Ozone distributions over southern Lake Michigan: Comparisons between ferry-based observations, shoreline-based DOAS observations and air quality forecast models

P.A. Cleary[1], N. Fuhrman[1], L. Schulz[2*], J. Schafer[3], J. Fillingham[3], H. Bootsma[3], J. McQueen[4], Y. Tang[4†], T. Langel[5], S. McKeen[6], E.J. Williams[5,6], S.S. Brown[5]

[1]{University of Wisconsin-Eau Claire, Department of Chemistry, 105 Garfield Ave, Eau Claire, WI 54702}

[2]{University of Wisconsin- Parkside, 900 Wood Road, Kenosha, WI 53144}

[3]{University of Wisconsin- Milwaukee, School of Freshwater Science, 600 E Greenfield Ave, Milwaukee, WI 53204}

[4]{National Centers for Environmental Prediction/Environmental Modeling Center, 5830 University Research Court, College Park, MD 20740}

[5]{Chemical Sciences Division, NOAA Earth System Research Laboratory, Boulder, CO 80305}
[6]{Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 809309}
[*]now at University of Wisconsin-Madison College of Agricultural Life and Sciences, 1450 Linden Drive, Madison, WI 53706
[†] Now at Air Resources Laboratory, NOAA, 5830 University Research Court, College Park, MD 20740

Correspondence to: P.A. Cleary (clearypa@uwec.edu)

Abstract

Air quality forecast models typically predict large summertime ozone abundances over water relative to land in the Great Lakes region. While each state bordering Lake Michigan has dedicated monitoring systems, offshore measurements have been sparse, mainly executed through specific short-term campaigns. This study examines ozone abundances over Lake Michigan as measured on the Lake Express ferry, by shoreline Differential Optical Absorption Spectroscopy (DOAS) observations in southeastern Wisconsin, and as predicted by the Community Multiscale Air Quality (CMAQ) model. From 2008-2009 measurements of O_3,

SO_2, NO_2 and formaldehyde were made in the summertime by DOAS at a shoreline site in Kenosha, WI. From 2008-2010 measurements of ambient ozone conducted on the Lake Express, a high-speed ferry that travels between Milwaukee, WI and Muskegon, MI up to 6 times daily from spring to fall. Ferry ozone observations over Lake Michigan were an average of 3.8 ppb higher than those measured at shoreline in Kenosha with little dependence on position of the ferry or temperature but with highest differences during evening and night. Concurrent 1-48h forecasts from the CMAQ model in the upper Midwestern region surrounding Lake Michigan were compared to ferry ozone measurements, shoreline DOAS measurements and EPA station measurements. The bias of the model O_3 forecast was computed and evaluated with respect to ferry-based measurements. Trends in the bias with respect to location and time of day were explored showing non-uniformity in model bias over the lake. Model ozone bias was consistently high over the lake in comparison to land-based measurements with highest biases for 25-48h after initialization.

1 Introduction

Air quality near Lake Michigan has been under study for more than 30 years (Lyons and Cole, 1976; Keen and Lyons, 1978; Dye et al., 1995). The shoreline air quality has gone from a highly impacted environment for surface ozone in the 1970's-80's to persistent non-attainment status in the 2008 ground-level ozone standards for counties near to Lake Michigan in Wisconsin (Sheboygan and Kenosha), Illinois (Cook, Lake, Grundy, Kane, Kendall, McHenry, Will) and Indiana (Lake, Porter). The number of critical ozone events in the Chicago metro area region has been reduced in the past 20 years (EPA, 2014), but stricter measures for particulates have maintained a steady pattern of particulate matter exceedances for this region (Katzman et al 2010, Stanier 2012). Non-attainment of federal ozone standards are still of concern. Kenosha remains in marginal non-attainment of federal ozone standards (as of 2012) and Sheboygan County, north of Milwaukee remains in non-attainment. The proposed rule as of Nov. 26th, 2014 is to reduce the 8-hour primary standard to between 65 and 70 ppb ozone, which has the possibility of maintaining the non-attainment status for these counties in the future (EPA, 2014). These Wisconsin counties in non-attainment are unique in that they are both suburban, Lake

Michigan shoreline counties as opposed to urban or rural counties. Studies have been addressing the role of lake breeze in air quality near the Great Lakes of North America (Levy et al., 2010; Sills et al., 2011; Makar et al., 2010), with a whole campaign, BASQ-MET, dedicated to the evaluation of lake breezes. Complexities in the reduction of precursors and continued increases in ozone are of current concern in the Toronto area (Pugliese et al., 2014). This paper evalutates the Lake Michigan ozone mixing ratios off-shore with those on-shore, including agreement with ozone forecast models overwater and at the shoreline.

Ozone is generated in the troposphere by the reaction of precursors (nitrogen oxides (NO_x) and volatile organic compounds (VOCs)) in a photochemical cycle under conditions which support it (high temperatures, sunlight, stable inversions). The Milwaukee-Chicago-Gary urban corridor constitutes a large emissions source for ozone precursors and is home to significant populations impacted by poor air quality. The understanding of ozone production and distribution around Lake Michigan requires monitoring of land-based sites year-round, but no regular observations of offshore air quality exist. Some land-based monitors are situated farther from Lake Michigan than others, but no specific quantification of the difference between surface level offshore air quality and onshore air quality exists on a routine basis. Forecast models typically produce large ozone mixing ratio maxima over Lake Michigan (Lennartson and Schwartz, 1999, 2002). The nature of the distribution of ozone precursor emissions near to the Lake Michigan shoreline from an urban corridor is in stark contrast to the reduced anthropogenic and biogenic emissions over the lake. This, combined with the unique meteorological effects from this large body of water, like the lake breeze, which can trap, stratify and reciculate air offshore, highlights the need for ozone measurements at a near shore site and across the lake.

The study of high ozone events in the region has centered around mesoscale meteorological effects that contribute to the formation of ozone and the movement of air masses over land (Lennartson and Schwartz, 2002; Lyons and Cole, 1976). Lyons and Cole (1976) outlined the influence of the land-breeze effect on shoreline air quality. Lennartson and Schwartz (2002) indicated a pattern of high pressure anticyclonic events as coincident with higher ozone abundances at land-based sites. Recently, Levy et al. (2010) investigated the impact of local-scale flows in Great Lakes air quality in the region of Lake Erie. Levy et al. determined that local-scale emissions play a significant role in ozone production, and the meterological constraints on air movement aid in isolating and stratifying air pockets from which ozone is generated on a next-day basis.

A few studies have investigated offshore air quality in regional-scale monitoring of ozone around Lake Michigan. The Lake Michigan Air Quality Study in 1991, where aircraft were used for monitoring (Dye et al., 1995) and the LADCO Aircraft Project (Foley et al., 2011) are the two most notable. Dye et al. (1995) determined that stratification over Lake Michigan leads to limited vertical and horizontal mixing beyond the lake area during the summer, allowing for the confinement of ozone precursors. The LADCO Aircraft Project (LAP) was a 9-year aircraft-based study to evaluate air quality in the region, where flights were conducted on days of suspected high ozone which would be in non-attainment of hourly federal standards (Foley et al., 2011). The work from LAP is consistent with the interpretation presented by Dye et al. in that inversions over the lake created stable layers of urban plumes, and that air sampled at greater distance from the Chicago - Milwaukee shoreline tended to be more processed. Foley, et al. (2011) determined in the late 1990's and early 2000's that in lower altitude air (< 200 m above ground level (AGL)) ozone formation switched between VOC-limited conditions in the morning to NO_x-limited in the afternoon, and that above 200 m AGL, ozone formation was always NO_x limited. The observations from LAP showed a progression of the "photochemical clock" during northward aircraft transects over the lake where more aged plumes were found farther north of Chicago. Fast and Heilman (2003, 2005) developed a regional coupled meteorological and chemical model to describe ozone formation on or near the Great Lakes. For offshore measurements they used ozone observations from the SS *Badger*, which operates between Luddington, Michigan and Manitowoc, Wisconsin. The comparison between the model and measurements was restricted to specific times of the day due to the ferry movement where the agreement of model to measurement was poorest for the eastern side of Lake Michigan in 1999 (Fast and Heilman, 2003). Their model results from 1999 and 2001 showed distinct features in the ozone spatial distribution over Lake Michigan but did not reproduce eastern Wisconsin shoreline observations when ozone mixing ratios were high (>60 ppb) (Fast and Heilman, 2005).

The Lake Michigan land/lake breeze is a well-documented phenomenon that influences local scale air flow due to differential heating of air masses over land and water on a daily basis (Lyons and Cole, 1976; Foley et al., 2011; Hanna and Chang, 1995; Lennartson and Schwartz, 2002). Offshore flow (the land breeze) is dominant during the nighttime during summer when surface waters are higher in temperature than land surface temperatures. For counties along the western side of Lake Michigan, this westerly pattern follows typical westerly synoptic flow for the region. Onshore flow (the lake breeze) is more common in the summer daytime when land temperatures exceed water surface temperatures. The lake breeze has been seen to coincide with higher ozone and the transport of aerosol in Chicago (Harris and Kotamarthi, 2005; Lyons and Olsson, 1973) and larger-scale high pressure anticyclonic flows have been implicated in the higher Lake Michigan shoreline ozone observations (Lennartson and Schwartz, 1999), which enhance the flow of photochemically aged air from the Chicago urban plume northward along the Lake Michigan shoreline to southeastern Wisconsin.

In this study, the deployment of both a long path Differential Optical Absorption Spectrometer (DOAS) at the shoreline and an ozone monitor on a ferry has several benefits: the long path length for the DOAS instrument creates an averaged signal that is unaffected by small spatial scale point-source emissions, and allows for simultaneous observations of several compounds (NO_2, SO_2, O_3, formaldehyde). This combination of species provides relevant information about air masses, where O_3 is the pollutant of interest to compare with offshore observations, NO_2 is a proxy for NO_x and a precursor to O_3 production, formaldehyde is a proxy for total VOC which are other necessary ozone precursors, and SO_2 is used as a tracer for industrial emissions and electric power generation. The use of a DOAS instrument for monitoring atmospheric species at a shoreline has proven effective in other environments, such as the observatory on the west coast of Ireland, (Carpenter et al., 1999; Seitz et al., 2010), Crete (Vrekoussis et al., 2004), Galapagos Islands (Martin et al., 2013), Okinawa Island (Takashima et al., 2011), Houston (Rivera et al., 2010), Helgoland (Martinez et al., 2000) and Appledore Island, NH (White et al., 2008), to name a few. In the study described here, the four constituents measured by DOAS are used to show the change in chemical composition of air masses from offshore and onshore evaluate the spatial distribution of the species at the Lake Michigan shoreline. The routine monitoring of ozone over Lake Michigan on the ferry platform allows for an evaluation of the spatial distribution of ozone over the lake, comparison of over-water ozone to shoreline ozone, and comparison to forecast models of surface-level ozone. This investigation is the first to present high resolution, regular observations of ozone at the surface over Lake Michigan in comparison to air quality model output. Results have been analyzed to show the difference between shoreline and over-water ozone as a function of time of year, time of day, location over the lake and meteorology.

2 Methods

Kenosha, Wisconsin is located along the shoreline of Lake Michigan in the southeast corner of the state, bordering Illinois (Figure 1). The commercial DOAS instrument was mounted to two municipal buildings at the Kenosha Harbor along Lake Michigan spanning the harbor with a one-way single-beam path length of 596 m. The light source was mounted to the roof of the Kenosha Municipal Building at 625 52nd St and the detector was housed at the Kenosha Water Utility Water Production Plant located at 100 51st Place on Simmons Island. The beam passed over land and water at 10-14 meters above ground level. At this location, the shoreline of Lake Michigan is oriented North-South, with a small residential area directly south of the measurement site (see inset of Figure 1). Historic downtown Kenosha, a city of 100,000 located 35 miles south of Milwaukee (metropolitan area population 2 million) and 50 miles north of Chicago (metropolitan area population 9.5 million), lies to the west end of the site. The DOAS unit was calibrated with known standards in Sept. of 2008 (±4% yearly drift). In-beam standards were used to test the calibration Nov 7, 2008 and Aug 8, 2009. The instrument was operated from Sept. 19 to Nov. 24, 2008 and April 28, to Nov. 10, 2009. Meteorological data (temperature, relative humidity, wind speed and direction) were obtained in 2009 by the addition of a meteorological station at the Kenosha Harbor site of the DOAS detector. The meterological was mounted to a pole extending 3 meters above the rooftop where the DOAS detector was mounted. Data were collected as 1-minute averages for each compound (NO_2, SO_2, O_3 and formaldehyde) sequentially, which resulted in single data points every 5 minutes (1% precision). Data was filtered for low light levels when the instrument required realignment. No post-processing filters, (e.g. omitting data with low wind speeds) were placed on meteorological measurements.

