Point-by-point response to all referee comments

Acp-2014-480

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

P.A. Cleary et al.

We thank the reviewers for the thoughtful comments to this manuscript. Because of the common concern brought up by both reviewers on the methodology we used for the model comparison, we revised the manuscript and analysis methods to conduct the model comparison using CMAQ model output grid values directly. We wish to acknowledge the contributions of 3 new co-authors that have aided in this new CMAQ comparison: J. McQueen, Y Tang and Stu McKeen. This analysis will hopefully lay the referees' concerns to rest, although it has not changed the conclusions from our analysis. Responses to the reviewer questions are below, with the caveat that the model comparison section has been significantly revised along with the figures in that section, to best reflect the changes in analysis. The substantial changes to the manuscript are from page 16 line 22-page 20 line 4. Changes/additions were also made to Figures 9-15.

Referee comments are in italics.

Author responses to referees include paginations from the ACPD manuscript and page numbers from the revised manuscript which are numbered from 1-39.

Response to Reviewer 1 Comments:

Reviewer 1: 1) The authors discuss many "trends" and "patterns" in their data but provide no statistical analysis despite the large sample size. For instance in figure 1, they have at least 75 observations going into each of 12 wind direction bins yet the authors never bother to determine whether the differences between bins are statistically significant. In addition, patterns in box plots shown in Figures 5, 6, 7, 10, 11, and 12 are discussed but the authors do not quantify the differences. Figures 5 and 6 show the difference in measured ozone between ferry measurements and shoreline DOAS which is used as a proxy for the onshore/offshore gradient. Although median values are sometimes above or below zero, the interquartile range crosses zero in almost all cases suggesting that the difference in ozone may not be statistically different from zero. Similarly In figures 11 and 12 the authors break down model bias spatially and temporally. There is not a single boxplot with a mean or median value that is outside the interquartile range of any other boxplot. Again, this suggests that the spatial and temporal differences are not likely to be statistically significant. Adding some simple statistical analysis would not be a large effort. The authors should do this to add rigor to the analysis. I do believe that the spatial/temporal patterns identified by the authors are of interest even if they are not statistically significant but authors should at least acknowledge which results are significant in this discussion

1. We have added a statistical analysis (Kruskal-Wallis test, for non-parametric distributions) to the paper for figures 5, 6 and 7 to describe the significance in the differences in box plots given in the figures. The text has been modified to reflect these tests (p 15 lines 18-24 in the revised manuscript). A Kruskal-Wallis test was used because we need to rank the observed distributions by median instead of by mean due to the fact that we cannot assume they are normal distributions. The correlation coefficient was also computed for agreement between model and

measurement and included in the revised manuscript in Figure 12 and described in the revised manuscript on p 18 lines 10-12.

Reviewer 1: 2) The authors do not discuss uncertainties in measurements or limitations/ uncertainties in the comparisons between instruments or between the observations and the model predictions. The authors should add a brief discussion of all major uncertainties and limitations.

2. Statistical Comparisons are described above (using a Kruskal-Wallis test). The accuracy of the DOAS instrument was included on p7 line 13. The accuracy of the ozone monitor on the ferry was included in the methods section of the paper (p 8 lines 18-22). The method for extracting the CMAQ output was changed but an estimate of the uncertainties in selecting a model grid point associated with the ferry position is in the revised manuscript. Quantification of the correlation in terms of correlation coefficient was given in the text (p 18 lines 10-12) and in Figure 12. Added language to describe uncertainties was added to discussions in the intercomparison of ferry and shoreline DOAS observations.

Reviewer 1: 3) The case study presented in Figure 4 should be better integrated into the overall analysis. The authors choose 6 days out of 6 months to analyze in detail. Why was this particular episode chosen? Does this episode demonstrate general trends that are seen throughout the entire measurement period? Is this episode interesting because it is unique within the period or because it represents typical patterns? Can any broader conclusions be drawn about pollutant fate and transport in this area from these 6 days? Some connection should be made between these six days and the study period as a whole.

3. The episode given in Figure 4 was chosen because concentrations of higher max ozone mixing ratios (70 ppb) in a short time period which also shows differences in max ozone as measured at the shoreline and over the lake. 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. This figure captures a particularly strong change in conditions on August 14th that depicts a strong temperature change, wind direction change and ozone mixing ratio change at the shoreline. This has been addressed in the revised manuscript p11 line 24 through p12 line 3.

Reviewer 1: 4) A major part of this article is the comparison between modeled and measured ozone over Lake Michigan yet the authors do not describe the model or even give a reference for it. Some basic information about how the model is run is essential to understand what any biases mean.

4. A description of the model has been added to the revised manuscript (p 16 line 23 – p17 line 12). We changed the method for model comparison and used the CMAQ experimental model output directly in this revision (which was obtained by the help of individuals we are including as co-authors in the revised manuscript). We are also including evaluation of the model meta-data at Kenosha, and forecast ozone with other air quality monitoring stations in the area.

Specific comments:

Page 23209, line 7: Was binning done for 30 minute averaged values? This is implied in the figure caption but never stated explicitly. Please state in the text.

23209: Yes. The text was modified to state that 30-min average data was used

Page 23209, line 9: It might be of interest to also look at variability and max values by wind direction. As stated above, a statistical analysis could be performed to determine whether concentrations associated with different wind directions are statistically different.

We conducted a Kruskal-Wallis test for different times of day and determined that there are differences in distribution across the times of day, as stated in the manuscript on p 15, lines 18-22.

Page 23210, line 11: Can any quantitative comparisons be made with older studies to show how pollution levels/processes have changed in the 10 years since the previous studies?

23210: We have included some more references in the introduction to describe trends in the area and trends near the Great Lakes (e.g. Pugliese, et al 2014) that are relevant to this study (p 3 of revised manuscript).

Page 23210, lines 26-28: Were any instrument inter-comparisons made? For instance, were the DOAS and the ferry O3 instrument ever co-located to determine instrument bias/variability between the two? Since this comparison is used to imply differences in onshore and offshore concentrations, it is important to know how the instruments perform when measuring at the same location. The authors should at least discuss this as a limitation if no instrument inter-comparison was ever done.

P 23210: This was addressed on p12 line 8 and assigned an uncertainty.

Page 23210, lines 26-28: Are there any ground-based ozone observations from the ozone monitoring network in Kenosha and Milwaukee that could be compared to give a sense for how much shoreline ozone concentrations typically vary between these locations. This is also an important piece of information for interpreting differences between the DOAS and the ferry. Are the onshore/offshore differences greater that typical differences in ozone concentrations along the Wisconsin shoreline? If not, then these differences may be representing spatial variability of ozone but not necessarily typical lake versus onshore differences.

23210 we used the metadata from the CMAQ experimental model to evaluate the shoreline observations.

Page 23210, line 18: When the authors say "daily maximum" are they referring to 1-hr daily maximum, 30 minute daily maximum, or 8-hr daily maximum values?

23210 Daily max refers to the 30 minute averaged data and not 1 hour max.

Page 23211: In figure 4, it appears that there is a pattern in the second half of the episode where the peak ozone occurs later in the day for the ferry measurements than for the DOAS. Is

this pattern seen at other times in the study period? Does this temporal difference in the timing of peak ozone tell us anything about physical/chemical processes leading to high ozone? Is it a result of offshore flow during the day?

23211: Median observations of offshore ozone peak in the region of 14-17 h CDT and that trend is very similar in the ozone observations. Comparisons of day-to-day peaks can be complicated by wind shifts at the shoreline (like on August 14th of Figure 5), therefore we don't believe there to be much difference in the peak ozone time of day offshore versus onshore. This has been addressed on (p 12, second paragraph and p 13 first paragraph of the revised manuscript).

Page 23212, line 1: add "shoreline" before "NO2"

23212: "shoreline" has been added (p 13 line 1 of revised manuscript)

Page 23212, lines 14-15: Are wind direction and temperature correlated? Again, a quick statistical test could be used to answer this question quantitatively.

23212: wind direction and temperature are not correlated over the whole campaign as the variations in temperature day-to-day are higher than that between the over-water air masses and over-land air masses. A wider range in temperatures are observed from air masses arriving at the shoreline site from land, and a smaller range in temperatures are observed from air masses arriving from offshore. Some correlations can be seen on smaller timescales (day-to-day variations). Also a higher median temperature can be observed from air masses arriving from on land than over water. This has been addressed on p. 14 lines 9-12 of the revised manuscript.

Page 23212, line 16: Should 18:00-02:00 actually be 18:00-22:00? Page 23208 line 8 states that the last Ferry trip of the day occurs at 22:00.

23212. No. Sometimes the ferry arrived in Milwaukee after midnight. A 2.5 hour trip starting at 22:00 CDT will get into port after midnight.

Page 23214: The authors should consider also looking to see if there was a seasonal dependence in the DOAS/ferry differences. They could recreate figure 5-7 except split them by season (spring, summer, fall) rather than time of day to investigate.

23214: There is a statistically significant difference in the distribution of differences (Kruskal-Wallis p=0.05) in ozone from summer (June, July, August) to fall (September, October) with median difference of 3.3ppb for summer and 1.6 ppb for all points. Instead of adding a figure this was included in the text on p. 11 lines 18-21 of the revised manuscript.

Page 23215: The authors need to provide a reference for the National Air Quality Forecast model and also provide a few key details about this model. The authors should discuss some of the largest uncertainties in providing this type of comparison but before they do so they need to provide some information about how the model was run.

* Is this the forecast that is provided by NOAA? What photochemical model is it based on? CMAQ? Please provide a reference.
* What is the model resolution? 12km? If the resolution was much coarser than 12km (36km or larger) then comparisons between coarse model grids and point measurements might not be appropriate.
* What emissions inventory year was used to project the emissions? I think it is likely that the 2009 model runs were performed using a 2005 base emissions inventory year.
When the emissions were projected from 2005 to 2009 was any adjustment made for the economic recession or for new national and state emissions control programs that had been implemented in this time period? If not, it is likely that the emissions for the 2009 forecast were substantially higher than reality and this may explain some of the model bias.
* What meteorological model was used to drive the forecast model? How often was the met model re-initialized?

> 23215: The section has been modified to include more details about the CMAQ model that was used. Please see p 16 line 23 – p17 line 12 of revised manuscript.

Page 23215, lines 12-13: I may be misunderstanding, but it sounds like the authors took image files and attempted to translate georeferenced ozone concentrations from the color scale shown in the image. This seems like an odd way to obtain the model data as it potentially adds an unnecessary source of error and a lot of work! Why didn't the authors simply ask NOAA for the raw model output so that they could use the actual model data? How precise is the translation of colors to ppb? For instance the authors would be limited by the resolution of the color scale used in the images. What resolution was used for the color scale? 1ppb? 5ppb? The raw data would give exact values down to several decimal places. How accurate was the image program at distinguishing between adjacent colors on the color scale for translating colors to concentrations? Would this be impacted by how the computer monitor interprets colors? In addition, the gridded model output comes with information about the geographic projection used to create the model domain. It seems like goereferencing the images would add error if the authors did not use information about how the model grid was projected. Please further clarify if this is indeed what was done to obtain model data and add a discussion about the added uncertainty/error introduced by this process.

> 23215: The model output has since been obtained directly and used for analysis. This has been updated in the revised manuscript. Please see p 16 line 23 – p17 line 12 of revised manuscript.

Page 23215, lines 22-23: Were model grid cells averaged when the ferry traversed multiple cells?
   23215 lines 22-23. No grid cells were averaged. The new figures represent the model comparison as the ferry transects each grid cell. Please see Figure 10 on p34 for the number of comparison points per grid cell in the model comparison analysis.

Page 23216, lines 5-7: Was the model data for the bias calculation in daily maximum ozone matched in time and space with the observations? I.E. was the model data the maximum daily ozone in the model or was is the model ozone at the time and location of the observed daily maximum ozone. If it was the latter, the authors should consider looking at the former as well to see if perhaps the model had a similar maximum value that was displaced in time or space.

