The Pennsylvania State University
The Graduate School
College of Earth and Mineral Sciences

BAY BREEZE IMPACT ON SURFACE OZONE
AT TWO COASTAL SITES ALONG THE CHESAPEAKE BAY FROM 1986-2010

A Thesis in
Meteorology
by
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ABSTRACT

Hourly surface meteorological measurements were coupled with U.S. Environmental Protection Agency (EPA) surface ozone (O₃) mixing ratio measurements at Hampton, Virginia and Baltimore, Maryland, two sites along the Chesapeake Bay, to determine the behavior of surface ozone during bay breeze events and quantify the importance of the bay breeze in a manner similar to Martins et al. (2012). Analyses were from the months of May through September for the years 1986 to 2010. The years were split into three groups to account for recent reductions in emissions of nitrogen oxides (NOₓ): 1986-1994, 1995-2002, and 2003-2010. Each day was marked either as a bay breeze day, a non-bay breeze day, or a rainy/cloudy day based on the meteorological data, and ozone analyses were separated likewise. Eight hour averaged surface ozone values were typically 3 to 5 ppbv higher at Hampton and Baltimore during bay breeze events compared to days without a bay breeze. Average ozone anomalies in the afternoon were highest at both sites during bay breeze days in the study period 2003-2010. In conjunction with an overall lowering of ozone levels, the percentage of total exceedances of the EPA eight hour standard of 75 ppbv of ozone during bay breeze days increased dramatically at Hampton for 2003-2010, while remaining relatively the same at Baltimore. These results suggest that bay breeze circulations are becoming more important to causing pollution events at particular sites in the region, and support the hypothesis of Martins et al. (2012) that highly localized meteorology increasingly drives air quality events at Hampton.
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Chapter 1

Introduction

Ozone (O₃)

Ozone (O₃) is a naturally occurring reactive trace gas that has many vital implications for the earth’s radiation budget, as well as life at the surface. In a column of atmosphere, approximately 90% of the total ozone is located in the stable stratosphere, a layer stretching from about 10 – 18 kilometers (km) depending on latitude to 50 km (Seinfeld and Pandis, 2006). This maximum in ozone is known colloquially as the “ozone layer.” Stratospheric ozone absorbs harmful UV-A as well as the more biologically active UV-B radiation (λ = 290-320 nanometers, nm), which damages cells and can lead to skin cancer in animals and humans. Lower-altitude stratospheric and tropospheric column ozone has also been discovered to respond to climate changes and oscillations such as ENSO (Lee et al. 2010; Hitchman and Rogal 2010; Randel and Thompson 2011; Thompson et al. 2011; Wang et al. 2011). For these reasons, atmospheric ozone is closely monitored across many different regions from the tropics (see Thompson et al., 2003) to the poles (see Environment Canada) by instruments ranging from ground-based surface and column measurements, to airplanes and balloons, to satellites (WMO, 2008). While necessary in the stratosphere to protect and sustain life, ozone produced at the surface becomes an environmental and health issue. Figure 1-1 presents a profile of the differing layers of ozone measured from a balloon-borne ozonesonde instrument.
Figure 1-1. Profile of atmospheric ozone. A profile of ozone partial pressure in milliPascals (mPa) with near surface mixing ratios in parts per billion by volume (ppbv; inset) highlighted taken by a balloon-borne ozonesonde from Hampton, Virginia on 25 June, 2010. The “ozone layer” can be seen maximizing at about 25 kilometers (km) and surface pollution is evidenced by mixing ratios beyond 75 ppbv.

Surface ozone is a United States Environmental Protection Agency (EPA) regulated pollutant that has been shown to have adverse affects on the human respiratory system and photosynthesis in vegetation, leading to crop destruction (Fishman et al., 2010 references within). The molecule is a secondary pollutant and is formed through a combination of nitrogen oxides (NO_x), volatile organic compounds (VOCs), and sunlight. Natural background mixing ratios of ozone at the surface are usually between 10 and 40 ppbv, but such mixing ratios are only found in the Arctic and pristine marine environments (Seinfeld and Pandis, 2006). The formation of ozone in the boundary layer has been shown to be dependent on several, often complex processes such
as incoming solar radiation and cloud cover, temperature, precursor compound mixing ratios, wind speed, and boundary layer height (Comrie, 1990; Sillman and Samson, 1995; Bloomer et al., 2009; Steiner et al., 2010; Banta et al., 2011). The general chemical production cycle for surface ozone pollution can be outlined in the equations:

1) \( \text{VOC} + \text{OH} \rightarrow \text{RO}_2 + \text{H}_2\text{O} \)
2) \( \text{RO}_2 + \text{NO} \rightarrow (\text{Radical or HO}_2) + \text{NO}_2 \)
3) \( \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \)
4) \( \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \)

Here, OH is the hydroxyl radical, RO\(_2\) is the alkylperoxy radical, \( \text{hv} \) represents a photon of a sufficient energy to photolyze NO\(_2\), M is any molecule that absorbs excess vibrational energy (most likely Nitrogen, \( \text{N}_2 \)), and O and \( \text{O}_2 \) are monatomic and diatomic oxygen, respectively.