The *Lake Express* ferry runs from May to October from Milwaukee, WI to Muskegon, MI (Figure 1) at 06:00 (eastbound), 09:15 (westbound), 12:30 (eastbound), 15:45 (westbound)

CDT and in late July/August also at 19:00 (eastbound) and 22:00 (westbound) CDT. Time zones for Wisconsin and Michigan differ, but all times given here are in Central Daylight Time. The ferry stays in port overnight in Milwaukee and the average trip duration of the ferry for this study was 2.25 hours. The inlet for air monitoring was installed at the bow above the wheelhouse (3 m starboard of center and 10 m above water line) and approximately 15 meters of ¼“ PTFE tubing was routed through the interior conduit into a utility closet where a commercial CO_2 (Li-Cor) and O_3 (Thermo Scientific Model 49) monitor were housed. The sample line had a teflon cartridge filter (changed approx. weekly) and tee fitting to the two instruments (each with independent pumps) with a sampling time lag of approximately 10s. The inlet was positioned to the stern so as to minimize water spray entering the sample lines, with intake tubing surrounded by a larger tubing as a rain/spray cover. The O_3 instrument was installed on the ferry from July 9-Sept 21, 2008, May 12 to Oct. 28, 2009 and June 23-Nov. 1, 2010. GPS coordinates and gas measurements were recorded every 30 seconds., resulting in a frequency/spatial resolution of ~1 min/km, with an average speed of ferry at 30 knots. Zeros on the ozone monitor were conducted during powerdown of the ferry (typically twice per day when ferry was docked in port). Ozone data was excluded from data set when the ferry was in port because measurements were also influenced by engine emissions of NO. On occasion, due to inclement weather or mechanical problems, the ferry did not follow its posted schedule. The ozone instrument had a manufacturer stated accuracy of ± 2 ppbv. The ozone instrument was calibrated at NOAA before and after deployment each year by comparison of the instrument deployed on the ferry to a standard ozone monitor (Thermo Scientific Model 49i-PS) maintained in the laboratory for comparison purposes. Comparisons were always within 2%.

3 Results

3.1 Shoreline DOAS Observations as a function of wind direction

Observations from the Kenosha Harbor DOAS instrument were evaluated with respect to offshore versus onshore airmass origin by sorting the data with respect to observed wind direction in 2009. For 2009, all 30-minute averaged data were binned to median mixing ratio per 30 degree increment of wind direction. Figure 2 shows the distribution of gases O_3, NO_2, SO_2 and formaldehyde median mixing ratios with respect to wind direction. The highest median ozone and SO_2 mixing ratios observed at the Kenosha Harbor location arise from air masses flowing from the lake (0-180° are from offshore), whereas the highest NO_2 and formaldehyde observations arise from air masses originating on land. So few formaldehyde measurements in the onshore flow were above the detection limit that average data from those wind directions were omitted from Figure 2d. The observation of NO_2 from land-based air masses is consistent with localized fossil-fuel combustion sources of short-lived NO_x (=NO+NO_2) coming from land-based mobile and point sources as NO_x oxidizes rapidly to other nitrogen species during the daytime. Formaldehyde can serve as a proxy for VOCs, with anthropogenic and biogenic emissions arising from sources on land, and can also be produced *in situ* as an oxidation product of VOCs. Formaldehyde can be lost to reaction with OH and photolysis during the day. The longer-lived atmospheric species of O_3 and SO_2 were observed in higher abundance from offshore. The O_3 and SO_2 mixing ratios were otherwise not correlated in individual days, which is typical as the chemistry and emissions driving the evolution of each were quite different. O_3 is produced by catalytic photochemical cycles which require the presence of NO_x and VOCs and can be titrated by fresh emissions of NO. Sulfur dioxide is most commonly emitted by fossil fuel combustion at coal-fired power plants, many of which lie at the Lake Michigan shoreline in the Gary-Chicago-Milwaukee urban corridor from Indiana to Wisconsin. The diurnal wind patterns (Figure 3) at the Kenosha Harbor site also contribute to the apparent higher mixing ratios of ozone and SO_2 over the lake because the lake breeze wind pattern drives winds from land offshore at night (when NO_2 and formaldehyde losses by photolysis and reaction with OH were minimized) and from the lake onshore during the day (when ozone mixing ratios were at a maximum). Night time losses of NO_x can be as significant as daytime losses (Brown et al., 2004), although in this context we expect the mobile land-based sources of NO_2 to also be higher during the daytime, thus the larger NO_2 observations from off-shore are an artifact of NO_2 minima mid-day from the combination of photolysis losses and reaction with OH.

These DOAS observations align with past studies of Lake Michigan air quality in that they implicate higher O_3 mixing ratios over Lake Michigan (Dye et al., 1995;Foley et al., 2011;Lennartson and Schwartz, 1999, 2002). The higher SO_2 mixing ratios may show the influence of power plant emissions mixing over longer distances and timescales over the lake. The nearest power plants to the DOAS site are located to the southwest (Pleant Prairie), north (Oak Creek) and south (Waukegan) and yet SO_2 observations are highest from the southeastern quadrant – including from the south and east. The lifetime of SO_2 is long enough (approx 1 week) that sources from other powerplants neighboring Lake Michigan (see Fig. 1) may contribute to these observations. Foley et al described (2011) sampling high NO_x plumes over Lake Michigan that appeared to remain aloft. They suggested that these plumes originated from power plants in the region, which would also be a source of SO_2. The shoreline observations presented here do not constrain the extent to which ozone was higher over the lake, nor the distribution of ozone across the lake, but only show that air with enhanced ozone was observed during afternoon hours when the air moved inland during the lake breeze. At the intersection between the offshore environment and the onshore environment, titration of O_3 occurs via emissions from local NO_x sources, and therefore the additional offshore processing cannot be distinguished from chemistry at the shoreline with this DOAS measurement alone.

3.2 Comparison between shoreline DOAS and ferry observations

Kenosha shoreline DOAS observations of O_3 were compared with the *Lake Express* ferry O_3 observations in order to understand the regional distribution of ozone. The two measurements were compared by averaging the ferry measurements to 30 minute intervals at the timescale of the Kenosha harbor DOAS measurements. The two instruments were never intercompared at the same location so we estimate an uncertainty in their intercomparison at 5% (which is higher than the stated drift of either instrument as evaluated independently). The differences in 30-minute averaged data from 2009, as measured as $O_{3\,\text{(Lake Express Ferry)}} - O_{3\,\text{(Kenosha Harbor)}}$, fluctuated from as high as 45 ppb to -37 ppb, with a median difference of 2.8 ppb, mean of 3.8 ppb and standard deviation of 9.1 ppb. The daily maximum data (30-minute average) had a range of 39 ppb to -9 ppb, a median of 4.2 ppb, mean of 5.0 ppb, standard deviation 7.6 ppb. The time of peak ozone for ferry measurements was approximately 14-17h CDT for the whole campaign and for the DOAS measurements was from 14-16h CDT, which are not considerably different. Day-to-day variations in the time of peak ozone off-shore versus onshore can occur from changes in wind direction and local NO_x sources at the shoreline Kenosha site, and therefore cannot be used to indicate differences in chemical processing over the day. There is a statistically significant difference in the O_3 distribution over land vs. lake from summer (June, July, August) to fall (September, October) with median difference of 3.3 ppb for summer and 1.6 ppb for fall (Kruskal-Wallis $p=0.05$).

In order to demonstrate the agreement between ozone measurements of both platforms, Figure 4 shows the wind direction, O_3 measurements, the difference in ozone measurements, temperature, NO_2, SO_2 and formaldehyde for Aug. 12 to Aug. 18, 2009. This week was chosen because of the range of ozone maxima depicted (with daily maxima ranging from 40-70ppb) and the example of a wind shift event that correlated to temperature and atmospheric composition changes at the shoreline on August 14th. In the example of Aug. 12, 2009 in Figure 4, the ozone mixing ratios for both instruments appear quite similar.. Note that the discontinuities in ferry data represent times when the ferry was in port, and each of the segments between the data gaps represents an entire transect of Lake Michigan. In some cases, such as Aug. 12, there was very little variation in the difference between ferry and shoreline O_3 with respect to the location of the ferry. For Aug. 13, the maximum ozone as measured at the shoreline (~50 ppb) was observed by the ferry upon return to the western side of Lake Michigan and again when it left with roughly a 15 ppb difference between the eastern and western sides of Lake Michigan in the afternoon hours. NO_2 measurements in Figure 4d peaked at night as high as 30 ppb and at were at a minimum during the day, particularly after noon. The mixing ratios of NO_2 for this period do not correlate with SO_2 mixing ratios and so can be considered to be from different emissions sources, such as urban non-point source NO_x and power-plant or industrial sources of SO_2.

Evidence of lake breeze shifts in the data was most clearly shown on Aug 14th (indicated by dotted lines in Fig. 4). The wind direction shifted abruptly from southwest (offshore flow) until about 10:00 CDT, when it shifted to southeast (onshore flow). The temperature change between these two air masses is evident in Figure 4c, where the ambient temperature dropped 3 ^{o}C as the wind direction shifted. The NO_2 mixing ratio increased to 30 ppb after the wind shift, which may be evidence of recent land-based NO_2 emissions from the northern Chicago area flowing offshore during rush-hour and then returning onto land after the wind shift. Following the rapid NO_2 decrease, O_3 increased as measured at the shoreline and also as measured on the ferry. By 18:00 CDT, the wind shifted back to arriving at the Kenosha Harbor site from the southwest, the shoreline ozone decreased precipitously but the ferry observations of ozone remained high. The shoreline NO_2 mixing ratios also rebounded to 12 ppb. In this case, the maximum SO_2 observations arrived at the Kenosha harbor site from offshore later in the afternoon before the wind shifted. A Hysplit back trajectory model was calculated for the morning of Aug 14th for synoptic winds at 250 m AGL and indicated an air mass arriving from the northeastern suburbs of Chicago, Illinois which would intercept the rush-hour traffic emissions. Thus, the low O_3 mid-morning was a result of near-source and early-day NO_x titration. On Aug. 13, 14 and 15, NO_2 increased following the wind shift between south-westerly and south-easterly wind flows. Hysplit back trajectories were generated for each of these days, which showed air mases from Chicago transported northward along the shoreline at the same time of day. Emissions were likely brought back on land from lake breezes which could not be resolved from back trajectories.

