrations decreased steadily over 2–3 km inland before leveling off at lower concentrations inland. This analysis confirms that the lake breeze front only reached about halfway to the inland monitor on this day. Four causal factors that can contribute to decreasing ozone across the lake breeze front are dilution, chemical loss, deposition and the presences of a front. While dilution across the lake breeze front appears to be a reasonable assessment for the decreased ozone concentrations, additional vertical flux measurements and higher resolution NO_x observations could elucidate the contributions of each factor more clearly. However, these analyses confirm that ozone concentrations at inland monitors during near-shore lake breeze events remain low because the ozone-rich marine layer from the lakeshore never impacts the monitors.

CRediT authorship contribution statement

Patricia A. Cleary: wrote significant portions of this manuscript and was responsible for data collection, analysis and funding of this document. **Angela Dickens:** rote significant portions of this manuscript and was responsible for data analysis and methodology. **Molly McIlquham:** were responsible for data acquisition. **Mario Sanchez:** were responsible for data acquisition. **Kyle Geib:** were responsible for data acquisition. **Caitlin Hedberg:** was responsible for data analysis. **Joe Hupy:** were responsible for figure generation and formatting and the editing of this document. **Matt W. Watson:** responsible for figure generation and formatting and the editing of this document. **Marta Fuoco:** was responsible for data acquisition. **Erik R. Olson:** was responsible for data acquisition. **R. Bradley Pierce:** was responsible for editing this document and structuring the 2017 LMOS Field Campaign. **Charles Stanier:** was responsible for editing this document and structuring the 2017 LMOS Field Campaign. **Russell Long:** was responsible for data acquisition. **Lukas Valin:** was responsible for data acquisition and assisted in editing this document. **Stephen Conley:** were responsible for data acquisition. **Mackenzie Smith:** were responsible for data acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2021.118834.

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