23216. Figures that depict daily maximum ozone have been modified. This is no longer relevant.

Page 23216, lines 16-17: Although the authors report no ozone exceedances in 2008-2010 of the federal standard in their data, this is not consistent with ozone values reported by Wisconsin's ground-based monitoring network. For instance, the Kenosha monitor (#55-059-0019) reported one day in late July 2008, two days in late June 2009 and 7 days throughout the summer of 2010 that had 8-hr daily maximum ozone values above 75 ppb. There are four monitors located in Milwaukee County (55-079-0010, 55-079-0026, 55-079-0041 and 55-079-0085). Each of these shows one or more exceedance in the 2008-2010 time period. So the authors should qualify their statement that the model is predicted too many exceedances since independent nearby measurements do show multiple exceedances during the study period. Data from the groundbased monitoring networks is available online at: www.epa.gov/airdata

23216: We have included more comparisons of the air quality monitoring stations from the ground-based monitoring network to compare how off-shore air masses are modeled as compared to shoreline observations (see Figure 15 on p 39 and p19 lines 14-19). There is no longer a discussion of 8-hour ozone in the model versus measurements.

Response to Reviewer 3 comments

Major Comments:

Referee 3: 1) It is not clear to me what new information is being presented in this paper that is not already in the literature. The authors describe previous work in the Lake Michigan area and indicate that there has been O3 reduction in the past 20 years, but are there still problems with non-attainment? How significant are the current problems? What was the impetus for this particular study? The need for routine offshore comparisons with onshore measurements has been highlighted, but the reasons why are not described. This study may be the first to present regular O3 measurements over Lake Michigan and compare with national air quality forecasts (p. 23207 L. 11), but what new information does this study provide in that is any different from previous studies? This needs to be highlighted. As an aside, why do the authors not make use of other land-based air quality measurements that exist in this region to help characterize the onshore air quality, sources, and the behaviour of the lake breeze? This would also provide context for the measurements presented in this paper.

1. 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. These counties in non-attainment in Wisconsin are unique in that they are both suburban, Lake Michigan shoreline counties as opposed to urban or rural counties. The relationship between Chicago emissions, and meteorology of Lake Michigan in air quality in Wisconsin is being evaluated by this.

Other papers have been addressing the role of Lake Breeze in air quality near the Great Lakes of North America (Levy, Makar, Sills, Pugliese), with a whole campaign dedicated to the evaluation (BASQ-MET) of lake breezes. This paper is a first step in associating Lake Michigan ozone mixing ratios off-shore with those on-shore, but a full assessment of lake breezes as they cross different land-based stations is

beyond the scope and focus of this paper. We don't doubt that our experiment will be meaningful to contextualize the research being done near/over the Great Lakes, but we are not interested in generating a different analysis for assessing the presence of Lake Breeze at this time as it is outside the scope of this paper. We have included more language on pages 2-3 of the manuscript to describe how this study fits in with modern studies on the role of the Great Lakes on shoreline air quality.

Referee 3: 2) Uncertainties and statistical comparisons are not presented and discussed. Particularly because comparisons (ie. differences) between DOAS and TECO O3 data and TECO O3 and model output are being presented, it is important to quantify uncertainties and statistically compare the data in order to ascertain whether differences are significant or not. What is the accuracy of the DOAS? Were the DOAS and O3 systems run side by side to intercompare and substantiate whether there is a bias in either measurement? This is a critical starting point to ensure the measurements are comparable. In addition, the uncertainties in digitizing the model images needs to be quantified.

2. The DOAS instrument is accurate to within 4% of calibration slope per year. For the observations made in this study, the measurements for ozone were made within 1 year of calibration. The DOAS instrument and TECO instrument were not co-located but each instrument was calibrated in 2009. The TECO instrument was calibrated against an ozone standard instrument at NOAA before and after the 2009 campaign. The DOAS instrument was evaluated with an in-beam absorption cell as outlined in the text. We assume all forecast ozone mixing ratios to be significant to ±1 ppb, and the text has been modified to address this. We also stated that the two instruments were never intercompared on p 12 and estimated an uncertainty because of this.

Referee 3: 3) The model comparison with the ferry O3 measurements in Section 3.3 is very limited. Interpretation of measurements versus model requires an in depth understanding of the model itself. Little information is provided about the model used in this paper. What emissions inventory is being used? How often is the meteorology updated? What chemistry is in the model? What is the spatial resolution i.e. can lake breeze circulations be captured and how does this impact the comparisons? What can the model tell us about the vertical O3 structure over the lake? What are the most significant model limitations in the context of these comparisons? Also, it is odd to me why the authors needed to digitize model images – why would the data not be available to presumably obtain much better quality comparisons with presumable much better accuracy than using images. No information is provided about the uncertainty associated with digitizing these images. If this paper is to include a large section on model comparisons as it does, then a much more comprehensive comparison needs to be done, most preferably using direct model output. Otherwise interpretation is left completely to speculation with an all-encompassing list of possible causes of discrepancies - meteorology, emissions, and chemistry. The authors are referred to Makar et al. (2010), reference provided below, for work that is relevant to this paper.

3. The text of the paper has been changed to respond to the questions outlined here. The national air quality forecast model is made up of the North American Mesoscale (NAM) meteorological model and the EPA's Community Multiscale Air Quality modeling system. The NAM produces meteorological parameters which are used within the CMAQ model to simulate gas-phase chemistry. The output of this model was not the experimental CMAQ model (CBIV Carbon Bond Mechanism 05) which has since been implemented (Saylor 2012). The emissions inventory is based on the EPA's 2005 National Emissions

Inventory (Pan et al 2014). The meteorology forecasts are run every 12 hours to input into the CMAQ and may not adequately capture changes in lake breeze circulation due to its smaller temporal resolution than the forecast model. The section on model comparison has been changed to reflect a comparison using the CMAQ experimental model. We intend to include 3 new authors (Stu McKeen, Jeff McQueen, and Youhua Tang) in this paper who aided in acquiring the CMAQ experimental model output in 2009 and provided additional analysis of these new model ozone forecasts.

Minor comments:

In order to better understand the O3 measurements presented in this paper, it would be helpful to have further information and interpretation of emission sources and possible impacts. The following comments (1-5) are related to this:

1. p. 23206, L.24- p. 23207 L. 5 How does the combination of DOAS species provide a 'unique breadth of information about air masses'? and What is meant by this 'measurement strategy'?

1. P23206: The text has been modified to address the reviewer's comments. The DOAS instrument is a multi-species monitor and so is a strategy to obtain multiple, relevant, measurements with one device. See P6 lines 1-5 of the revise manuscript.

2. p. 23204 L. 21 What is unique about the distribution of o3 precursor emissions and why not state more explicitly what and where they are? A figure depicting emission sources might be helpful.

2. P23204: The text has been modified to address this point (p3 lines 18-23). We also added points to the map in Figure 1 to depict coal-fired power plants in the map, which are sources of NO_x and SO_2.

3. p. 23210 L 1-2, Not a very comprehensive picture for the reader to know where the major sources are located and what they are.

3. 23210: text was modified (p10 lines 14-18) and power plants were added to Figure 1.

4. p. 23210 L9-11 'may implicate influence of power plant emissions over longer distances'… where are the sources implicated? Any attempt at connecting the measurements to these sources through e.g. back trajectories, calculating time scales etc.

4. 23210: Text has been modified (p 10 lines 14-18).

5. p. 23207, L. 5-7 I don't see in this study how the DOAS measurements used to determine changes in chemical composition to describe emissions, processing and transport of plumes over Lake Michigan.

5. 23207: Text has been modified to address reviewer's comments (p 6 line 15).

6. p 23211, L 16-18 so why not discuss the different sources that impact your measurements How were the meteorological measurements made? What are their uncertainties?

Was a minimum wind speed criteria used for the wind direction measurement to avoid stagnant conditions which may be unreliable (Fig 2)? The O3 inlet seems like it would be a fairly lengthy line – what are the details on this e.g. residence time, subsampled off faster flow? Was an inlet filter used and how often was it changed? Was there some kind of 'rain cover'? How often were the O3 zeros done? Should indicate in the Figure 1 caption that the ferry path is shown in the inset.

6. 23211 Details were added to the manuscript to answer these questions. No filter was used for the meteorological measurements. (p 8 line 7-11)
The ferry path in Figure 1 is the line across the lake. The path of the light for the DOAS measurement is given in the inset. This was clarified in the caption on p 25.

Figure 2, SO2 also looks like it is elevated from the south (land) in addition to over water

Discussion of Figure 2 was modified to include larger mixing ratios being observed from the south (p 10 lines 15-16)

Change concentrations to mixing ratios throughout manuscript.

Mixing ratios is used instead of concentration throughout the revised manuscript

p. 23204 L. 20 Please add references for forecast models predicting high lake O3

23204. A reference was added.

p. 23209 L 15-26 description here doesn't seem to lead to any interpretation of the measurements and thus why is this even discussed?

23209. We added CMAQ analysis of measurements conducted at that site, so we do feel that it is relevant to the discussion.

p. 23210 L 3-5 what about night time losses of NO2?

23210: We addressed this question in the revised manuscript. The sources of NO_2 are expected to also be highest during the day (mobile sources and powerplants, all primarily land-based) but the losses from photolysis and reaction with OH bring the diurnal profile of NO_2 to a minimum mid-day consistently over this experiment. Based on our observations, either there is a consistent large source of NO_2 offshore (which is unlikely – this would require a lot of shipping exhaust only at night offshore) or land-based sources of NO_2 produce local NO_2 which is lost mid-day. We note that formation of NO_3 and N_2O_5 at night can be a considerable loss of NO_x, as outlined in the paper Brown et al 2004, for a marine boundary layer experiment. Because we only measure NO_2, we do not have a fully comprehensive constraint on all NO_x but that NO_2 is photolyzed in the day and has losses with OH which can lead to a minimum mid-day (which was observed). If losses of NO_2 at night were high, we would also require a high emissions rate from off-shore at night to compensate for these high losses to describe the observations (as a function of wind direction and time of day). Because we do not expect there to be regular sources of NO_x at night offshore that are higher than

daytime emissions, we believe the most reasonable explanation for high NO_2 at night from offshore being a reduction in losses at night.

Figures 11, 12 and 14, Differences between west and east: how does the 2.5 hour time period for a trip factor into the data interpretation? I would expect changes in O3 chemistry over this time period. How much uncertainty is estimated from these changes?

Figures 11, 12 and 14 and have been modified based on our new evaluation of the model.

p. 23214, L 10-13, sentence doesn't make sense

P 23214 line 10-13. The sentence has been modified.

Figure 13 – need to clarify what 'number' represents (ie number of days) on both the y-axis and the caption

Figure 13 has been modified.

Reference Makar, P.A., J. Zhang, W. Gong, C. Stroud, D. Sills, K. L. Hayden, J. Brook, I. Levy, C. Mihele, M. D. Moran, D. W. Tarasick, H. He, and D. Plummer, Mass tracking for chemical analysis: the causes of ozone formation in southern Ontario during BAQSMet 2007, Atmos. Chem. Phys., 10, 11151-11173, 2010.

Reference of Makar 2010 has been added.

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

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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,

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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.

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1   The study of high ozone events in the region has centered around mesoscale

2   meteorological effects that contribute to the formation of ozone and the movement of air masses

3   over land (Lennartson and Schwartz, 2002; Lyons and Cole, 1976). Lyons and Cole (1976)

4   outlined the influence of the land-breeze effect on shoreline air quality. Lennartson and

5   Schwartz (2002) indicated a pattern of high pressure anticyclonic events as coincident with

6   higher ozone abundances at land-based sites. Recently, Levy et al. (2010) investigated the

7   impact of local-scale flows in Great Lakes air quality in the region of Lake Erie. Levy et al.

8   determined that local-scale emissions play a significant role in ozone production, and the

9   meterological constraints on air movement aid in isolating and stratifying air pockets from

10   which ozone is generated on a next-day basis.