Differences between ferry O_3 and shoreline DOAS O_3 mixing ratios were evaluated with respect to temperature (Figure 5), location of the ferry (Figure 6) and wind direction (Figure 7). Each figure shows the data for all times of the day, and for distinct time windows (06:00-12:00 CDT, 12:00-18:00 CDT, 18:00-02:00 CDT) in box plots which represent mean (line), median (□), 25-75% (box), and 10-90% (whiskers) for the 30-minute average difference between $O_{3\ (\text{Lake Express})}$ and $O_{3\ (\text{Kenosha Harbor})}$. Differences between ozone observations from the ferry and shoreline with respect to temperature were investigated (Figure 5). There was no observed trend in difference in ozone versus temperature for all data, a minor trend for morning times (06:00-12:00 CDT, 5b) where the difference changed from a positive difference to a more negative difference with increasing temperature above 15.5 °C, and an opposite trend toward higher ozone over the lake in the afternoon (12:00-18:00 CDT) and for temperatures above 26 °C. Ozone differences after 18:00 CDT show consistently higher ozone mixing ratios over the lake for all temperatures, but with larger differences above 21.1°C. While the chemistry can drive more ozone production at higher temperatures, the fact that the largest differences were observed in the evening and at night can arise from the isolation of air masses at this time from the lake/land breeze effects. If the airmasses observed at the shoreline arrived from inland in the late evening, they could have been chemically different from those found far offshore. The only time when shoreline DOAS ozone observations tended to be higher than those from the ferry was at 06:00-12:00 CDT for temperatures above 26.7 °C. This may be due to days when temperatures were high in the morning, thus stagnating the air and limiting the influence of lake/land breeze on horizontal movement of airmasses. Differences in offshore and shoreline observations of ozone with respect to temperature were largest later in the day and at higher temperatures when ozone was typically at a maximum. The range in temperatures observed from different wind directions was higher in wind arriving from land (180^{o}-360^{o}) in comparison to over water (0^{o}-180^{o}), such that the median temperature of all masses arriving at the site from the east was 12.8^{o}C and from the west was 9.3^{o}C. The highest differences depicted in Figure 7 then are showing the highest ozone differences between shoreline and offshore measurements from a wind direction where temperatures are not as extreme.

Investigations into the ozone differences between shoreline and ferry observations with respect to ferry location were conducted as a test of the east-west gradient over Lake Michigan. Figure 6 depicts the difference of $O_{3\ (\text{Lake Express})} - O_{3\ (\text{Kenosha Harbor})}$ with respect to ferry distance from Milwaukee. For all data the mean and median difference was positive (i.e., greater as measured over water from the ferry). The median differences were not significantly positive or negative for the morning, slightly positive for the early afternoon time window, and consistently positive for the late afternoon/evening. In the case of the late evening time window, the mean, median and extremes (25%-75%) of the data all lie above 0, which is a strong suggestion that at these times the ozone mixing ratios over the lake are consistently higher than at the shoreline. However, there does not appear to be a significant variation with respect to longitude, meaning that evaluated as a whole, the land-lake differences in ozone did not depend on the ferry's distance from the shoreline. This demonstrates a widely regional distribution of ozone once over the lake.

In order to distinguish between meteorological effects at the shoreline, the differences in ozone observations from the ferry and shoreline DOAS ozone mixing ratios with respect to wind direction at Kenosha Harbor were evaluated. All data (Figure 7a) show a trend in which the differences between offshore and onshore observations of ozone are positive (i.e., greater ozone over water as measured from the ferry) when wind arrives at the Kenosha Harbor site from 180-360 degrees (inland) where the median and mean lie above 0. When broken up into time windows of morning, afternoon and evening/night, the largest differences were observed after 18:00 CDT if winds were arriving from 180-360^o. This picture is consistent with land breezes developing in the evening and producing surface winds which draw from land and move over the lake. The sampled air masses at the shoreline, thus, were of different origin (or sampled air masses over the lake were isolated from land-based air masses). The number of data points ($n<15$) were acquired when the wind blew from 30-160^o from 18:00-02:00 CDT were insufficient for analysis. For the morning and early afternoon times, the trend with respect to wind direction was not large.

The differences between ferry and shoreline ozone observations were largest after 18:00 CDT and into the night, as shown in Figures 5, 6, and 7. For each of these graphs, we conducted a Kruskal-Wallis statistical test to the distributions at a given temperature, distance or wind direction in comparison to time of day (comparing the box plots vertically in the figures) and determined that they are all significantly different across the 3 different times of the day (95% confidence). Figure 5 d) was the only figure that demonstrated the distributions could be considered unequal across different temperatures (K-W, 95% confidence). The rest of the trends discussed are not statistically significant. The difference between the ferry and shoreline trend with the wind direction for all times of the day with the mean difference for wind directions from 0-180° at 0.2 ppb and for wind directions from 180-360° at 6.3 ppb. This trend in the dependence of the observed ozone difference with respect to wind direction is magnified after noon. One possible key driver of differences between observed offshore and shoreline ozone could be the differences in NO_x emissions from each wind direction. The trends with respect to temperature are small in comparison to the trends with respect to wind direction and may be a subtle indicator of the strength of lake breeze effects. Both temperature and location may demonstrate some differences in photochemistry, where some aspects of photochemical ozone production are enhanced with temperature (water vapor content, VOC emissions), the distance from emissions sources (where titration of O_3 can occur) could be represented by the distance from the western Lake Michigan shoreline, and lower losses of O_3 to water surfaces compared to terrestrial surfaces (Levy et al., 2010). One complicating factor is that the ferry intercepted air near the surface, whereas urban plumes might reside aloft over an inversion above the lake (Foley et al., 2011; Dye et al., 1995). However, the subtleties of these effects appear to be outweighed by the magnitude of air-mass isolation effects due to local meteorology, as indicated by the large ozone mixing ratio trends with wind and time of day. More complex yet similar observations near Lake Erie were made in summer 2007 during BAQS-Met by Levy et al. (2010) where oscillations in inland ozone were observed at times associated with lake-breeze front movement. The extent to which inversion occurs over the lake at night and ozone precursors and ozone mixing ratios remain high aloft, as suggested by Dye et al. and Foley et al. (Foley et al., 2011; Dye et al., 1995) cannot be evaluated by our measurements at the surface.

3.3 Comparison of ferry ozone with CMAQ experimental model forecasts

The National Air Quality Forecast Model (NAQFM) was developed with the collaboration of the National Oceanic and Atmospheric Administration (NOAA) and the

Environmental Protection Agency (EPA) (Eder 2009). The NAQFM is made up of two components: the National Center for Environmental Prediction's (NCEP) North American Mesoscale (NAM) meteorological model and the Environmental Protection Agency's (EPA) Community Multiscale Air Quality (CMAQ) modeling system (Janjic, 2003, Eder 2009, Byun and Schere 2006). The NAM is used to input meteorological conditions into the CMAQ to generate 48h forecasts. Initialization steps to the forecasts are conducted every 12 hours at 06 and 12 UTC (Eder 2009, Chai 2010). The NAQFM provides real-time predictions for ground-level ozone mixing ratios over the contiguous US (Eder 2009) with a 12 km grid size. The NAQFM CMAQ runs in 3 modes: operational, experimental and developmental, with the operational prodect displayed publicly on the NAQFM web-site. Figure 8 shows an example of the operational product for June 24, 2009, along with the Lake Express Ferry measurements on that day, illustrating a clear model overprediction on the east side of the lake. During 2009 the operational model used the Carbon Bond Mechanism version IV (CBMIV) gas-phase chemical mechanism. Here we compare observations with the developmental model product which used the Carbon Bond Mechanism 5 (CB05). The emissions inventory used in both model forecasts is adopted from from the EPA's 2005 National Emissions Inventory (NEI) (Pan 2014). Figure 8 depicts an image of the NAQFM ozone forecast with a sample ferry transect with ozone observations.

Hourly output from the developmental CMAQ forecasts were saved for the monitoring season of 2009 from June 18-Sept. 15 2009. The CMAQ output ozone mixing ratios were reported to 1 ppb precision. Figure 9 depicts O_3 forecast levels consistently higher than ferry measurements with 57 days of overlapping data. These forecasts produce a distinct ozone maximum over the water surfaces of the Great Lakes and, in particular, southern Lake Michigan (e.g. Figure 8). Statistical comparsions with the Lake Express observations use model grid and time values determined from ship tracks through the model domain, and with no spatial or temporal interpolation.. Figure 10 depicts the sample numbers within distinct model grid cells for the 3 month time period according to model longitude and central daylight time for the tferry transects. The extreme western and eastern points are within ports and the Milwaukee model grid are over land. The statistics may not be reliable for the shoreline grids due to local sources and contamination by the ferry exhaust. The median ozone values for the forecast (Figure 11a) 1-24 hours after model initialization, (11b): 25-48 hours after initialization, and *Lake Express* monitor (Figure 11c) show distinct higher model median O_3 forecasts in comparison to observations. The maxima in the model forecast O_3 are mid-lake from 15:00-18:00 CDT. The forecast O_3 mixing ratios are highest after 25-48 hours after initialize, especially between 2pm and 9pm. The location of the daily maximum ozone from the ferry is similar distribution given by the CMAQ for 1-24 h since initalization (Figures 11a,c). The CMAQ predicts the highest median daily maximum O_3 just offshore on the eastern side of Lake Michigan for 1-24 hour initialization (Figure 11a) and a larger area for 25-48h after initialization (Figure 11b). The correlation coeffficients between model and measurement are high (R=0.85 to 0.95) from 14:00 - 17:00 h CDT for the 1-24 hour forecast (Figure 12a). The correlations were reduced for the 25-48-hour forecast (Figure 12b).

The comparison between the ozone forecast and the ferry observations were computed as bias:

$$\text{bias} = p_i - o_i \qquad (1)$$

where p_i is the model-predicted O_3 concentration and o_i is the observed O_3 concentration on the ferry, was determined for each sample location and time referenced in Figure 10. Model bias is shown in Figure 13. The forecast from 1-24 hours after initialization in Figure 13a shows an 11-16 ppb median O_3 bias for offshore locations, which is highest between 12:00 and 17:00 h CDT. The 24-48 hour forecast (Figure 13b) has a much higher bias between 14:00-21:00h CDT.

Components of the model were investigated to evaluate differences that may lead to the higher model bias to the eastern side of Lake Michigan. Winds tend to start the day with a north-to-south median wind component, with a switch to south-to-north wind component in the region of 11:00-15:00h CDT for the 1-24 hour forecast, and an earlier at 8:00h CDT for the 25-48 h CDT forecast. This difference in occurrences in Chicago's plume travelling northward in the 25-48 hr forecast may lead to the higher O_3 biases for that forecast.

CMAQ developmental model biases were also determined for the Kenosha site for ozone along with NO_2, SO_2 and formaldehyde (Figure 14). Ozone was overpredicted in the model for this shoreline measurement for most daylight times, with correlations lower than those obtained over water ($R^2 = 0.67$ 1-24h, $R^2 = 0.58$ 25-48h). NO_2 is underpredicted during daylight hours, but not of the same magnitude as the overprediction of ozone ($R^2=0.38$ 1-24h, $R^2=0.30$ 25-48h). Formaldehyde is consistently underpredicted when it is measured, with effectively no correlation ($R^2=0.03$ for both 1-24h and 25-48h forecasts). Gaps in formaldehyde bias are from gaps in formaldehyde data at the Kenosha site. Bias in SO_2 show little trend with respect to time of day and little correlation ($R^2=0.16$ 1-24h, $R^2=0.18$ 25-48h).

The mid-afternoon O_3 (20:00 UTC) was also determined for all EPA station monitors in the region (Figure 15). The *Lake Express* ferry data were also used to obtain the bias at a similar time (12:30-15:00 h CDT transect), shown in squares in Figure 15. Note that there is an upwind bias in central in western Wisconsin of ~7-8ppb and igh biases are observed at some locations near Chicago and the northern Indiana region. The high biases seen over Lake Michigan don't appear to extend too strongly inland.

Others have also found the CMAQ to predict ozone mixing ratios that were biased high (Eder et al., 2009; Tang et al., 2009; Zhang et al., 2012a, b; Wilczak et al., 2006). Simon et al. (2012) completed an exhaustive comparison of photochemical performance statistics reported from 2006-2012, whereby national median in mean bias for hourly ozone was approximately 4 ppb, for 1-hour maximum ozone was approximately 8 ppb (Simon et al., 2012). In comparison, the bias determined in this study would be higher than 75th percentile of studies of hourly ozone mean bias for 40 studies compiled by Simon et al. (2012), between the median and 75th percentile for the 22 studies of 1-hour maximum ozone. The work presented here represents the first study of CMAQ model bias over the water of Lake Michigan and show a higher bias than over the surrounding land.