Ozone pollution is formed from the oxidation of VOCs and the production of NO\(_2\). The oxidation of VOCs is important because the formation of NO\(_2\) is possible without consuming an ozone molecule in the process:

5) \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)

This is a component of the photostationary steady state where \( \text{O}_3 \) and NO\(_2\) cycle with no net ozone production (Seinfeld and Pandis, 2006).

Given surface ozone’s strong dependence on solar radiation for photochemical production, the eastern U.S. “ozone season” is typically found from the months of May to September, and is the time period when locations are most susceptible to higher ozone mixing ratios.
The Bay Breeze

A bay or sea breeze (from here on, bay breeze) is a small-scale circulation that arises from a pressure gradient that forms from the temperature contrast of air over land and water (Miller et al. 2003). This phenomenon has been widely studied and has shown to have multiple effects on coastal areas. Bay breezes can provide relief from excessively hot weather, provide convergence to breed thunderstorms, and either improve or worsen air quality in varying regions of the world (Miller et al. 2003; Lin et al. 2007; Banta et al. 2011).

During the daytime, solar radiation heats the land, and thus the air directly above the land, more quickly than a water surface and adjacent air. A hydrostatic pressure gradient results and, given weak synoptic background winds, air is forced from the water surface over the land. This motion continues as long as the temperature difference and pressure gradient exists, usually breaking down around sunset. A schematic of the typical conditions observed before and during a bay breeze event are shown in Figure 1-2.
Motivation

The meteorological conditions needed to form a bay breeze and produce ozone go hand in hand. The combination of warm conditions needed to cause a temperature gradient from land to water and intense sunlight can lead eventually to a bay breeze at coastal locations. The heat and incoming solar radiation, in the presence of high mixing ratios of ozone precursors NOx and VOCs, can produce high amounts of ozone both over land and over water. Over water, the sun’s inability to heat the surface quickly leads to lower boundary layer heights via mixing, concentrating ozone production in a smaller volume compared with over the warm land. The stagnant conditions necessary to allow a bay breeze to become the dominant circulation during the daytime also allows a buildup of ozone in the boundary layer due to lack of venting and accumulation of pollutants at the bay breeze front (Rappenglück, 2008; Banta et al. 2011; Wu et al. 2010; Loughner et al. 2011). The ozone-rich air masses over the water can then transport
pollution well inland as the bay breeze front propagates (Darby, 2005; Lin et al. 2007). Previous studies have found the bay or water-body breeze to be a mechanism through which emissions and ozone from urbanized areas are transported to more rural locations (Darby et al., 2007; White et al., 2007).

In addition to similar meteorology controlling both of these processes, the behavior of ozone over water surfaces is quite different than over land. Whereas ozone deposits readily to surfaces and vegetation over land, its deposition velocity over water ($\sim 0.07$ cm s$^{-1}$) is five to six times slower than over a terrestrial ($\sim 0.4$ cm s$^{-1}$) surface (Lenschow et al., 1981; Lenschow et al., 1982; Hauglustaine et al., 1994; Wesely and Hicks 2000). This weaker deposition velocity produces less of a flux of ozone onto the water surface where it is effectively removed from the system. Because of this, higher near-surface ozone mixing ratios may accumulate over the water than over an adjacent land area. In addition to the reduced deposition of ozone, minimal nighttime oxidation over the emission-lacking water surface will also lessen O$_3$ loss, leading to frequently higher ozone observations over a water body (Mao et al. 2006).

Participation in two recent projects examined these effects and provided the motivation for a long term historical analysis of bay breezes and ozone. During the Chemistry of the Atmospheric Boundary Layer Experiment (CAPABLE; http://capable.larc.nasa.gov/) project in July 2010 in Hampton, Virginia ($37.07^\circ$, -76.36$^\circ$) near the mouth of the Chesapeake Bay, we observed several instances of bay breezes, with some of them leading to elevated ozone and violations of the EPA eight hour ozone mixing ratio standard of 75 ppbv. This standard is what locations in the U.S. are held to by the National Ambient Air Quality Standard (NAAQS; U.S. EPA). The only two violations of the NAAQS at Hampton in July 2010 occurred on bay breeze days (Martins et al. 2012), when ozone was found to spike just after the passage of the bay breeze front. These observations imply that there may be an increasing role for highly localized meteorology events in air quality violations.
The Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ; http://nasa.gov/discover-aq) project is a multiyear campaign to capture surface variability of air quality measurements with total column observations for satellite applications. Both DISCOVER-AQ and CAPABLE projects were designed to improve satellite retrievals of trace gases for NASA's upcoming Geostationary Coastal and Pollution Events (GEO-CAPE; http://geo-cape.larc.nasa.gov/) satellite mission. The summer 2011 deployment that was located in the Baltimore-Washington metropolitan area included several ground sites that were susceptible to bay breeze meteorology.