11   A few studies have investigated offshore air quality in regional-scale monitoring of

12   ozone around Lake Michigan. The Lake Michigan Air Quality Study in 1991, where aircraft

13   were used for monitoring (Dye et al., 1995) and the LADCO Aircraft Project (Foley et al., 2011)

14   are the two most notable. Dye et al. (1995) determined that stratification over Lake Michigan

15   leads to limited vertical and horizontal mixing beyond the lake area during the summer,

16   allowing for the confinement of ozone precursors. The LADCO Aircraft Project (LAP) was a

17   9-year aircraft-based study to evaluate air quality in the region, where flights were conducted

18   on days of suspected high ozone which would be in non-attainment of hourly federal standards

19   (Foley et al., 2011). The work from LAP is consistent with the interpretation presented by Dye

20   et al. in that inversions over the lake created stable layers of urban plumes, and that air sampled

21   at greater distance from the Chicago - Milwaukee shoreline tended to be more processed. Foley,

22   et al. (2011) determined in the late 1990's and early 2000's that in lower altitude air (< 200 m

23   above ground level (AGL)) ozone formation switched between VOC-limited conditions in the

24   morning to NO_x-limited in the afternoon, and that above 200 m AGL, ozone formation was

25   always NO_x limited. The observations from LAP showed a progression of the "photochemical

4

1   clock" during northward aircraft transects over the lake where more aged plumes were found

2   farther north of Chicago. Fast and Heilman (2003, 2005) developed a regional coupled

3   meteorological and chemical model to describe ozone formation on or near the Great Lakes.

4   For offshore measurements they used ozone observations from the SS *Badger*, which operates

5   between Luddington, Michigan and Manitowoc, Wisconsin. The comparison between the

6   model and measurements was restricted to specific times of the day due to the ferry movement

7   where the agreement of model to measurement was poorest for the eastern side of Lake

8   Michigan in 1999 (Fast and Heilman, 2003). Their model results from 1999 and 2001 showed

9   distinct features in the ozone spatial distribution over Lake Michigan but did not reproduce

10 eastern Wisconsin shoreline observations when ozone mixing ratios were high (>60 ppb) (Fast

11 and Heilman, 2005).

12   The Lake Michigan land/lake breeze is a well-documented phenomenon that influences

13 local scale air flow due to differential heating of air masses over land and water on a daily basis

14 (Lyons and Cole, 1976; Foley et al., 2011; Hanna and Chang, 1995; Lennartson and Schwartz,

15 2002). Offshore flow (the land breeze) is dominant during the nighttime during summer when

16 surface waters are higher in temperature than land surface temperatures. For counties along the

17 western side of Lake Michigan, this westerly pattern follows typical westerly synoptic flow for

18 the region. Onshore flow (the lake breeze) is more common in the summer daytime when land

19 temperatures exceed water surface temperatures. The lake breeze has been seen to coincide with

20 higher ozone and the transport of aerosol in Chicago (Harris and Kotamarthi, 2005; Lyons and

21 Olsson, 1973) and larger-scale high pressure anticyclonic flows have been implicated in the

22 higher Lake Michigan shoreline ozone observations (Lennartson and Schwartz, 1999), which

23 enhance the flow of photochemically aged air from the Chicago urban plume northward along

24 the Lake Michigan shoreline to southeastern Wisconsin.

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1   In this study, the deployment of both a long path Differential Optical Absorption

2 Spectrometer (DOAS) at the shoreline and an ozone monitor on a ferry has several benefits: the

3 long path length for the DOAS instrument creates an averaged signal that is unaffected by small

4 spatial scale point-source emissions, and allows for simultaneous observations of several

5 compounds (NO_2, SO_2, O_3, formaldehyde). This combination of species provides relevant

6 information about air masses, where O_3 is the pollutant of interest to compare with offshore

7 observations, NO_2 is a proxy for NO_x and a precursor to O_3 production, formaldehyde is a proxy

8 for total VOC which are other necessary ozone precursors, and SO_2 is used as a tracer for

9 industrial emissions and electric power generation. The use of a DOAS instrument for

10 monitoring atmospheric species at a shoreline has proven effective in other environments, such

11 as the observatory on the west coast of Ireland, (Carpenter et al., 1999; Seitz et al., 2010), Crete

12 (Vrekoussis et al., 2004), Galapagos Islands (Martin et al., 2013), Okinawa Island (Takashima

13 et al., 2011), Houston (Rivera et al., 2010), Helgoland (Martinez et al., 2000) and Appledore

14 Island, NH (White et al., 2008), to name a few. In the study described here, the four constituents

15 measured by DOAS are used to show the change in chemical composition of air masses from

16 offshore and onshore evaluate the spatial distribution of the species at the Lake Michigan

17 shoreline. The routine monitoring of ozone over Lake Michigan on the ferry platform allows

18 for an evaluation of the spatial distribution of ozone over the lake, comparison of over-water

19 ozone to shoreline ozone, and comparison to forecast models of surface-level ozone. This

20 investigation is the first to present high resolution, regular observations of ozone at the surface

21 over Lake Michigan in comparison to air quality model output. Results have been analyzed to

22 show the difference between shoreline and over-water ozone as a function of time of year, time

23 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)

7

1 CDT and in late July/August also at 19:00 (eastbound) and 22:00 (westbound) CDT. Time

2 zones for Wisconsin and Michigan differ, but all times given here are in Central Daylight Time.

3 The ferry stays in port overnight in Milwaukee and the average trip duration of the ferry for this

4 study was 2.25 hours. The inlet for air monitoring was installed at the bow above the

5 wheelhouse (3 m starboard of center and 10 m above water line) and approximately 15 meters

6 of ¼" PTFE tubing was routed through the interior conduit into a utility closet where a

7 commercial CO_2 (Li-Cor) and O_3 (Thermo Scientific Model 49) monitor were housed. The

8 sample line had a teflon cartridge filter (changed approx. weekly) and tee fitting to the two

9 instruments (each with independent pumps) with a sampling time lag of approximately 10s.

10 The inlet was positioned to the stern so as to minimize water spray entering the sample lines

11 with intake tubing surrounded by a larger tubing as a rain/spray cover. The O_3 instrument was

12 installed on the ferry from July 9-Sept 21, 2008, May 12 to Oct. 28, 2009 and June 23-Nov. 1,

13 2010. GPS coordinates and gas measurements were recorded every 30 seconds., resulting in a

14 frequency/spatial resolution of ~1 min/km, with an average speed of ferry at 30 knots. Zeros on

15 the ozone monitor were conducted during powerdown of the ferry (typically twice per day when

16 ferry was docked in port). Ozone data was excluded from data set when the ferry was in port

17 because measurements were also influenced by engine emissions of NO. On occasion, due to

18 inclement weather or mechanical problems, the ferry did not follow its posted schedule. The

19 ozone instrument had a manufacturer stated accuracy of ± 2 ppbv. The ozone instrument was

20 calibrated at NOAA before and after deployment each year by comparison of the instrument

21 deployed on the ferry to a standard ozone monitor (Thermo Scientific Model 49i-PS)

22 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

9

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

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1 emissions from local NO_x sources, and therefore the additional offshore processing cannot be

2 distinguished from chemistry at the shoreline with this DOAS measurement alone.

3 **3.2   Comparison between shoreline DOAS and ferry observations**

4 Kenosha shoreline DOAS observations of O_3 were compared with the *Lake Express* ferry O_3

5 observations in order to understand the regional distribution of ozone. The two measurements

6 were compared by averaging the ferry measurements to 30 minute intervals at the timescale of

7 the Kenosha harbor DOAS measurements. The two instruments were never intercompared at

8 the same location so we estimate an uncertainty in their intercomparison at 5% (which is higher

9 than the stated drift of either instrument as evaluated independently). The differences in 30-

10 minute averaged data from 2009, as measured as O_3 (Lake Express Ferry) $- O_3$ (Kenosha Harbor), fluctuated

11 from as high as 45 ppb to -37 ppb, with a median difference of 2.8 ppb, mean of 3.8 ppb and

12 standard deviation of 9.1 ppb. The daily maximum data (30-minute average) had a range of 39

13 ppb to -9 ppb, a median of 4.2 ppb, mean of 5.0 ppb, standard deviation 7.6 ppb. The time of

14 peak ozone for ferry measurements was approximately 14-17h CDT for the whole campaign

15 and for the DOAS measurements was from 14-16h CDT, which are not considerably different.

16 Day-to-day variations in the time of peak ozone off-shore versus onshore can occur from

17 changes in wind direction and local NO_x sources at the shoreline Kenosha site, and therefore

18 cannot be used to indicate differences in chemical processing over the day. There is a

19 statistically significant difference in the O_3 distribution over land vs. lake from summer (June,

20 July, August) to fall (September, October) with median difference of 3.3 ppb for summer and

21 1.6 ppb for fall (Kruskal-Wallis p=0.05).

22   In order to demonstrate the agreement between ozone measurements of both platforms,

23 Figure 4 shows the wind direction, O_3 measurements, the difference in ozone measurements,

24 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 ºC 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

1 of ozone remained high. The shoreline NO_2 mixing ratios also rebounded to 12 ppb. In this

2 case, the maximum SO_2 observations arrived at the Kenosha harbor site from offshore later in

3 the afternoon before the wind shifted. A Hysplit back trajectory model was calculated for the

4 morning of Aug 14th for synoptic winds at 250 m AGL and indicated an air mass arriving from

5 the northeastern suburbs of Chicago, Illinois which would intercept the rush-hour traffic

6 emissions. Thus, the low O_3 mid-morning was a result of near-source and early-day NO_x

7 titration. On Aug. 13, 14 and 15, NO_2 increased following the wind shift between south-

8 westerly and south-easterly wind flows. Hysplit back trajectories were generated for each of

9 these days, which showed air mases from Chicago transported northward along the shoreline at

10 the same time of day. Emissions were likely brought back on land from lake breezes which

11 could not be resolved from back trajectories.

12   Differences between ferry O_3 and shoreline DOAS O_3 mixing ratios were evaluated with

13 respect to temperature (Figure 5), location of the ferry (Figure 6) and wind direction (Figure 7).

14 Each figure shows the data for all times of the day, and for distinct time windows (06:00-12:00

15 CDT, 12:00-18:00 CDT, 18:00-02:00 CDT) in box plots which represent mean (line), median

16 (□), 25-75% (box), and 10-90% (whiskers) for the 30-minute average difference between O_3

17 (Lake Express) and O_3 (Kenosha Harbor). Differences between ozone observations from the ferry and

18 shoreline with respect to temperature were investigated (Figure 5). There was no observed trend

19 in difference in ozone versus temperature for all data, a minor trend for morning times (06:00-

20 12:00 CDT, 5b) where the difference changed from a positive difference to a more negative

21 difference with increasing temperature above 15.5 °C, and an opposite trend toward higher

22 ozone over the lake in the afternoon (12:00-18:00 CDT) and for temperatures above 26 °C.

23 Ozone differences after 18:00 CDT show consistently higher ozone mixing ratios over the lake

24 for all temperatures, but with larger differences above 21.1°C. While the chemistry can drive

25 more ozone production at higher temperatures, the fact that the largest differences were

13

1 observed in the evening and at night can arise from the isolation of air masses at this time from

2 the lake/land breeze effects. If the airmasses observed at the shoreline arrived from inland in

3 the late evening, they could have been chemically different from those found far offshore. The

4 only time when shoreline DOAS ozone observations tended to be higher than those from the

5 ferry was at 06:00-12:00 CDT for temperatures above 26.7 °C. This may be due to days when

6 temperatures were high in the morning, thus stagnating the air and limiting the influence of

7 lake/land breeze on horizontal movement of airmasses. Differences in offshore and shoreline

8 observations of ozone with respect to temperature were largest later in the day and at higher

9 temperatures when ozone was typically at a maximum. The range in temperatures observed

10 from different wind directions was higher in wind arriving from land (180º-360º) in comparison

11 to over water (0º-180º), such that the median temperature of all masses arriving at the site from

12 the east was 12.8ºC and from the west was 9.3ºC. The highest differences depicted in Figure 7

13 then are showing the highest ozone differences between shoreline and offshore measurements

14 from a wind direction where temperatures are not as extreme.

15   Investigations into the ozone differences between shoreline and ferry observations with

16 respect to ferry location were conducted as a test of the east-west gradient over Lake Michigan.