4 Conclusions

Observations of shoreline O_3 and ferry O_3 in comparison to forecast O_3 by the developmental NAQFM show more agreement between shoreline and the ferry measurements than between ozone forecasts over the lake and ferry measurements. Shoreline Lake Michigan measurements of O_3, NO_2, SO_2 and formaldehyde demonstrated the differences between onshore and offshore air masses. The comparison between ferry-based O_3 observations and shoreline DOAS O_3 observations indicated that diurnal changes in ozone mixing ratio were larger than spatial gradients across Lake Michigan, and ozone tended to be higher over Lake Michigan, particularly in the evening. Mesoscale meteorological processes involving differential heating between the lake and land surfaces produced diurnal cycles of air mass flow between shoreline environments and offshore, which complicated the understanding of offshore ozone dynamics. Model forecast O3 is highly correlated with ferry monitor observations, but with afternboon median biases ranging from 11 to 16 ppb, compared to 6-9 ppbv biases for land-based monitors just west of Lake Michigan. The model O_3 overpredictions over water are similar to those determined for the Kenosha site, though formaldehyde and NO_2 are underpredcited. The developmental NAQFM showed a trends of increasing O_3 bias to the eastern side of Lake Michigan, and a larger bias for the second day forecast compared to the first 24 hours. Further analyses are required to determine whether NAQFM predictions might be improved by adjusting model parameters related to emission sources, localized shoreline meteorology, or atmospheric chemistry.

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References

Brown, S. S., Dibb, J. E., Stark, H., Aldener, M., Vozella, M., Whitlow, S., Williams, E. J., Lerner, B. M., Jakoubek, R., Middlebrook, A. M., DeGouw, J. A., Warneke, C., Goldan, P. D., Kuster, W. C., Angevine, W. M., Sueper, D. T., Quinn, P. K., Bates, T. S., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Nighttime removal of NOx in the summer marine boundary layer, Geophysical Research Letters, 31, 10.1029/2004gl019412, 2004.

Carpenter, L. J., Sturges, W. T., Penkett, S. A., Liss, P. S., Alicke, B., Hebestreit, K., and Platt, U.: Short-lived alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production, Journal of Geophysical Research-Atmospheres, 104, 1679-1689, 10.1029/98jd02746, 1999.

Dye, T. S., Roberts, P. T., and Korc, M. E.: Observations of transport processes for ozone and ozone precursors during the 1991 Lake Michigan Ozone Study, Journal of Applied Meteorology, 34, 1877-1889, 10.1175/1520-0450(1995)034<1877:ootpfo>2.0.co;2, 1995.

Eder, B., Kang, D. W., Mathur, R., Pleim, J., Yu, S. C., Otte, T., and Pouliot, G.: A performance evaluation of the National Air Quality Forecast Capability for the summer of 2007, Atmospheric Environment, 43, 2312-2320, 10.1016/j.atmosenv.2009.01.033, 2009.

EPA: National Air Quality Standards for Ozone; Proposed Rule, in: 40 CFR Parts 50, 51, 52, et al., 242, Federal Register, 75234-754111, 2014.

Fast, J. D., and Heilman, W. E.: The effect of lake temperatures and emissions on ozone exposure in the western Great Lakes region, Journal of Applied Meteorology, 42, 1197-1217, 10.1175/1520-0450(2003)042<1197:teolta>2.0.co;2, 2003.

Fast, J. D., and Heilman, W. E.: Simulated sensitivity of seasonal ozone exposure in the Great Lakes region to changes in anthropogenic emissions in the presence of interannual variability, Atmospheric Environment, 39, 5291-5306, 10.1016/j.atmosenv.2005.05.032, 2005.

Foley, T., Betterton, E. A., Jacko, P. E. R., and Hillery, J.: Lake Michigan air quality: The 1994-2003 LADCO Aircraft Project (LAP), Atmospheric Environment, 45, 3192-3202, 10.1016/j.atmosenv.2011.02.033, 2011.

Hanna, S. R., and Chang, J. C.: Relations between meteorology and ozone in the Lake Michigan region, Journal of Applied Meteorology, 34, 670-678, 10.1175/1520-0450(1995)034<0670:rbmaoi>2.0.co;2, 1995.

Harris, L., and Kotamarthi, V. R.: The characteristics of the Chicago Lake breeze and its effects on trace particle transport: Results from an episodic event simulation, Journal of Applied Meteorology, 44, 1637-1654, 10.1175/jam2301.1, 2005.

Keen, C. S., and Lyons, W. A.: Lake/Land Breeze circulations on the western shore of Lake Michigan, Journal of Applied Meteorology, 17, 1843-1855, 10.1175/1520-0450(1978)017<1843:lbcotw>2.0.co;2, 1978.

Lennartson, G. J., and Schwartz, M. D.: A synoptic climatology of surface-level ozone in Eastern Wisconsin, USA, Climate Research, 13, 207-220, 10.3354/cr013207, 1999.

Lennartson, G. J., and Schwartz, M. D.: The lake breeze-ground-level ozone connection in eastern Wisconsin: A climatological perspective, International Journal of Climatology, 22, 1347-1364, 10.1002/joc.802, 2002.

Levy, I., Makar, P. A., Sills, D., Zhang, J., Hayden, K. L., Mihele, C., Narayan, J., Moran, M. D., Sjostedt, S., and Brook, J.: Unraveling the complex local-scale flows influencing ozone patterns in the southern Great Lakes of North America, Atmospheric Chemistry and Physics, 10, 10895-10915, 10.5194/acp-10-10895-2010, 2010.

Lyons, W. A., and Olsson, L. E.: Detailed mesometeorological studies of air pollution dispersion in Chicago lake breeze, Monthly Weather Review, 101, 387-403, 10.1175/1520-0493(1973)101<0387:dmsoap>2.3.co;2, 1973.

Lyons, W. A., and Cole, H. S.: Photochemical oxidant transport - Mesoscale lake breeze and synoptic-scale aspects, Journal of Applied Meteorology, 15, 733-743, 10.1175/1520-0450(1976)015<0733:potmlb>2.0.co;2, 1976.

Makar, P. A., Gong, W., Mooney, C., Zhang, J., Davignon, D., Samaali, M., Moran, M. D., He, H., Tarasick, D. W., Sills, D., and Chen, J.: Dynamic adjustment of climatological ozone boundary conditions for air-quality forecasts, Atmospheric Chemistry and Physics, 10, 8997-9015, 10.5194/acp-10-8997-2010, 2010.

Martin, J. C. G., Mahajan, A. S., Hay, T. D., Prados-Roman, C., Ordonez, C., MacDonald, S. M., Plane, J. M. C., Sorribas, M., Gil, M., Mora, J. F. P., Reyes, M. V. A., Oram, D. E., Leedham, E., and Saiz-Lopez, A.: Iodine chemistry in the eastern Pacific marine boundary layer, Journal of Geophysical Research-Atmospheres, 118, 887-904, 10.1002/jgrd.50132, 2013.

Martinez, M., Perner, D., Hackenthal, E. M., Kulzer, S., and Schutz, L.: NO3 at Helgoland during the NORDEX campaign in October 1996, Journal of Geophysical Research-Atmospheres, 105, 22685-22695, 10.1029/2000jd900255, 2000.

Pugliese, S. C., Murphy, J. G., Geddes, J. A., and Wang, J. M.: The impacts of precursor reduction and meteorology on ground-level ozone in the Greater Toronto Area, Atmospheric Chemistry and Physics, 14, 8197-8207, 10.5194/acp-14-8197-2014, 2014.

Rivera, C., Mellqvist, J., Samuelsson, J., Lefer, B., Alvarez, S., and Patel, M. R.: Quantification of NO2 and SO2 emissions from the Houston Ship Channel and Texas City industrial areas during the 2006 Texas Air Quality Study, Journal of Geophysical Research-Atmospheres, 115, 10, 10.1029/2009jd012675, 2010.

Seitz, K., Buxmann, J., Pohler, D., Sommer, T., Tschritter, J., Neary, T., O'Dowd, C., and Platt, U.: The spatial distribution of the reactive iodine species IO from simultaneous active and passive DOAS observations, Atmospheric Chemistry and Physics, 10, 2117-2128, 2010.

Sills, D. M. L., Brook, J. R., Levy, I., Makar, P. A., Zhang, J., and Taylor, P. A.: Lake breezes in the southern Great Lakes region and their influence during BAQS-Met 2007, Atmospheric Chemistry and Physics, 11, 7955-7973, 10.5194/acp-11-7955-2011, 2011.

Simon, H., Baker, K. R., and Phillips, S.: Compilation and interpretation of photochemical model performance statistics published between 2006 and 2012, Atmospheric Environment, 61, 124-139, 10.1016/j.atmosenv.2012.07.012, 2012.

Takashima, H., Irie, H., Kanaya, Y., and Akimoto, H.: Enhanced NO2 at Okinawa Island, Japan caused by rapid air-mass transport from China as observed by MAX-DOAS, Atmospheric Environment, 45, 2593-2597, 10.1016/j.atmosenv.2010.10.055, 2011.

Tang, Y. H., Lee, P., Tsidulko, M., Huang, H. C., McQueen, J. T., DiMego, G. J., Emmons, L. K., Pierce, R. B., Thompson, A. M., Lin, H. M., Kang, D. W., Tong, D., Yu, S. C., Mathur, R., Pleim, J. E., Otte, T. L., Pouliot, G., Young, J. O., Schere, K. L., Davidson, P. M., and Stajner, I.: The impact of chemical lateral boundary conditions on CMAQ predictions of tropospheric ozone over the continental United States, Environmental Fluid Mechanics, 9, 43-58, 10.1007/s10652-008-9092-5, 2009.

Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., Crutzen, P. J., Lelieveld, J., Perner, D., Berresheim, H., and Baboukas, E.: Role of the NO3 radicals in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign, Atmospheric Chemistry and Physics, 4, 169-182, 2004.

White, M. L., Russo, R. S., Zhou, Y., Mao, H., Varner, R. K., Ambrose, J., Veres, P., Wingenter, O. W., Haase, K., Stutz, J., Talbot, R., and Sive, B. C.: Volatile organic compounds in northern New England marine and continental environments during the ICARTT 2004 campaign, Journal of Geophysical Research-Atmospheres, 113, 16, 10.1029/2007jd009161, 2008.

Wilczak, J., McKeen, S., Djalalova, I., Grell, G., Peckham, S., Gong, W., Bouchet, V., Moffet, R., McHenry, J., McQueen, J., Lee, P., Tang, Y., and Carmichael, G. R.: Bias-corrected ensemble and probabilistic forecasts of surface ozone over eastern North America during the summer of 2004, Journal of Geophysical Research-Atmospheres, 111, 10.1029/2006jd007598, 2006.

Zhang, Y., Bocquet, M., Mallet, V., Seigneur, C., and Baklanov, A.: Real-time air quality forecasting, part I: History, techniques, and current status, Atmospheric Environment, 60, 632-655, 10.1016/j.atmosenv.2012.06.031, 2012a.

Zhang, Y., Bocquet, M., Mallet, V., Seigneur, C., and Baklanov, A.: Real-time air quality forecasting, part II: State of the science, current research needs, and future prospects, Atmospheric Environment, 60, 656-676, 10.1016/j.atmosenv.2012.02.041, 2012b.

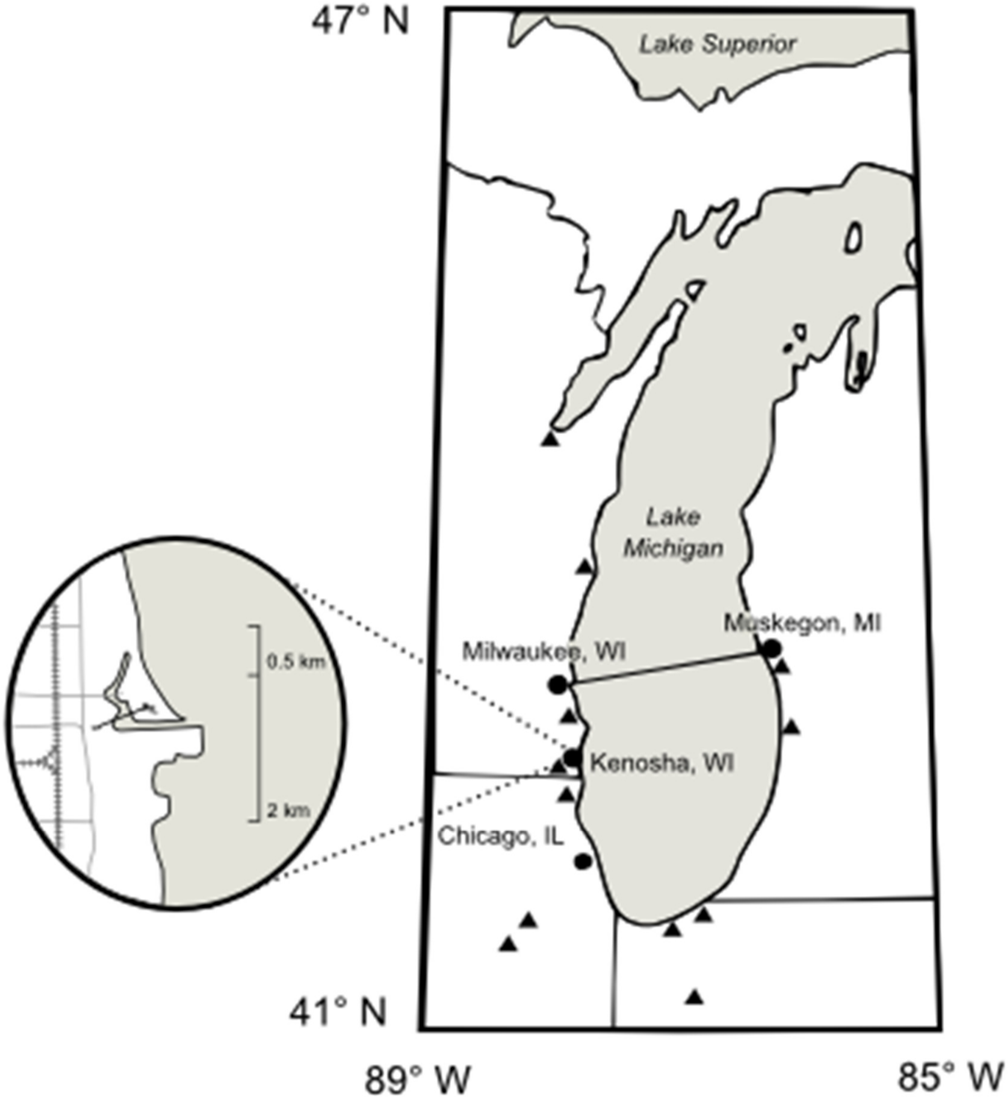


Figure 1: Map of experiment. Path of ferry from Milwaukee, Wisconsin to Muskegon, Michigan is shown with black line across the lake in the map. The DOAS instrument was placed at the Kenosha, Wisconsin harbor with the beam path shown (inset) as the dark line across the harbor. Coal fired power plants with power capacity greater than 400 MW are shown as black triangles.

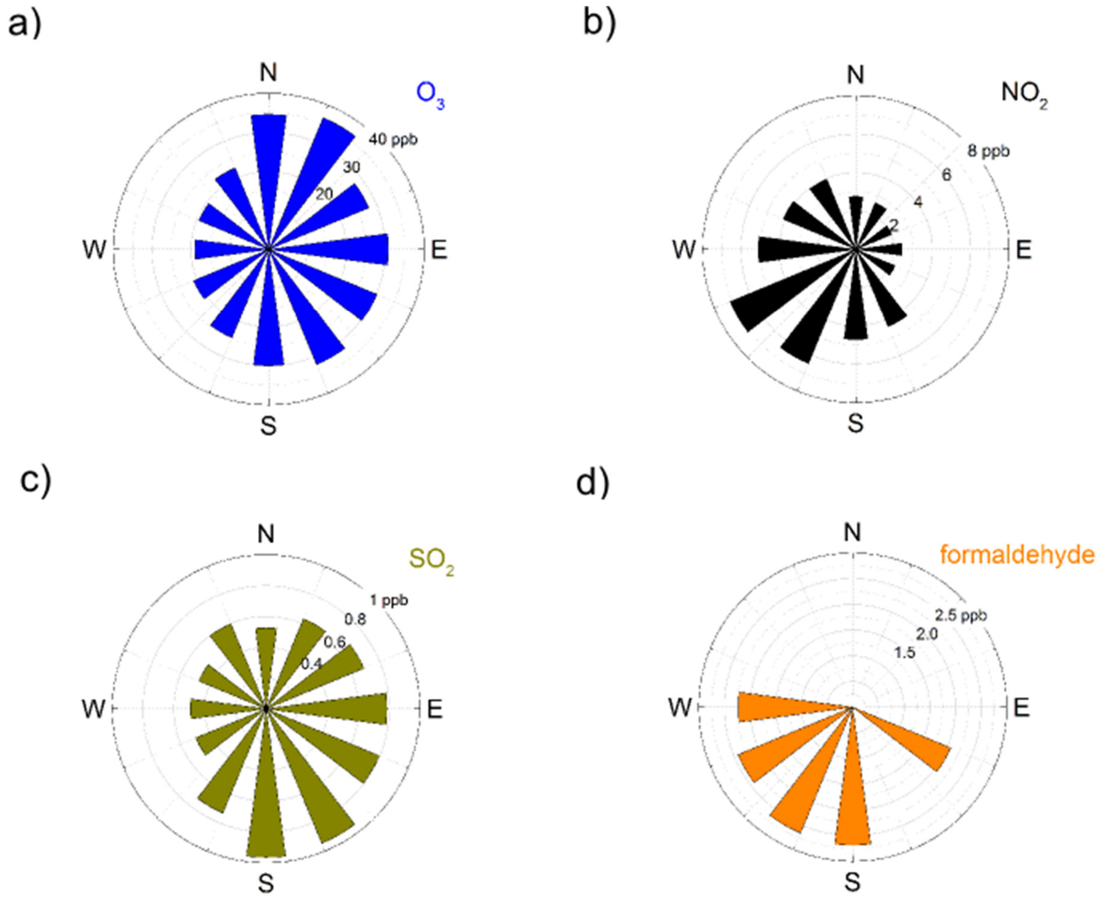


Figure 2. Wind rose depictions of median mixing ratio of a) O_3 b) NO_2 c) SO_2 and d) formaldehyde with respect to wind direction as measured by DOAS at Kenosha harbor from April-November of 2009. Medians are not reported for wind directions where few measurements (n<75 for 30 minute averaged data points) were above the detection limit (d.l. = 1.5 ppb for formaldehyde).

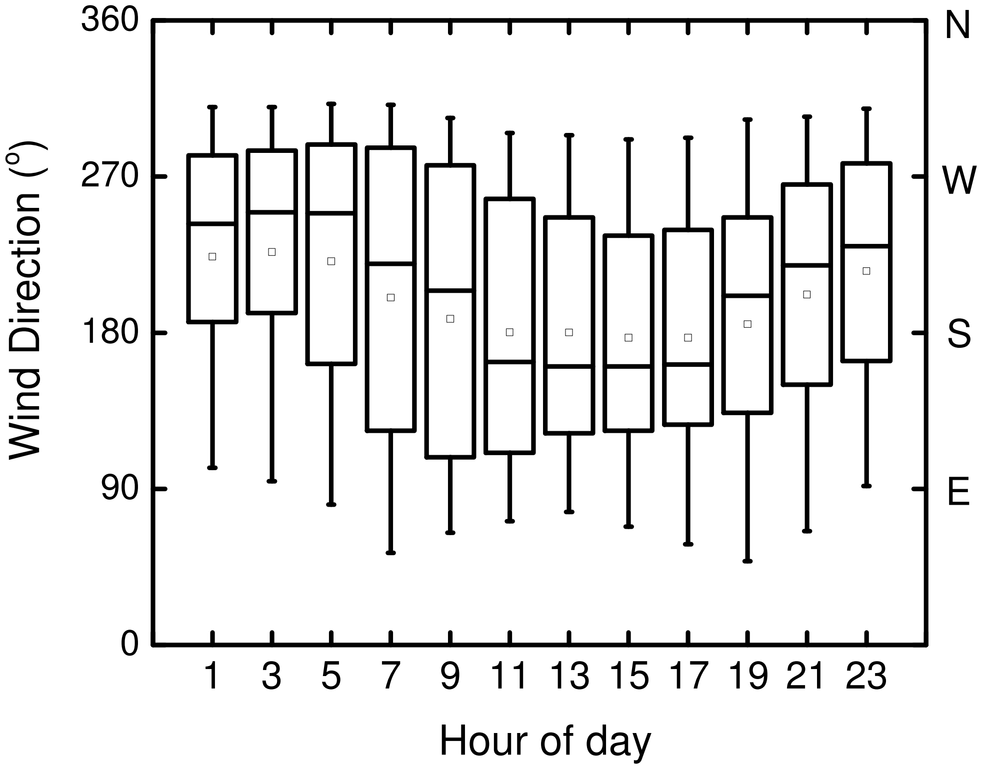


Figure 3: Wind direction as a function of time of day as measured at Kenosha harbor from April-November of 2009. Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers).

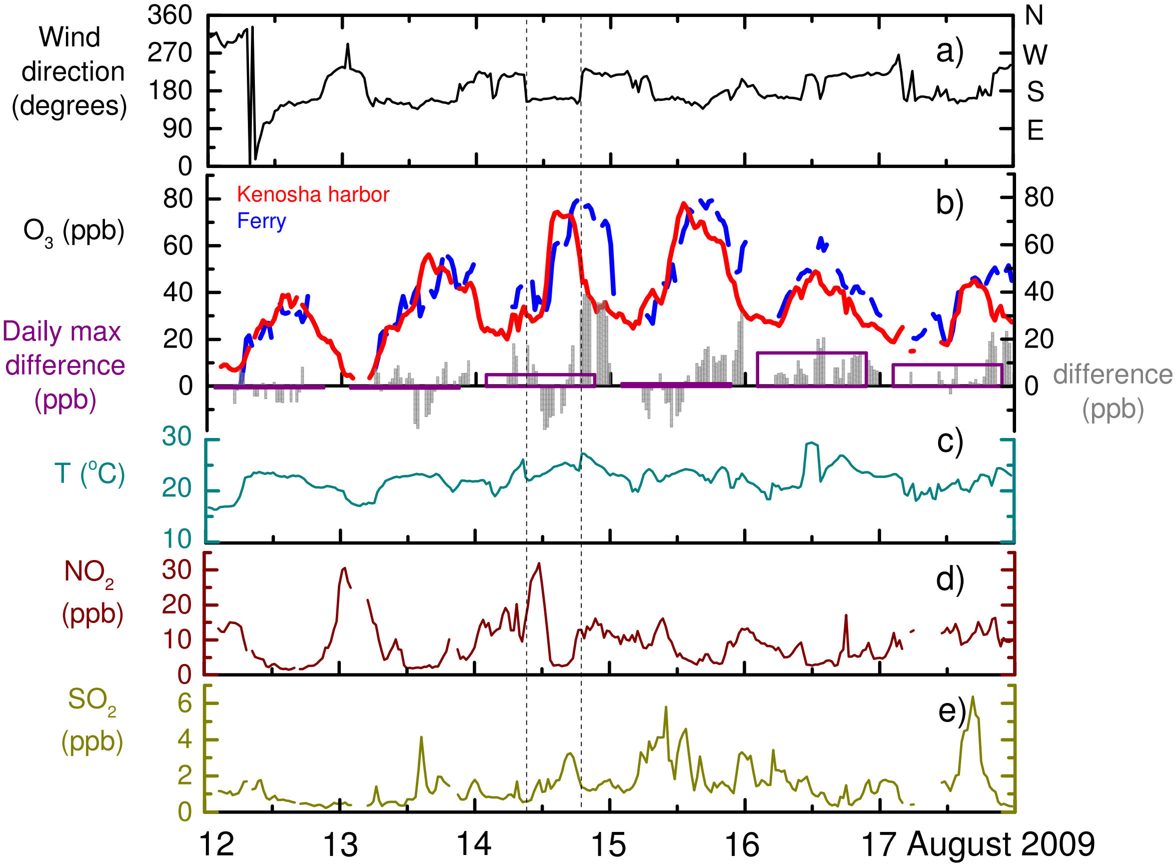


Figure 4: Example period of observations from Aug. 12, 2009 to Aug. 18, 2009 a) wind direction at Kenosha Harbor site, b) concurrent O_3 observations from Kenosha Harbor and *Lake Express* in transit, their 30 minute average O_3 (Ferry) - O_3 (Kenosha Harbor) difference and daily max difference c) temperature at Kenosha Harbor in Celsius d) NO_2 observations from Kenosha Harbor and e) SO_2 observations from Kenosha Harbor.