17 Figure 6 depicts the difference of $O_{3\,(Lake\,Express)} - O_{3\,(Kenosha\,Harbor)}$ with respect to ferry distance

18 from Milwaukee. For all data the mean and median difference was positive (i.e., greater as

19 measured over water from the ferry). The median differences were not significantly positive or

20 negative for the morning, slightly positive for the early afternoon time window, and consistently

21 positive for the late afternoon/evening. In the case of the late evening time window, the mean,

22 median and extremes (25%-75%) of the data all lie above 0, which is a strong suggestion that

23 at these times the ozone mixing ratios over the lake are consistently higher than at the shoreline.

24 However, there does not appear to be a significant variation with respect to longitude, meaning

25 that evaluated as a whole, the land-lake differences in ozone did not depend on the ferry's

14

1   distance from the shoreline. This demonstrates a widely regional distribution of ozone once

2   over the lake.

3   In order to distinguish between meteorological effects at the shoreline, the differences

4   in ozone observations from the ferry and shoreline DOAS ozone mixing ratios with respect to

5   wind direction at Kenosha Harbor were evaluated. All data (Figure 7a) show a trend in which

6   the differences between offshore and onshore observations of ozone are positive (i.e., greater

7   ozone over water as measured from the ferry) when wind arrives at the Kenosha Harbor site

8   from 180-360 degrees (inland) where the median and mean lie above 0. When broken up into

9   time windows of morning, afternoon and evening/night, the largest differences were observed

10   after 18:00 CDT if winds were arriving from 180-360°. This picture is consistent with land

11   breezes developing in the evening and producing surface winds which draw from land and move

12   over the lake. The sampled air masses at the shoreline, thus, were of different origin (or sampled

13   air masses over the lake were isolated from land-based air masses). The number of data points

14   (n<15) were acquired when the wind blew from 30-160° from 18:00-02:00 CDT were

15   insufficient for analysis. For the morning and early afternoon times, the trend with respect to

16   wind direction was not large.

17   The differences between ferry and shoreline ozone observations were largest after 18:00

18   CDT and into the night, as shown in Figures 5, 6, and 7. For each of these graphs, we conducted

19   a Kruskal-Wallis statistical test to the distributions at a given temperature, distance or wind

20   direction in comparison to time of day (comparing the box plots vertically in the figures) and

21   determined that they are all significantly different across the 3 different times of the day (95%

22   confidence). Figure 5 d) was the only figure that demonstrated the distributions could be

23   considered unequal across different temperatures (K-W, 95% confidence). The rest of the trends

24   discussed are not statistically significant. The difference between the ferry and shoreline trend

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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

16

1   Environmental Protection Agency (EPA) (Eder 2009). The NAQFM is made up of two

2   components: the National Center for Environmental Prediction's (NCEP) North American

3   Mesoscale (NAM) meteorological model and the Environmental Protection Agency's (EPA)

4   Community Multiscale Air Quality (CMAQ) modeling system (Janjic, 2003, Eder 2009, Byun

5   and Schere 2006). The NAM is used to input meteorological conditions into the CMAQ to

6   generate 48h forecasts. Initialization steps to the forecasts are conducted every 12 hours at 06

7   and 12 UTC (Eder 2009, Chai 2010). The NAQFM provides real-time predictions for ground-

8   level ozone mixing ratios over the contiguous US (Eder 2009) with a 12 km grid size. The

9   NAQFM CMAQ runs in 3 modes: operational, experimental and developmental, with the

10 operational prodect displayed publicly on the NAQFM web-site. Figure 8 shows an example of

11 the operational product for June 24, 2009, along with the Lake Express Ferry measurements on

12 that day, illustrating a clear model overprediction on the east side of the lake. During 2009 the

13 operational model used the Carbon Bond Mechanism version IV (CBMIV) gas-phase chemical

14 mechanism. Here we compare observations with the developmental model product which used

15 the Carbon Bond Mechanism 5 (CB05). The emissions inventory used in both model forecasts

16 is adopted from from the EPA's 2005 National Emissions Inventory (NEI) (Pan 2014). Figure

17 8 depicts an image of the NAQFM ozone forecast with a sample ferry transect with ozone

18 observations.

19   Hourly output from the developmental CMAQ forecasts were saved for the monitoring

20 season of 2009 from June 18-Sept. 15 2009. The CMAQ output ozone mixing ratios were

21 reported to 1 ppb precision. Figure 9 depicts O_3 forecast levels consistently higher than ferry

22 measurements with 57 days of overlapping data. These forecasts produce a distinct ozone

23 maximum over the water surfaces of the Great Lakes and, in particular, southern Lake Michigan

24 (e.g. Figure 8). Statistical comparsions with the Lake Express observations use model grid and

25 time values determined from ship tracks through the model domain, and with no spatial or

1   temporal interpolation.. Figure 10 depicts the sample numbers within distinct model grid cells

2   for the 3 month time period according to model longitude and central daylight time for the tferry

3   transects. The extreme western and eastern points are within ports and the Milwaukee model

4   grid are over land. The statistics may not be reliable for the shoreline grids due to local sources

5   and contamination by the ferry exhaust. The median ozone values for the forecast (Figure 11a)

6   1-24 hours after model initialization, (11b): 25-48 hours after initialization, and *Lake Express*

7   monitor (Figure 11c) show distinct higher model median O_3 forecasts in comparison to

8   observations. The maxima in the model forecast O_3 are mid-lake from 15:00-18:00 CDT. The

9   forecast O_3 mixing ratios are highest after 25-48 hours after initialize, especially between 2pm

10 and 9pm. The location of the daily maximum ozone from the ferry is similar distribution given

11 by the CMAQ for 1-24 h since initalization (Figures 11a,c). The CMAQ predicts the highest

12 median daily maximum O_3 just offshore on the eastern side of Lake Michigan for 1-24 hour

13 initialization (Figure 11a) and a larger area for 25-48h after initialization (Figure 11b). The

14 correlation coeffficients between model and measurement are high (R=0.85 to 0.95) from 14:00

15 - 17:00 h CDT for the 1-24 hour forecast (Figure 12a). The correlations were reduced for the

16 25-48-hour forecast (Figure 12b).

17   The comparison between the ozone forecast and the ferry observations were computed

18 as bias:

19      $$bias = p_i - o_i \qquad (1)$$

20 where p_i is the model-predicted O_3 concentration and o_i is the observed O_3 concentration on the

21 ferry, was determined for each sample location and time referenced in Figure 10. Model bias is

22 shown in Figure 13. The forecast from 1-24 hours after initialization in Figure 13a shows an

23 11-16 ppb median O_3 bias for offshore locations, which is highest between 12:00 and 17:00 h

24 CDT. The 24-48 hour forecast (Figure 13b) has a much higher bias between 14:00-21:00h CDT.

18

1 Components of the model were investigated to evaluate differences that may lead to the higher

2 model bias to the eastern side of Lake Michigan. Winds tend to start the day with a north-to-

3 south median wind component, with a switch to south-to-north wind component in the region

4 of 11:00-15:00h CDT for the 1-24 hour forecast, and an earlier at 8:00h CDT for the 25-48 h

5 CDT forecast. This difference in occurrences in Chicago's plume travelling northward in the

6 25-48 hr forecast may lead to the higher O_3 biases for that forecast.

7   CMAQ developmental model biases were also determined for the Kenosha site for

8 ozone along with NO_2, SO_2 and formaldehyde (Figure 14). Ozone was overpredicted in the

9 model for this shoreline measurement for most daylight times, with correlations lower than

10 those obtained over water ($R^2 = 0.67$ 1-24h, $R^2 = 0.58$ 25-48h). NO_2 is underpredicted during

11 daylight hours, but not of the same magnitude as the overprediction of ozone ($R^2=0.38$ 1-24h,

12 $R^2=0.30$ 25-48h). Formaldehyde is consistently underpredicted when it is measured, with

13 effectively no correlation ($R^2=0.03$ for both 1-24h and 25-48h forecasts). Gaps in formaldehyde

14 bias are from gaps in formaldehyde data at the Kenosha site. Bias in SO_2 show little trend with

15 respect to time of day and little correlation ($R^2=0.16$ 1-24h, $R^2=0.18$ 25-48h).

16   The mid-afternoon O_3 (20:00 UTC) was also determined for all EPA station monitors

17 in the region (Figure 15). The *Lake Express* ferry data were also used to obtain the bias at a

18 similar time (12:30-15:00 h CDT transect), shown in squares in Figure 15. Note that there is an

19 upwind bias in central in western Wisconsin of ~7-8ppb and jgh biases are observed at some

20 locations near Chicago and the northern Indiana region. The high biases seen over Lake

21 Michigan don't appear to extend too strongly inland.

22   Others have also found the CMAQ to predict ozone mixing ratios that were biased high

23 (Eder et al., 2009; Tang et al., 2009; Zhang et al., 2012a, b; Wilczak et al., 2006). Simon et al.

24 (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

20

adjusting model parameters related to emission sources, localized shoreline meteorology, or atmospheric chemistry.

Acknowledgements

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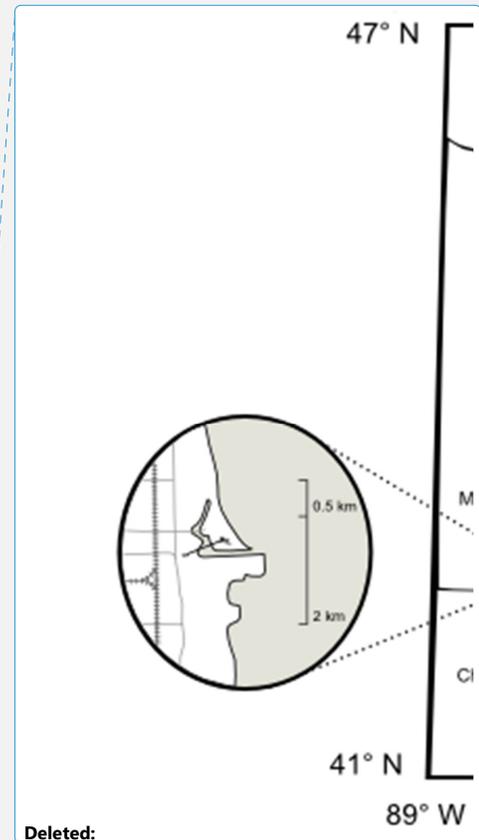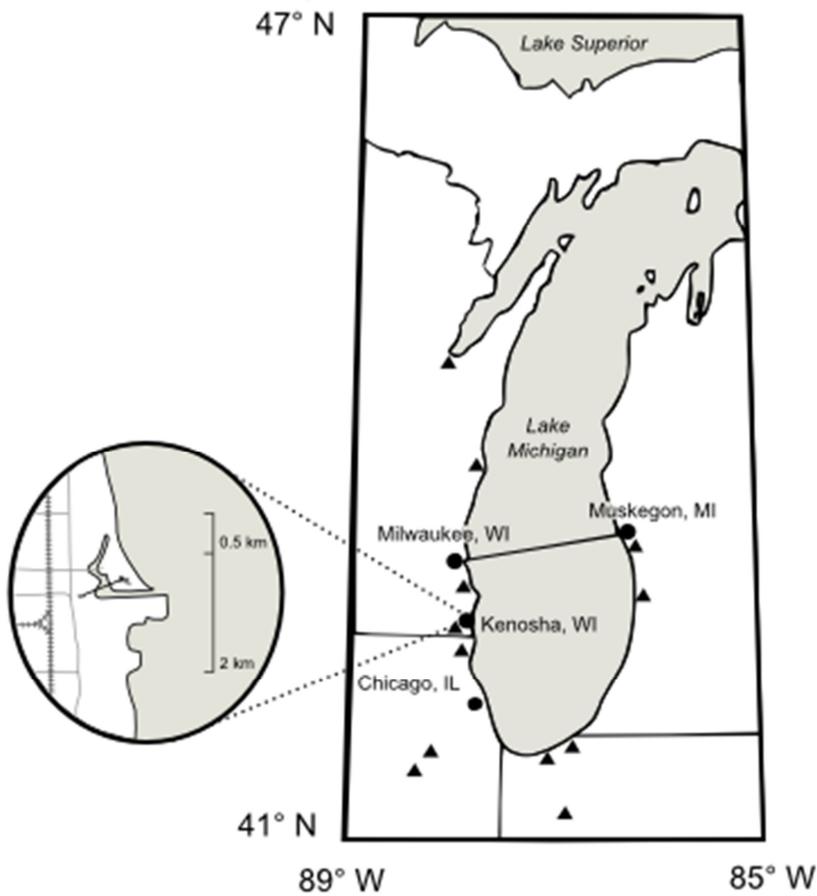
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2 **Figure 1**: Map of experiment. Path of ferry from Milwaukee, Wisconsin to Muskegon,
3 Michigan is shown with black line across the lake in the map. The DOAS instrument was placed
4 at the Kenosha, Wisconsin harbor with the beam path shown (inset)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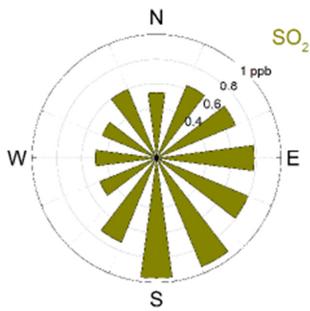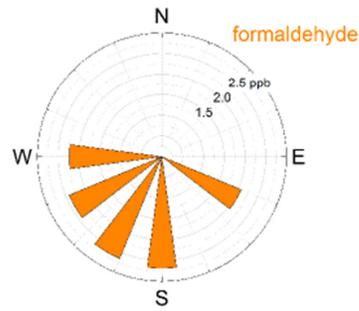6 triangles.

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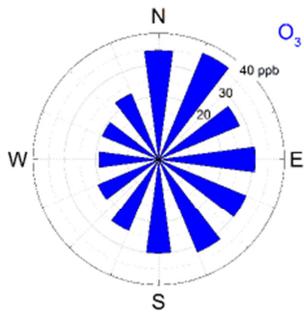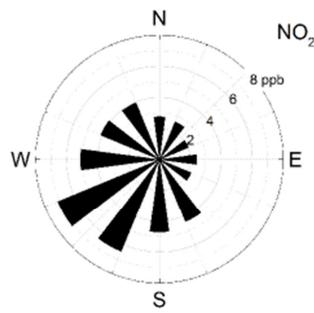
Figure 2. Wind rose depictions of median mixing ratio of a) O_3 b) NO_2 c) SO_2 and d) formaldehyde with respect to wind direction as measured by DOAS at Kenosha harbor from April-November of 2009. Medians are not reported for wind directions where few measurements (n<75 for 30 minute averaged data points)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

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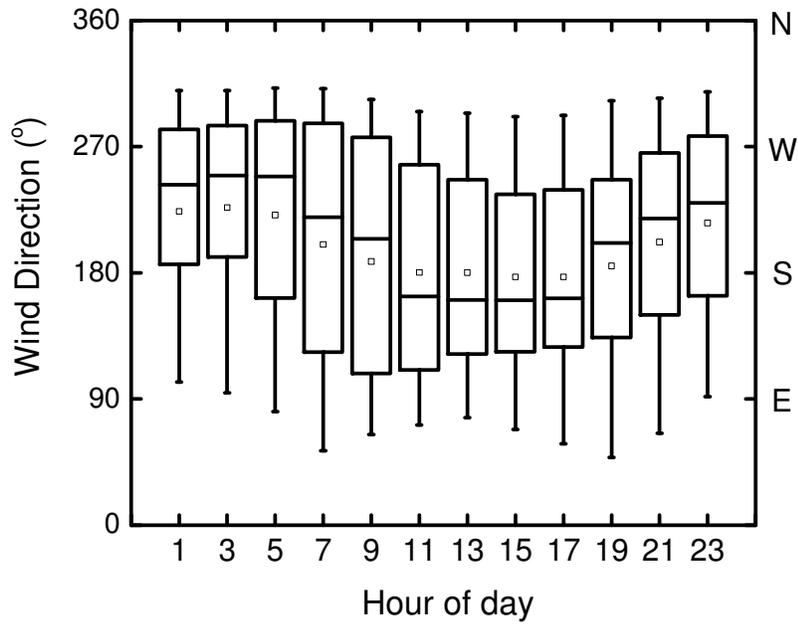
Figure 3: Wind direction as a function of time of day as measured at Kenosha harbor from April-November of 2009. Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers).

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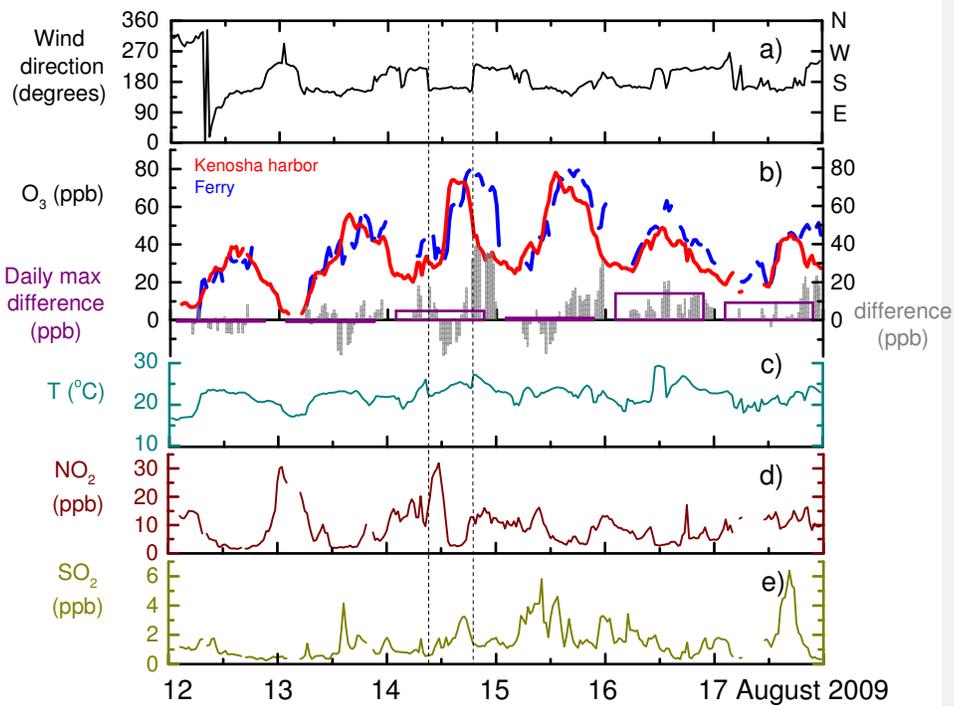
Figure 4: Example period of observations from Aug. 12, 2009 to Aug. 18, 2009 a) wind direction at Kenosha Harbor site, b) concurrent O_3 observations from Kenosha Harbor and *Lake Express* in transit, their 30 minute average O_3 (Ferry) - O_3 (Kenosha Harbor) difference and daily max difference c) temperature at Kenosha Harbor in Celsius d) NO_2 observations from Kenosha Harbor and e) SO_2 observations from Kenosha Harbor.
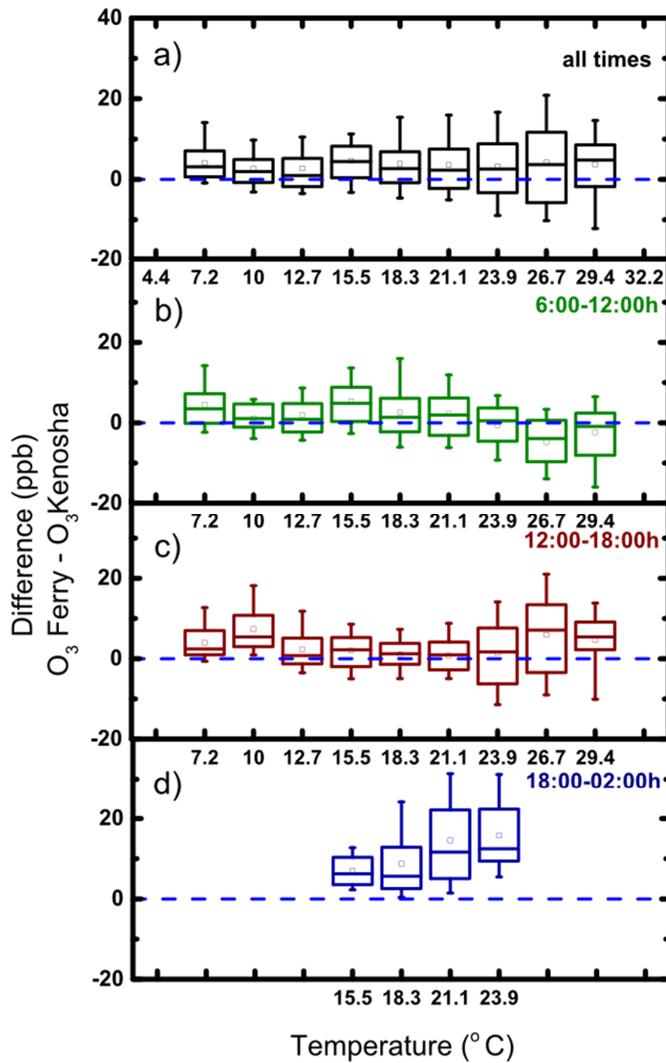
Figure 5: Difference in O_3 observations between platforms with respect to temperature (°C) measured at the shoreline for a) all times, b) morning (06:00-12:00h CDT), c) early afternoon (12:00-16:00h CDT) and d) late afternoon/evening (16:00-02:00h). Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box represents a minimum of 15 points.

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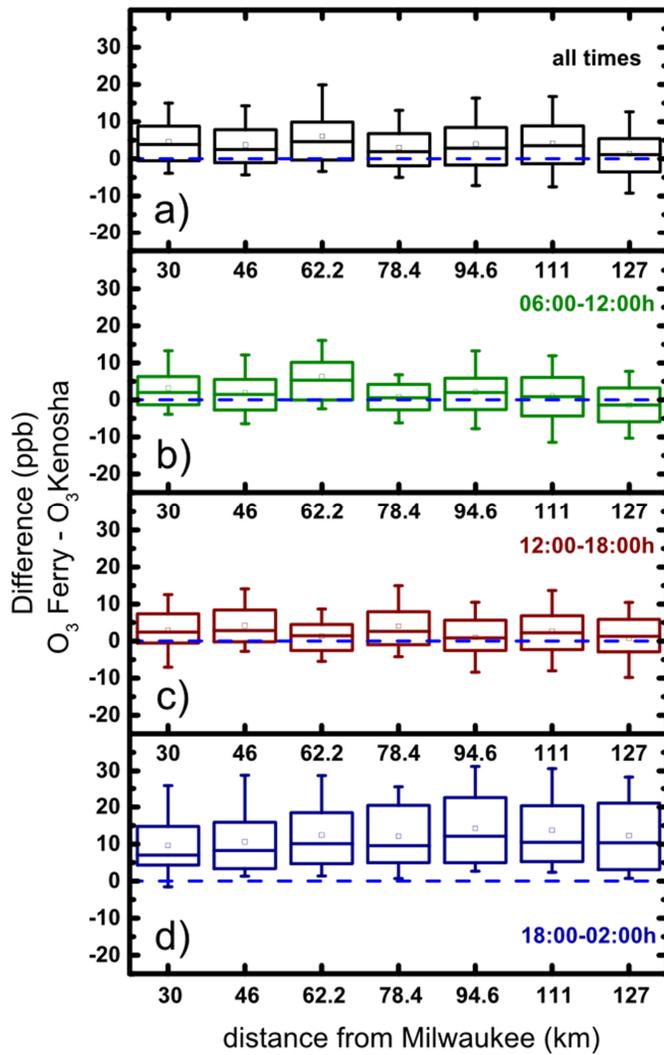
**Figure 6**: Difference in O_3 observations between platforms with respect to position of the ferry as indicated by km from Milwaukee along ferry path at: a) all times, b) morning (06:00-12:00h CDT), c) early afternoon (12:00-16:00h CDT) and d) late afternoon/evening (16:00-02:00h). Box plots show mean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