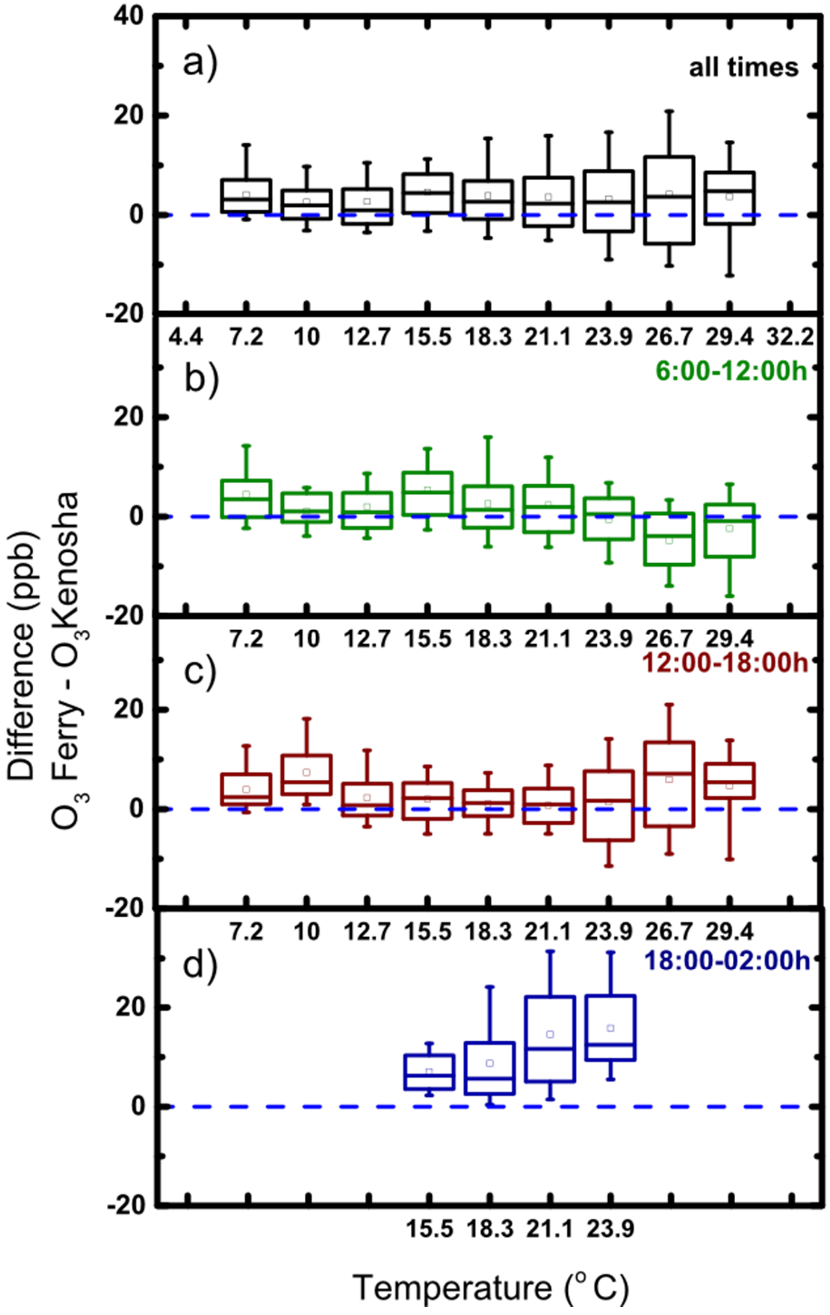


Figure 5: Difference in O_3 observations between platforms with respect to temperature (°C) measured at the shoreline for a) all times, b) morning (06:00-12:00h CDT), c) early afternoon (12:00-16:00h CDT) and d) late afternoon/evening (16:00-02:00h). Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box represents a minimum of 15 points.

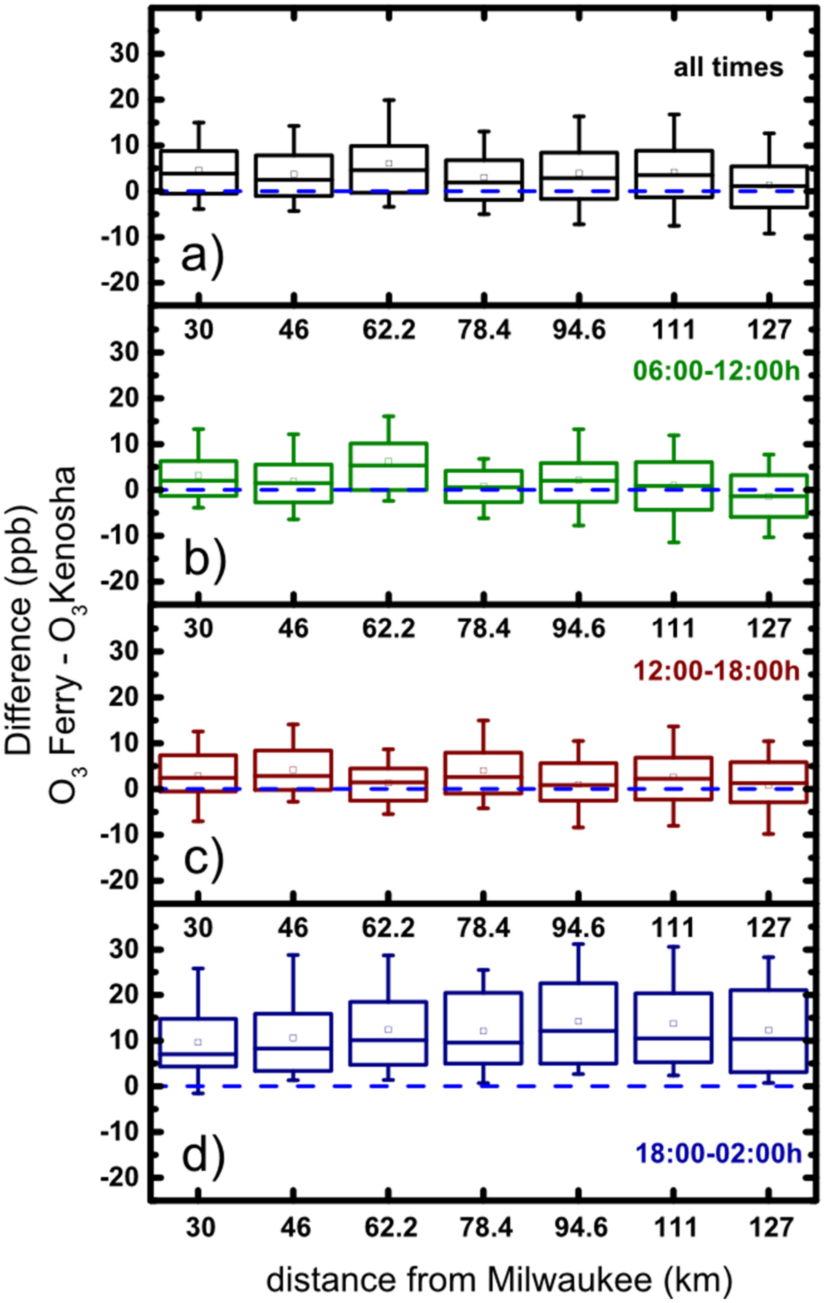


Figure 6: Difference in O_3 observations between platforms with respect to position of the ferry as indicated by km from Milwaukee along ferry path at: a) all times, b) morning (06:00-12:00h CDT), c) early afternoon (12:00-16:00h CDT) and d) late afternoon/evening (16:00-02:00h). Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box plot represents a minimum of 12 points.

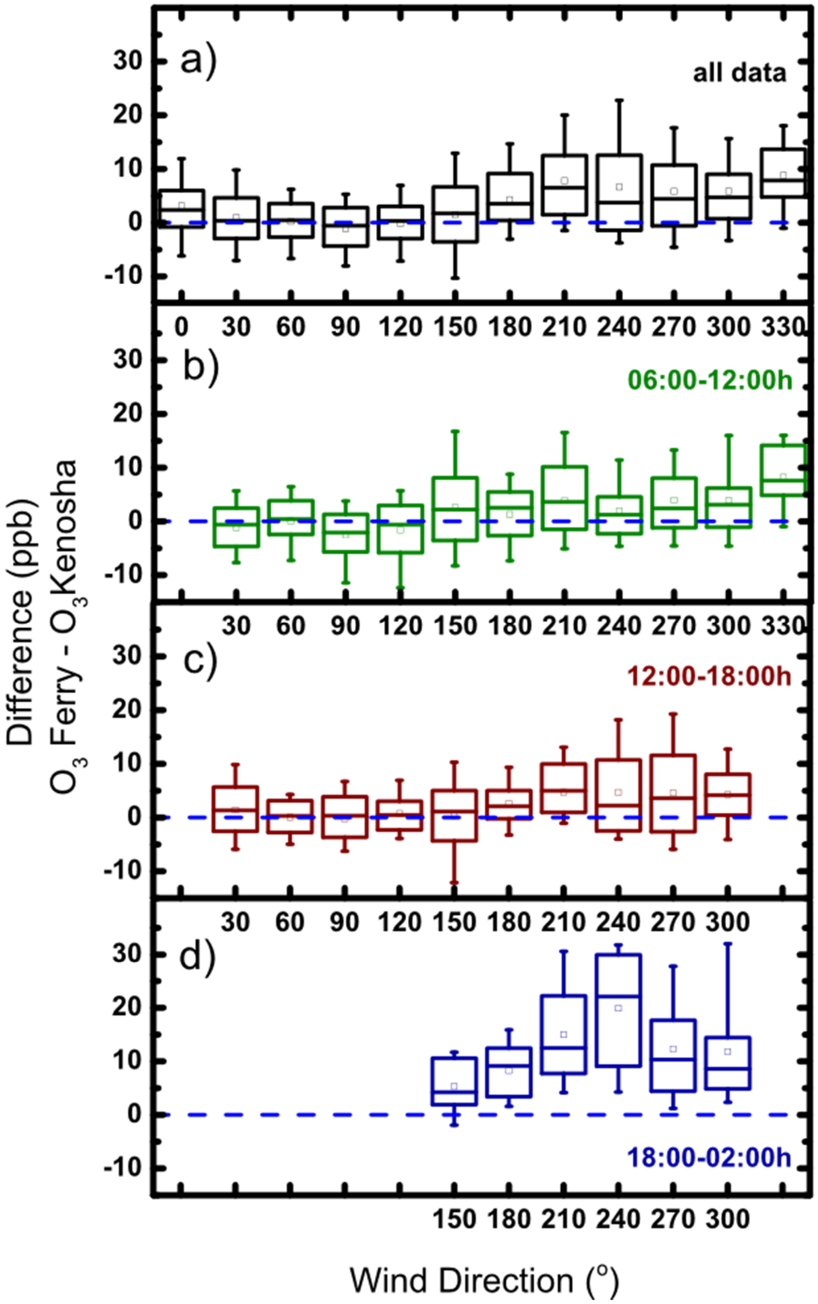


Figure 7 : Difference in O_3 observations between platforms with respect to wind direction measured at Kenosha harbor for a) all times, b) morning (06:00-12:00h CDT), c) early afternoon (12:00-16:00h CDT) and d) late afternoon/evening (16:00-02:00h). Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box represents a minimum of 15 points.