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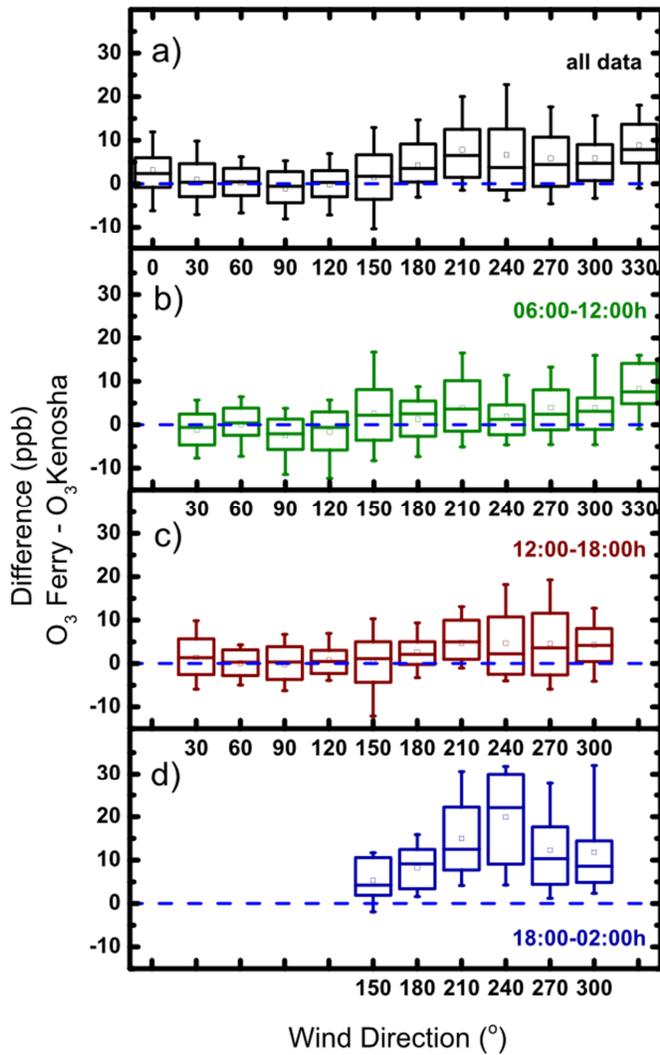
Figure 7 : Difference in O_3 observations between platforms with respect to wind direction measured at Kenosha harbor for a) all times, b) morning (06:00-12:00h CDT), c) early afternoon (12:00-16:00h CDT) and d) late afternoon/evening (16:00-02:00h). Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box represents a minimum of 15 points.
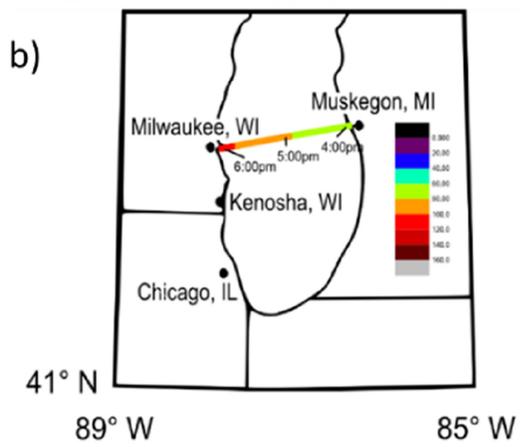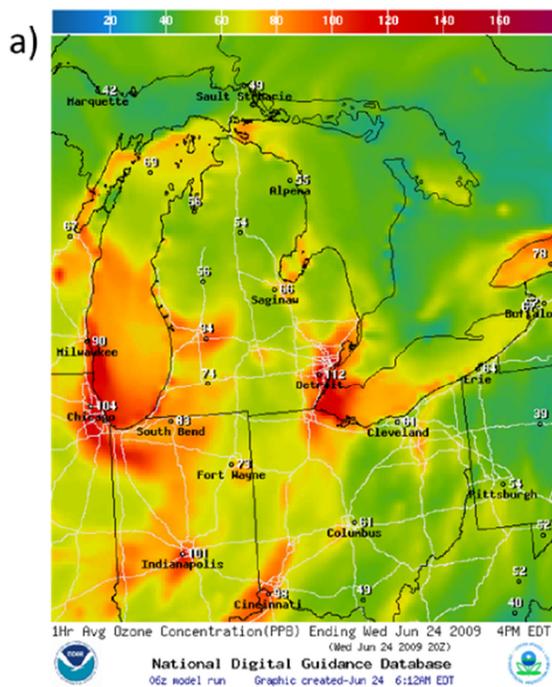
Figure 8: a) Sample image of National Air Quality Forecast Model (NAQFM) during the campaign period, b) O_3 measurements for one ferry trip on June 24, 2009 where the ferry was in transit from 3:50 pm (CDT) to 6:15 pm (CDT).

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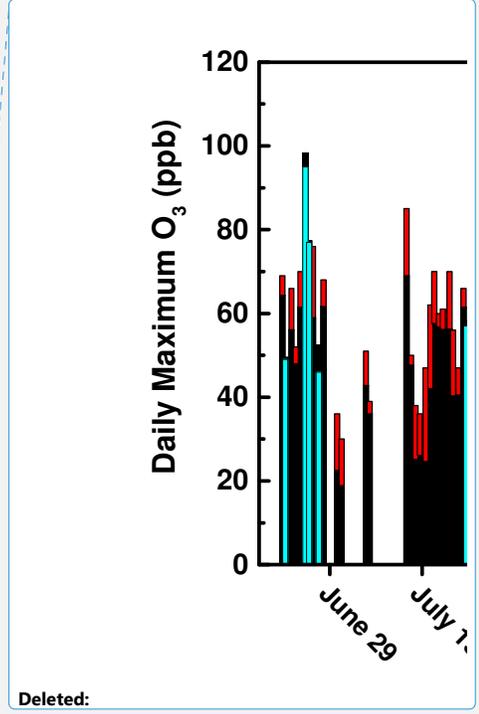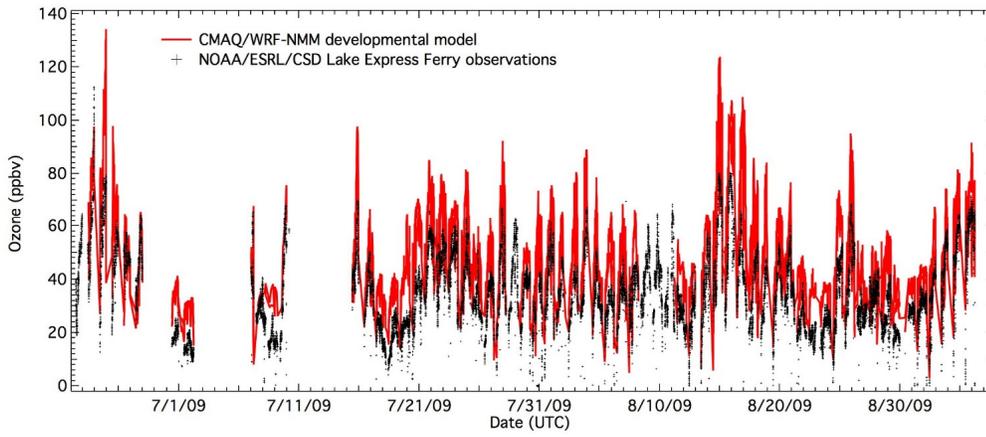
Figure 9: Graph of all CMAQ model forecast ozone mixing ratios in red with *Lake Express*
Ferry observations in black from 2009.

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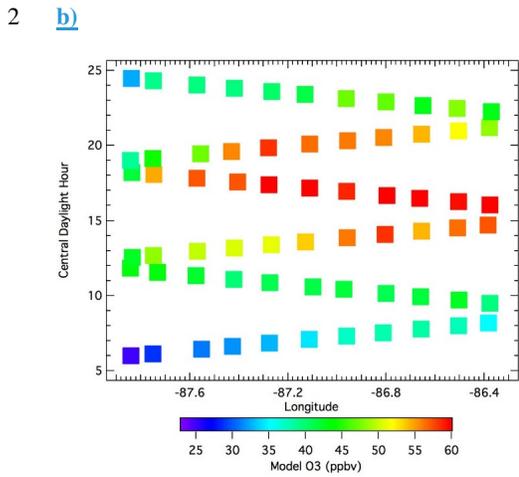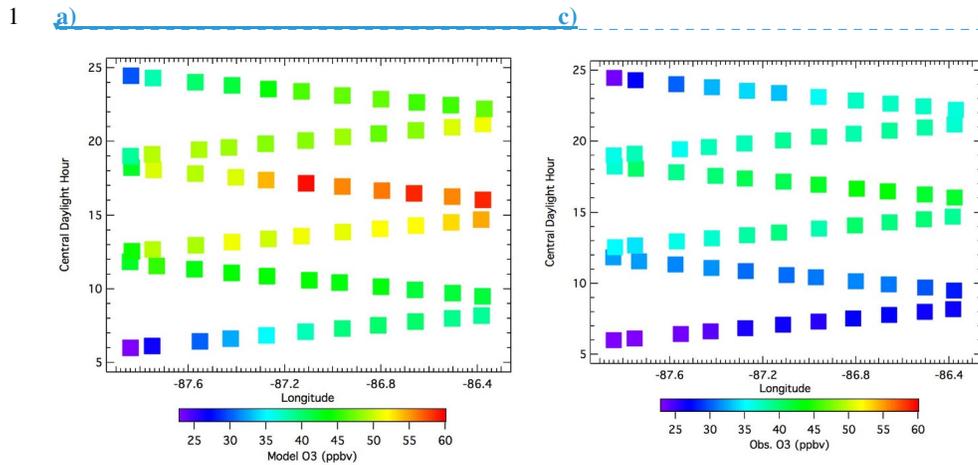
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Deleted: Oct. 29, 2009 with NAQFM forecast daily maximum ozone at the matched ferry location. Stacked bars indicate the extent of the over-prediction (red) or under-prediction (blue).
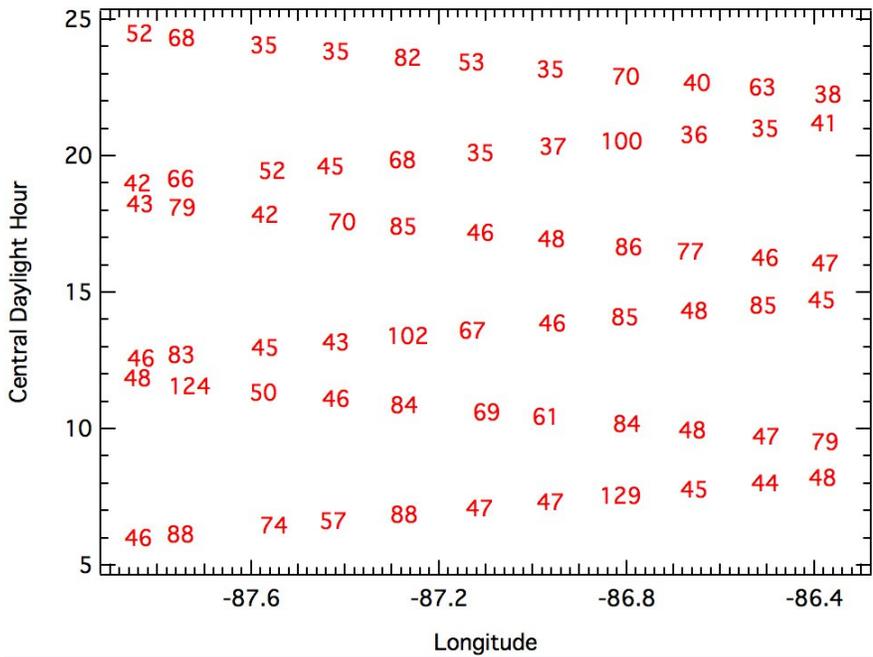
Figure 10: Statistical data for CMAQ model and ferry measurement comparison. Each model grid value and observation averages were binned according to model west-east grid number and CDT time of the ferry transect. The 1-min O_3 observations were averaged over model grid and hourly output. The numbers here are the number of hourly comparisons between model grid values and hourly averaged O_3 observations via ferry.

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1   a)   c)

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12   **Figure 11**: Median O$_3$ from a) 1-24hr CMAQ forecasts b) 25-48 CMAQ forecasts and c) ferry
13   observations.

14

Deleted: Figure 10: 8-hour average ozone concentrations as measured by the ferry between 10:00-18:00h CDT for a) 2008, b) 2009, and c) 2010. For 2009 (b), the shoreline Kenosha harbor and NAQFM forecast 8-hour average ozone concentrations are also given. ¶
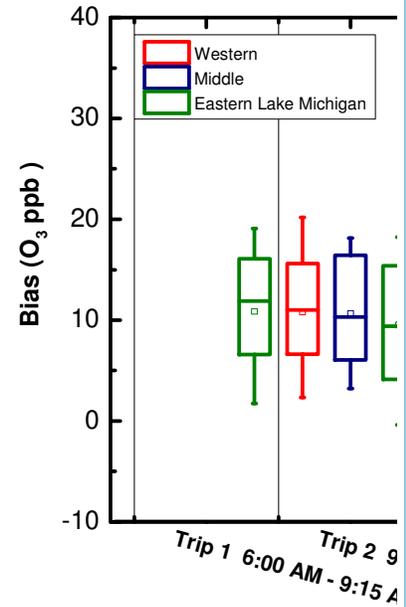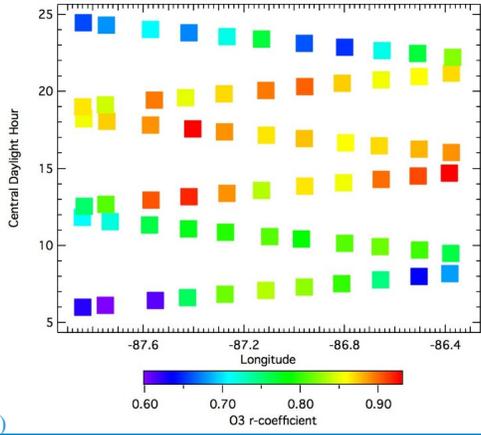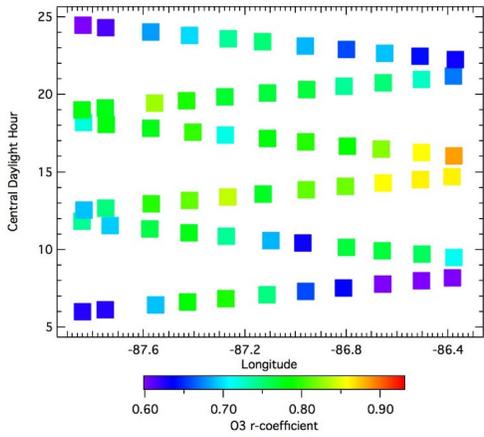-------------------------------Page Break-------------------------------

Figure 11: Bias in NAQFM ozone forecast compared to ferry measurement spatially matched to location of the ship with respect to time of day. The bias per trip was evaluated by selecting data only when the ferry trip was occurring in the typical trip time window given. The bias was evaluated for 3 regions of Lake Michigan: western Lake Michigan, ferry longitude > 87.3° W, middle Lake Michigan, ferry longitude between 87.3° W and 86.7° W, and eastern Lake Michigan, ferry longitude < 86.7 ° W. Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box plot represents a minimum of 47 data points.¶   ... [3]

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2 b)

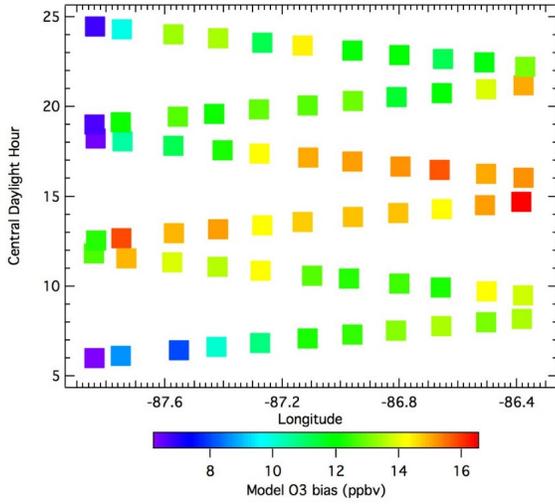
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4 **Figure 12**: Correlation coefficients for model-measurement comparison for each bin a) 1-24h
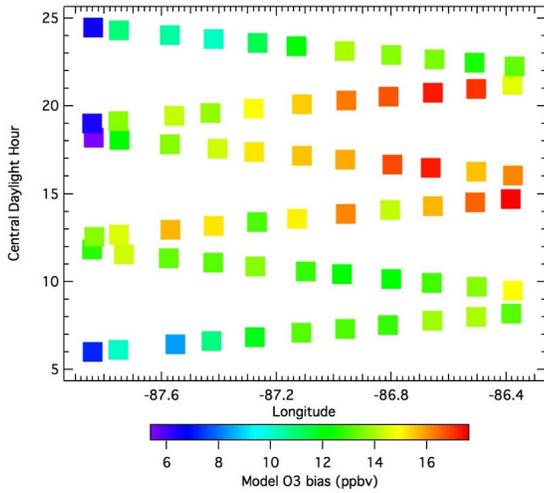
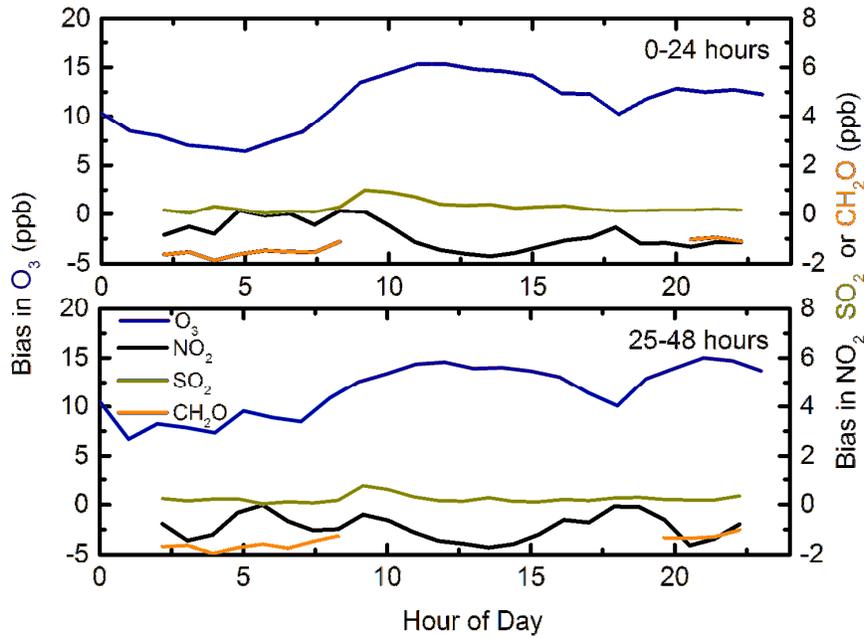5 forecast b) 25-48h forecast

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1   **a)**

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3   **b)**

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5   **Figure 13**: CMAQ model bias from a) 1-24h forecast and b) 25-48h forecast
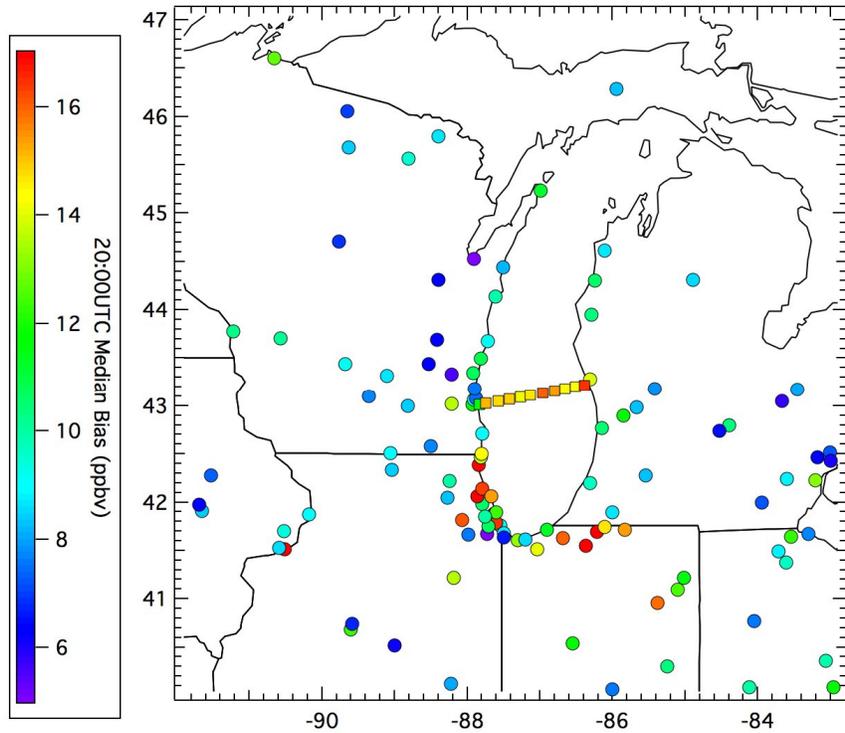
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Figure 14: CMAQ model bias at Kenosha for O_3 (in blue, left axis), NO_2 (black), SO_2 (brown),
or formaldehyde (orange) (right axis) for a) 1-24h forecast and b) 25-48 h forecast.

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2 **Figure 15**: CMAQ model O$_3$ bias for air quality EPA station monitors (circles) and *Lake*

3 *Express* ferry (boxes). EPA monitor biases are calculated at 20:00 UTC (3:00pm CDT), and

4 the data has been windowed for only those days when *Lake Express* ferry

5 data is available. For the *Lake Express* ferry data are from the 12:30 to 3:00 pm (CDT)

6 transect statistics.

7

at the eastern side of Lake Michigan in the afternoon may indicate insufficient ozone loss mechanisms in the forecast model, production of ozone extending farther away from emissions sources, or boundary layer or other meteorological confinement of the air mass properties that are not symmetric across the lake.

The model bias was also evaluated with respect to month for the 3 regions (Figure 12). The only two months which showed most significant differences in model bias with respect to ferry position were June and October. In June, the bias in the middle of Lake Michigan was higher than the western or eastern sides of Lake Michigan (which is observed in the 90th percentile, 75th percentile, median, mean and 25th percentile, 10th percentile). A similar trend was observed in July (as observed in 75th percentile, median, mean, 25th percentile and 10th percentile) and August (as observed in the 90th percentile, 75th percentile, median, mean and 25th percentile). The bias in the middle of Lake Michigan was smaller than the eastern and western sides for October (as seen in the 75th percentile, median, mean, and 25th percentile). A possible cause of this variation in bias is change in the strength of the lake-breeze effect and inversion meteorology between June (lake colder than overland air) and October (lake warmer than overland air). Also, O_3 production is limited in October and 8-hour average concentrations were around 30 ppb, so these differences could be attributed to the difference in chemistry (limited production versus loss mechanisms). The extent to which the parameterization of mesoscale meteorological effects or other model parameters like emissions and chemistry influence the O_3 model forecast cannot be extracted from this analysis. Without specific tests of the structure and parameterization of the NAQFM, these trends cannot be further dissected.

The time of day and position of the forecasted and observed daily maximum ozone concentrations are given in Figures 13 and 14. The data are presented as histograms that represent the number of days where the maximum ozone was located within a particular range of latitudes or within a given hour. The hour that most frequently corresponded to the maximum ozone concentration was 16:00 CDT for both the NAQFM and the ferry observations. Fewer total observations around 15:00 CDT may account for the small number of maximum ozone observations at that time because the ferry was typically in port at that time. The location of the daily maximum ozone from the ferry varies from the distribution given by the NAQFM (Fig. 14). The NAQFM predicts the highest frequency of daily maximum O_3 will most frequently be just offshore on the eastern side of Lake Michigan, whereas this was not observed by the ferry. However, the ferry may not have captured the time of maximum O_3 at the eastern side of Lake Michigan, as its typical trip began in Muskegon at 16:00 CDT.