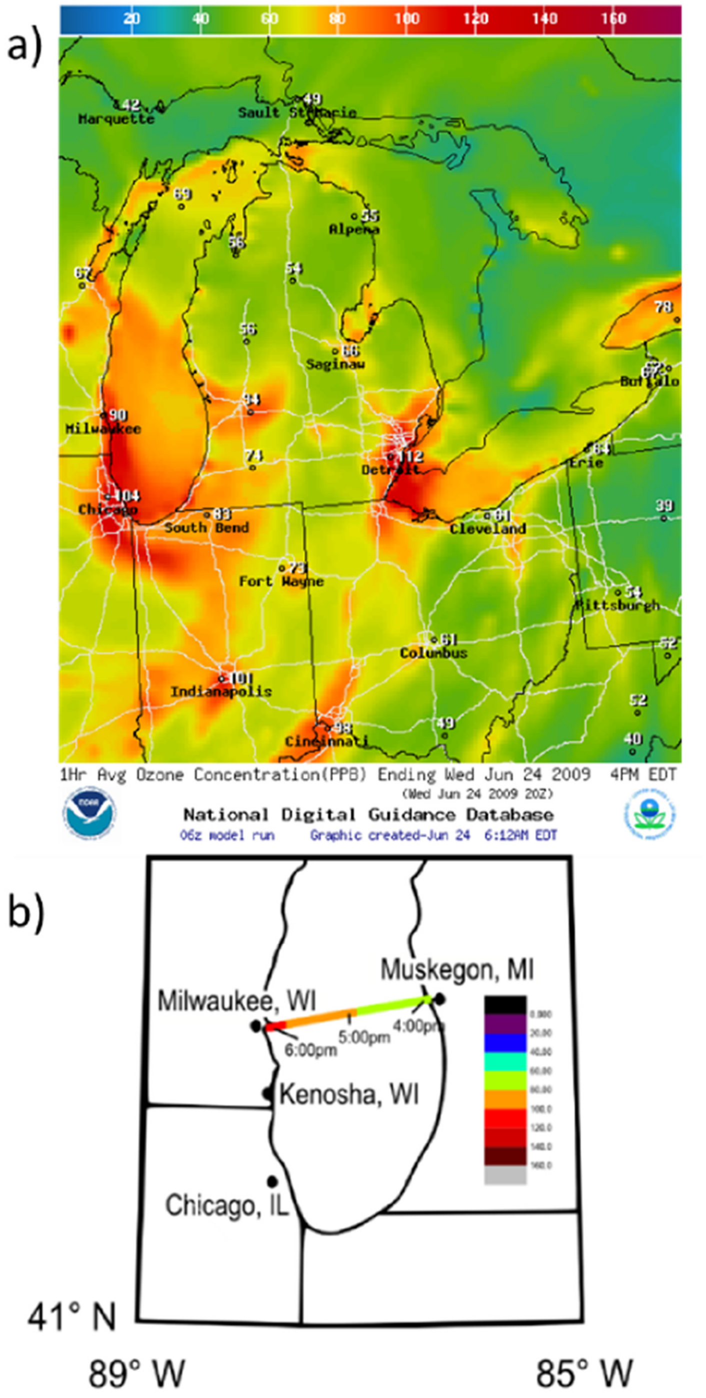


Figure 8: a) Sample image of National Air Quality Forecast Model (NAQFM) during the campaign period, b) O_3 measurements for one ferry trip on June 24, 2009 where the ferry was in transit from 3:50 pm (CDT) to 6:15 pm (CDT).

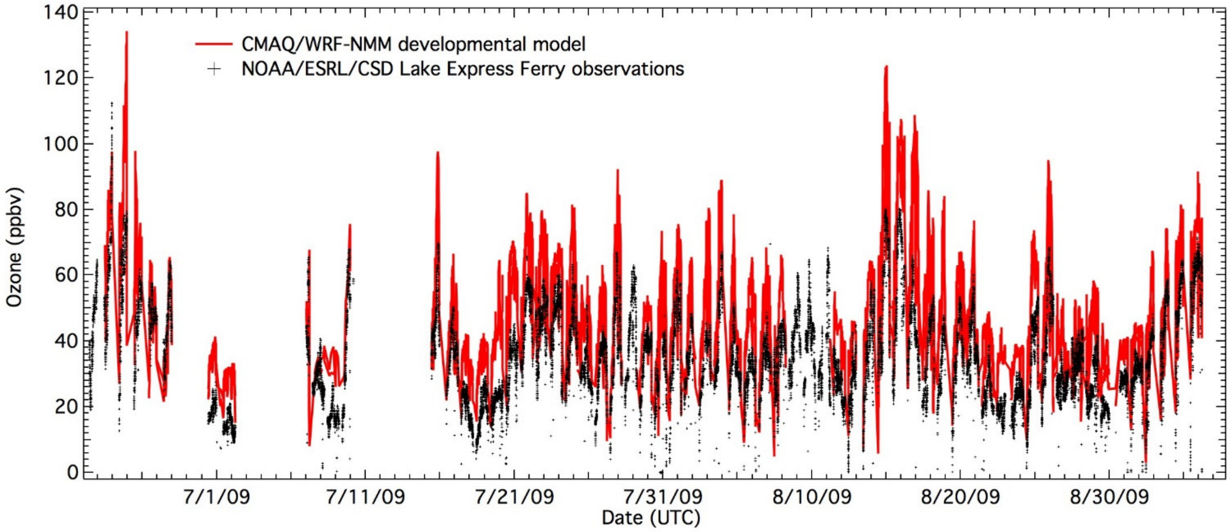


Figure 9: Graph of all CMAQ model forecast ozone mixing ratios in red with *Lake Express* Ferry observations in black from 2009.

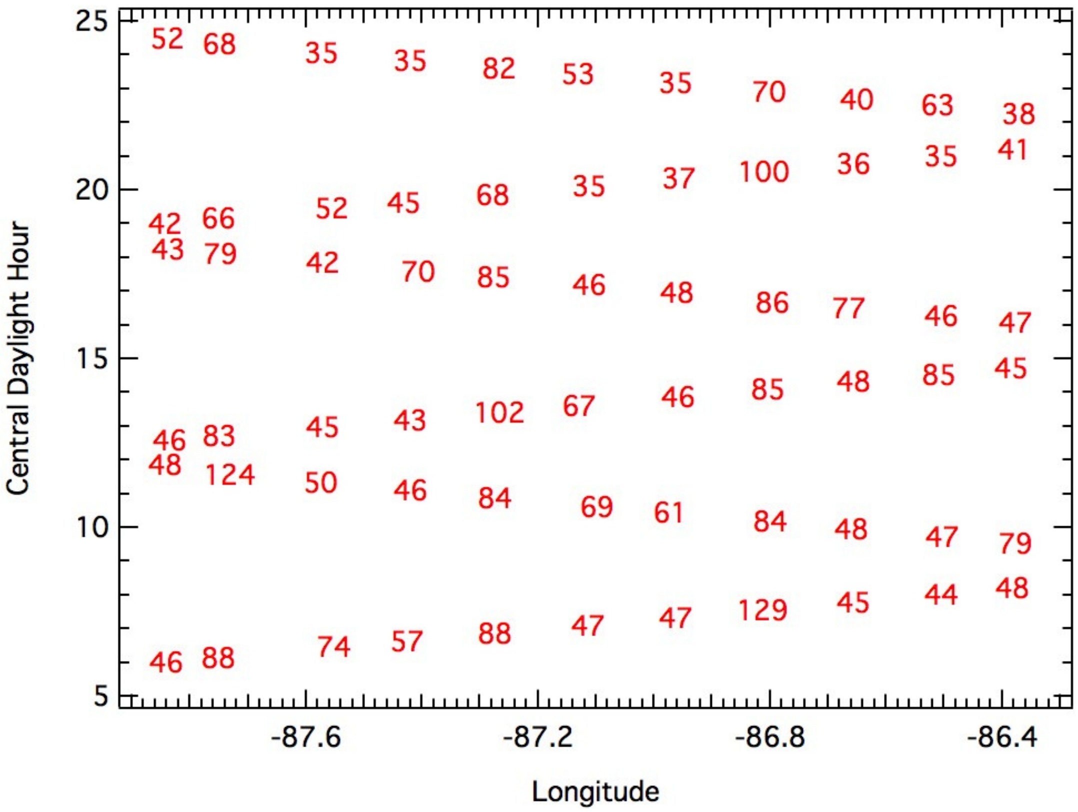


Figure 10: Statistical data for CMAQ model and ferry measurement comparison. Each model grid value and observation averages were binned according to model west-east grid number and CDT time of the ferry transect. The 1-min O_3 observations were averaged over model grid and hourly output. The numbers here are the number of hourly comparisons between model grid values and hourly averaged O_3 observations via ferry.

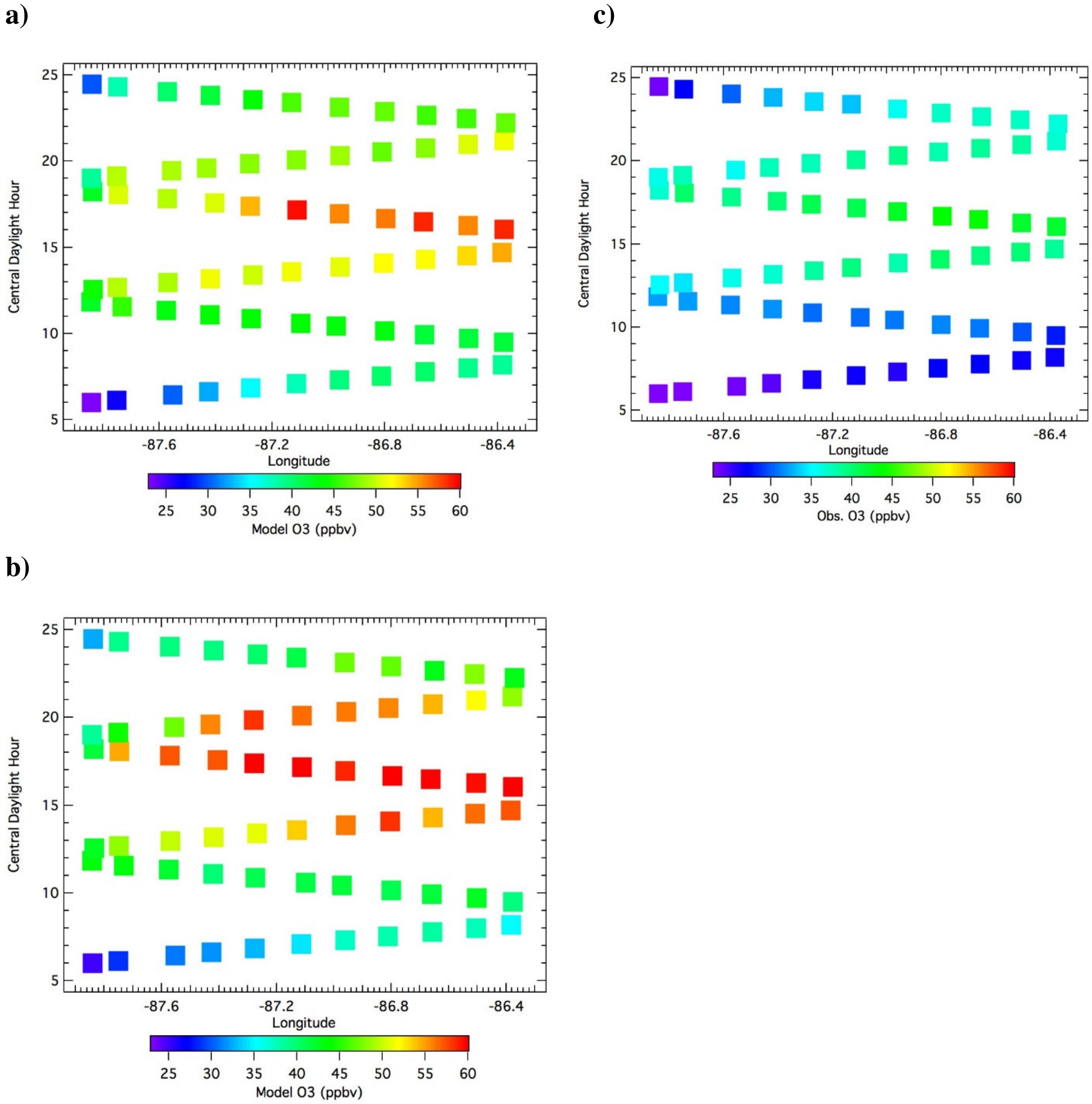


Figure 11: Median O_3 from a) 1-24hr CMAQ forecasts b) 25-48 CMAQ forecasts and c) ferry observations.