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when evaluated with respect to ferry trip, and a complicated bias of higher over-prediction mid-lake in the spring and summer, switching to a lower over-prediction mid-lake in fall. Ferry ozone observations captured 0 exceedances in 8-hour ozone versus 2 predicted by NAQFM.

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Figure 10: 8-hour average ozone concentrations as measured by the ferry between 10:00-18:00h CDT for a) 2008, b) 2009, and c) 2010. For 2009 (b), the shoreline Kenosha harbor and NAQFM forecast 8-hour average ozone concentrations are also given.
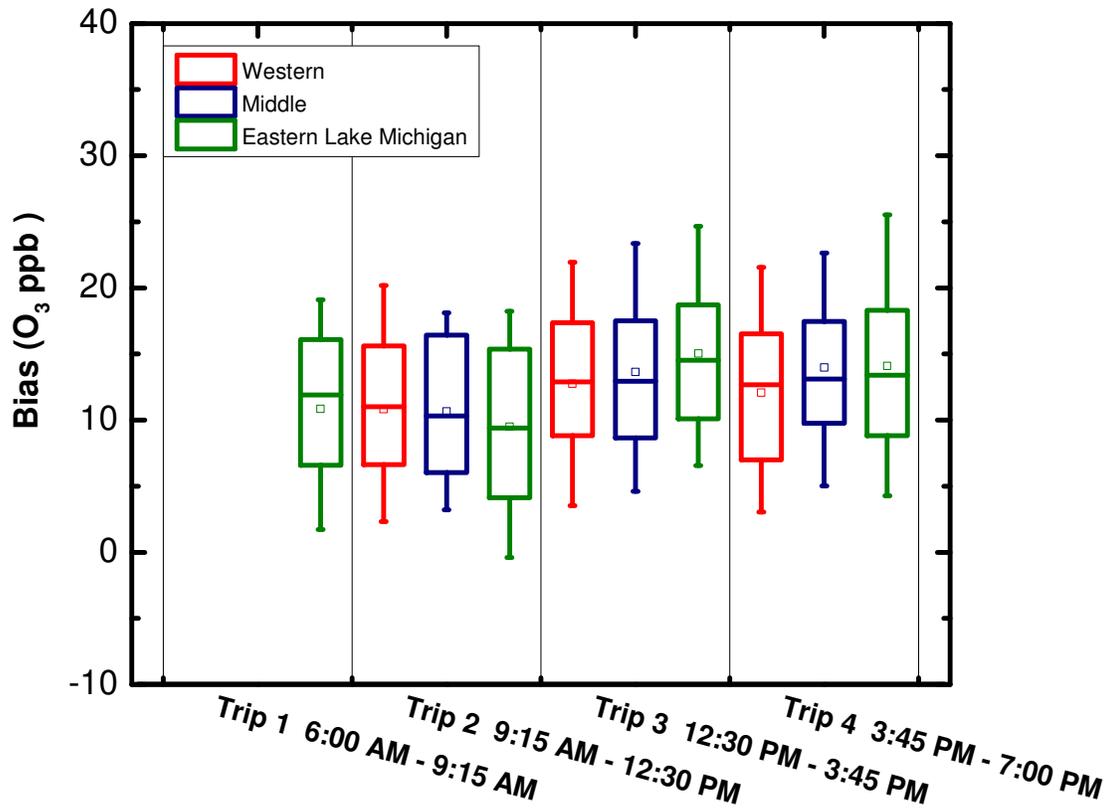
Figure 11: Bias in NAQFM ozone forecast compared to ferry measurement spatially matched to location of the ship with respect to time of day. The bias per trip was evaluated by selecting data only when the ferry trip was occurring in the typical trip time window given. The bias was evaluated for 3 regions of Lake Michigan: western Lake Michigan, ferry longitude > 87.3° W, middle Lake Michigan, ferry longitude between 87.3° W and 86.7° W, and eastern Lake Michigan, ferry longitude < 86.7 ° W. Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box plot represents a minimum of 47 data points.
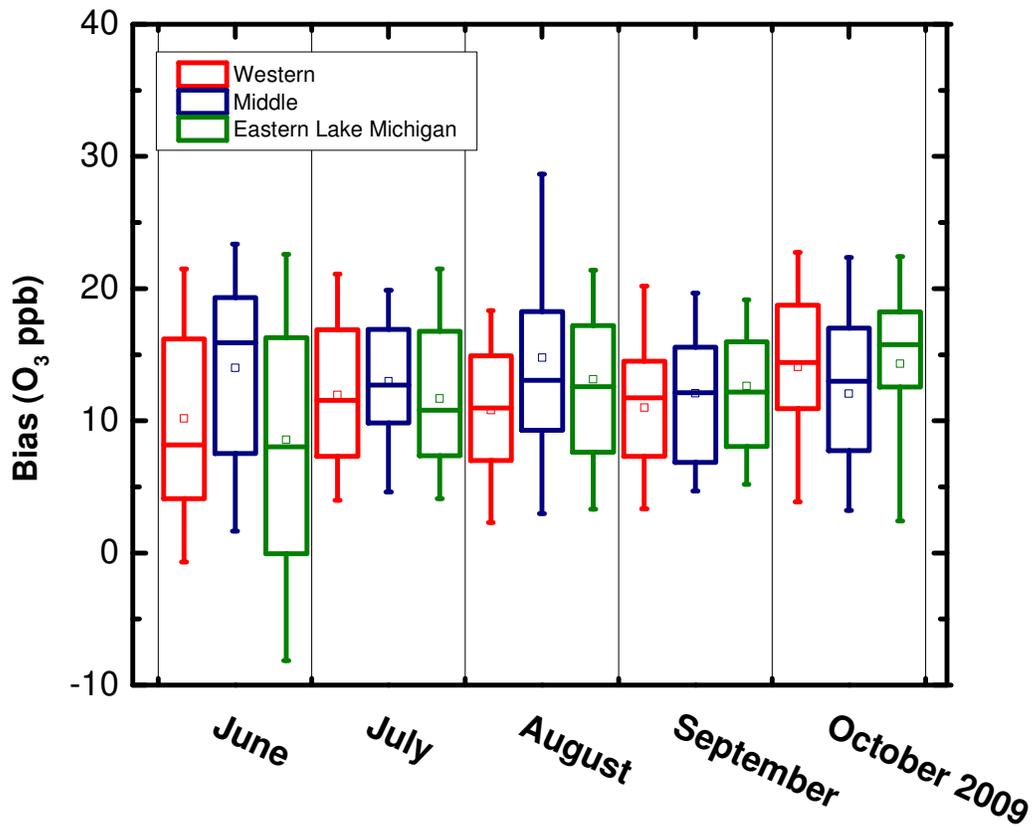
Figure 12: Bias in NAQFM ozone forecast compared to ferry measurement with respect to month. The bias was evaluated for 3 regions of Lake Michigan: western Lake Michigan, ferry longitude > 87.3° W, middle Lake Michigan, ferry longitude between 87.3° W and 86.7° W and eastern Lake Michigan, ferry longitude < 86.7 ° W. Box plots show mean (□), median (centerline), 25%-75% (box) and 10-90% (whiskers). Each box plot represents a minimum of 29 data points.
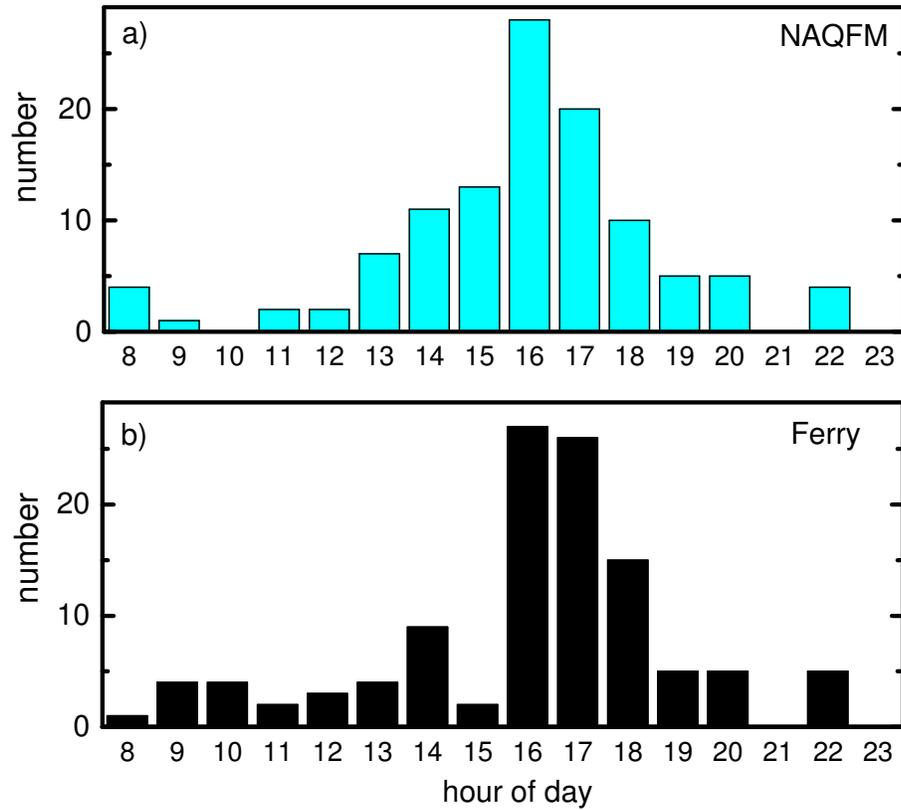
Figure 13: Time of day maximum ozone observation from a) NAQFM forecast b) ferry observations.
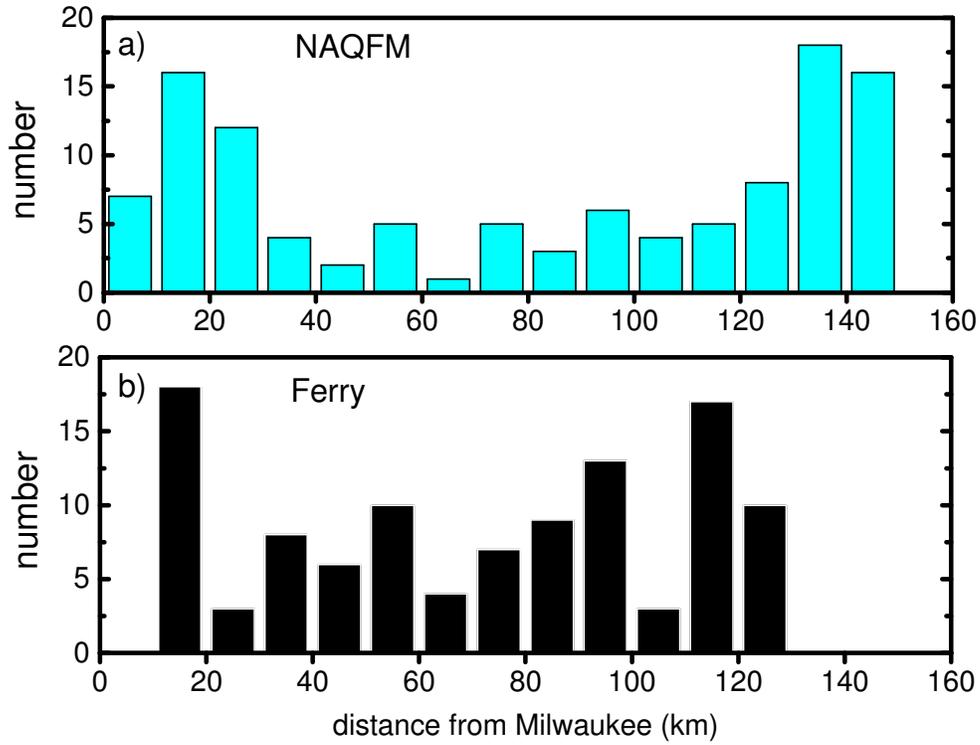
Figure 14: Location of daily maximum ozone from a) NAQFM and b) ferry observations