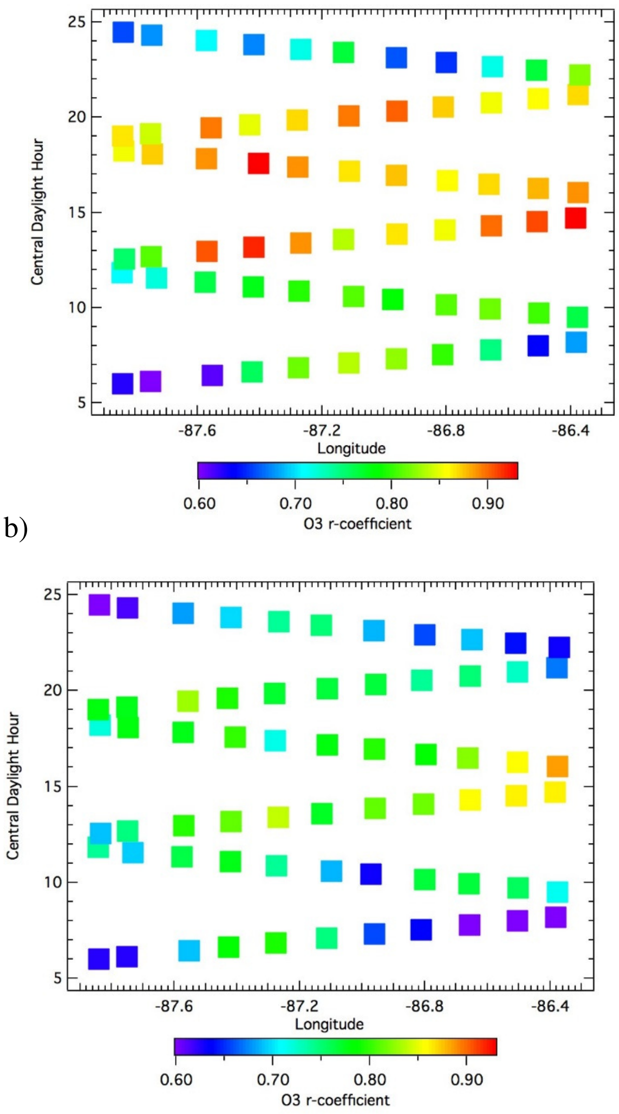
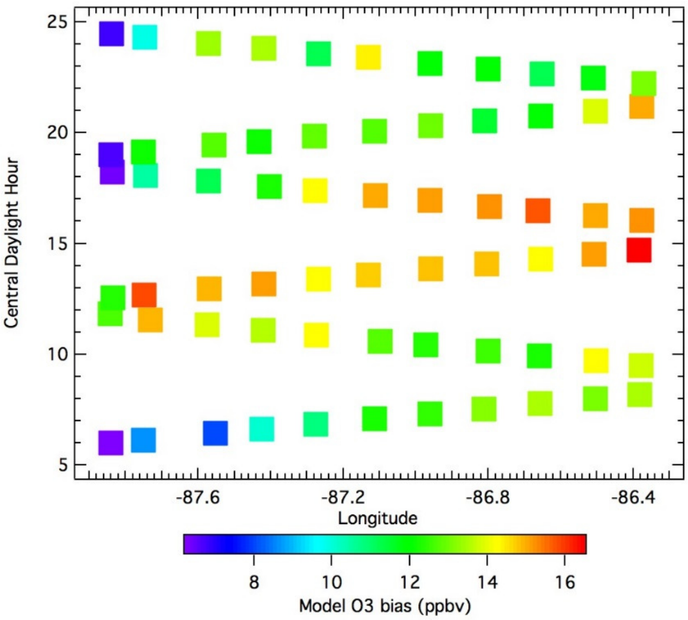


Figure 12: Correlation coefficients for model-measurement comparison for each bin a) 1-24h forecast b) 25-48h forecast

a)



b)

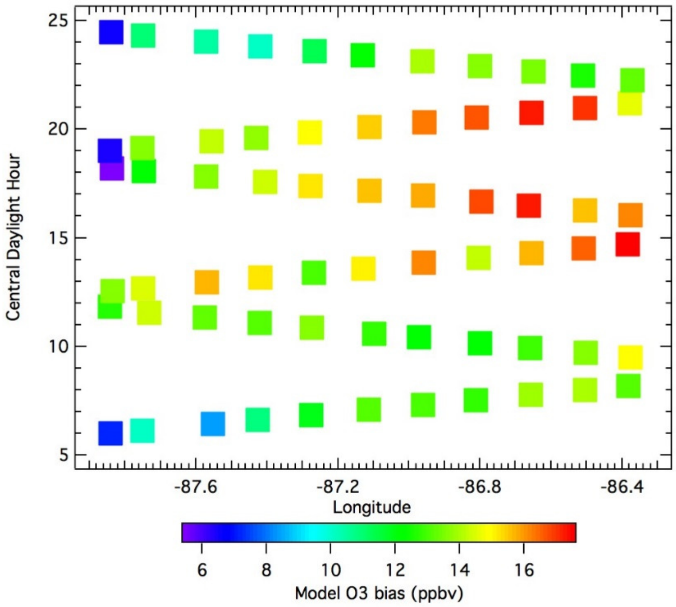


Figure 13: CMAQ model bias from a) 1-24h forecast and b) 25-48h forecast

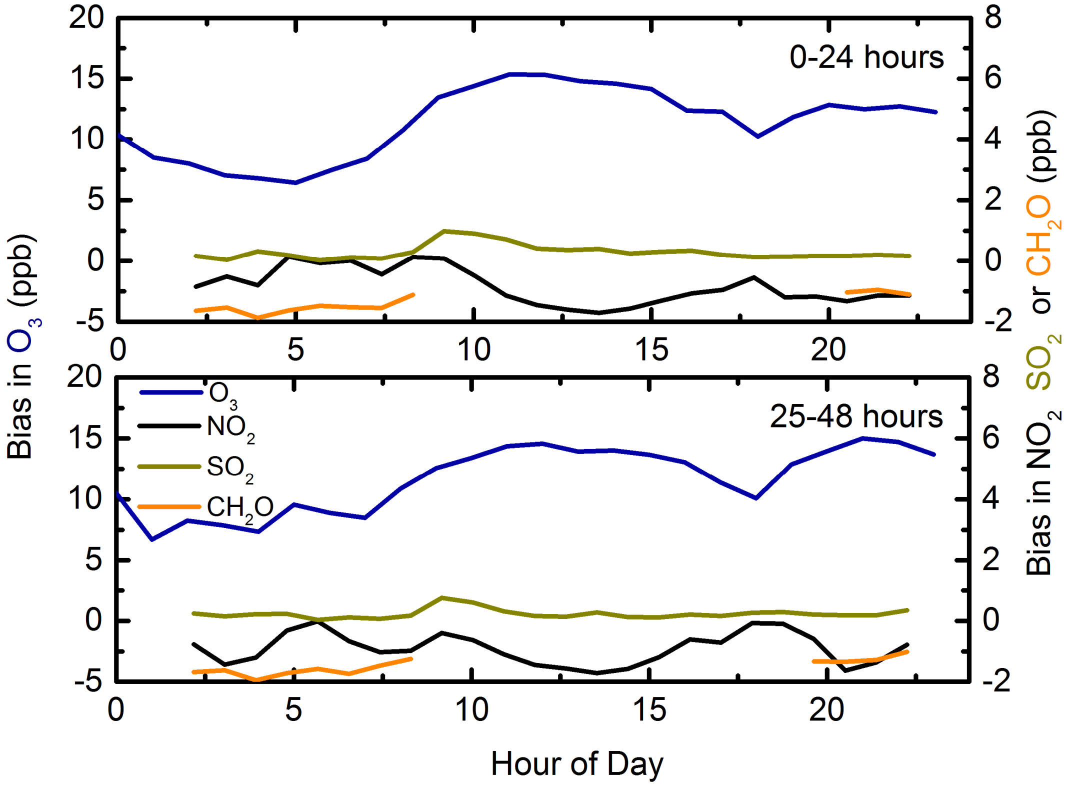


Figure 14: CMAQ model bias at Kenosha for O_3 (in blue, left axis), NO_2 (black), SO_2 (brown), or formaldehyde (orange) (right axis) for a) 1-24h forecast and b) 25-48 h forecast.

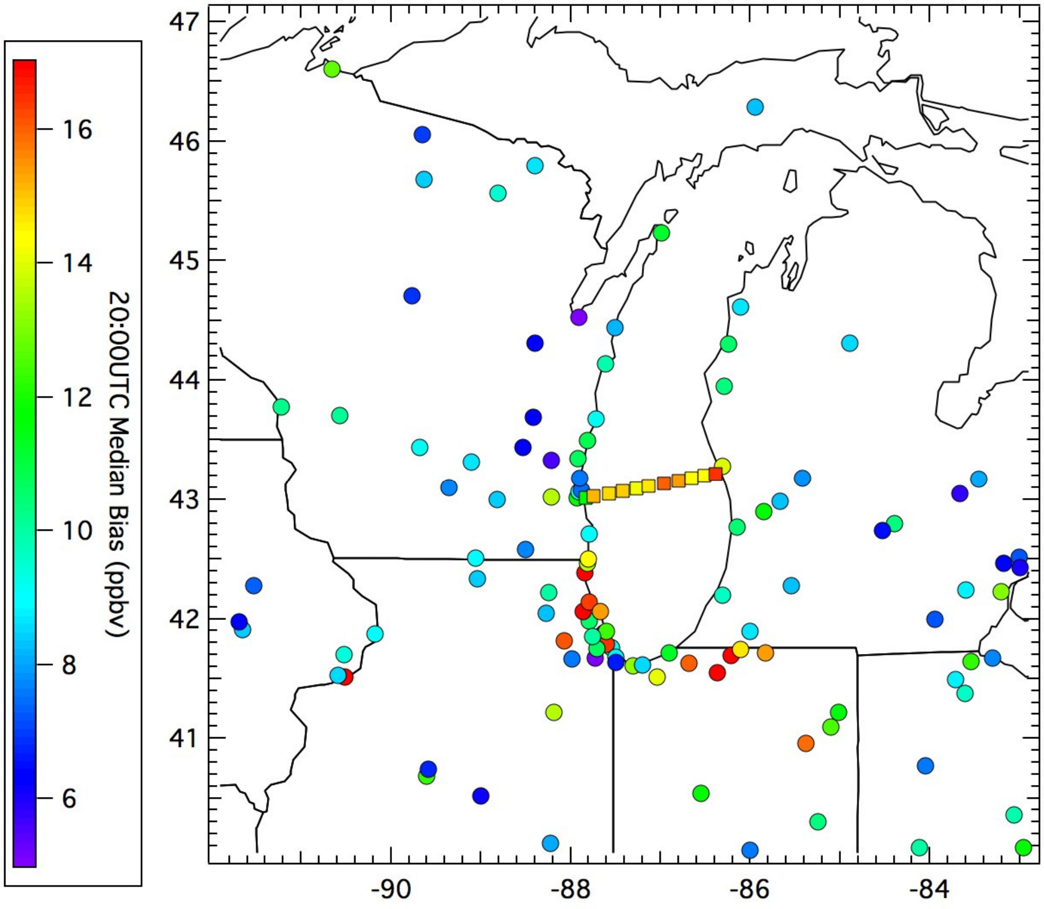


Figure 15: CMAQ model O_3 bias for air quality EPA station monitors (circles) and *Lake Express* ferry (boxes). EPA monitor biases are calculated at 20:00 UTC (3:00pm CDT), and the data has been windowed for only those days when *Lake Express* ferry data is available. For the *Lake Express* ferry data are from the 12:30 to 3:00 pm (CDT) transect statistics.