With recent deployments in part looking to characterize the impact of these small scale circulations on surface ozone, a broader look at the phenomena of ozone and bay breeze meteorology is warranted. Previous work has focused on regions such as New England, the Houston metropolitan area, and even the western Pacific. The focus here is on the Mid-Atlantic U.S., near the locations of the CAPABLE and DISCOVER-AQ field campaigns.

In this study, a climatological analysis of surface ozone on bay breeze days is performed, attempting to answer the question raised by Martins et al. (2012), whether days that exhibit a bay breeze correspond to a larger anomaly in surface ozone and a growing portion of total NAAQS violations at a given location. This is the first time a combined analysis of the Chesapeake Bay breeze and surface ozone data has been performed on time scales of this magnitude. The analysis is performed using meteorological data and surface ozone at Hampton, Virginia and Baltimore, Maryland, two sites near the Chesapeake Bay.
Chapter 2

Methodology

In order to perform this study of potential health impacts from O$_3$ during bay breeze events, co-located meteorological and ozone measurements with sufficient historical records were sought. Several coastal Chesapeake Bay locations were identified where hourly surface meteorological measurements and data from a co-located EPA ozone monitoring station were available.

Candidates for Study

To test the hypothesis that bay breeze days represent a growing portion of total exceedances at a location, a climatological analysis of bay breezes and surface ozone is conducted. While studies of Chesapeake Bay breeze climatology have been performed before (e.g. Sikora and Young, 2010), the results have never been combined with air quality data. The area of focus will be locations near the campaign study areas of CAPABLE and DISCOVER-AQ, at coastal locations along the Chesapeake Bay. This region was chosen because the 2010 and 2011 studies provided motivation for a broader, long term study into air quality during bay breeze events.

The airport at Aberdeen Proving Ground (KAPG) and Baltimore-Martin State Airport (KMTN) were both in consideration for analyses, but the spotty reporting of hourly meteorological variables made the data insufficient for characterizing bay breeze events.
Longstanding records of both ozone and meteorological variables were found at Hampton, Virginia (KLFI; 1981-present) and Baltimore, Maryland (KBWI; 1981-present) and these were chosen for bay breeze analysis. All sites considered in this study are presented in Figure 2-1.

Figure 2-1. Chesapeake Bay region and study candidates. Airport codes are listed for each hourly meteorological site deemed a candidate for climatological bay breeze analysis with those used in this study in red. Ozone monitoring locations considered for analysis are marked with red dots. The two monitors used in the study here are connected to their respective airport location.
Baltimore is the largest city in Maryland with a population of over 600,000 residents, and is located within and affected by pollution emissions from the Baltimore-Washington Metropolitan Area, a region with nearly 9 million people. Hampton, Virginia is a moderately urbanized area with population near 150,000, located within the “Hampton Roads” region of southeastern Virginia with 1 million residents. The differences in total population both in the cities proper and regionally affect the total anthropogenic NOx emissions, which aid in ozone formation. The Baltimore Non-Attainment Area (NAA) emitted an estimated 100,000 metric tons of NOx for the year 2005, while the Hampton Roads region produced approximately 65,000 metric tons of NOx for the same year (Region 3 Ozone Plan Summary; via http://yosemite.epa.gov/). These differences must be taken into account when analyzing and comparing surface ozone mixing ratios at each location.

**Identifying Bay Breezes**

To tell if a particular day exhibited a bay breeze, hourly surface meteorological measurements were analyzed from the two Chesapeake coastal stations, Hampton, Virginia and Baltimore, Maryland. A higher resolution map of each site is shown in Figure 2.2, along with what are defined as “onshore” and “offshore” wind directions. A station located inland, enough so as to be unaffected by the bay breeze, was picked for both sites as an additional reference in determining bay breeze days. These sites are Richmond International Airport (KRIC; for Hampton, VA) and International Airport at Dulles (KIAD; for Baltimore, MD). Table 2.1 shows
all meteorological Automated Surface Observing Systems (ASOS) and gives their International Civil Aviation Organization (ICAO) airport codes.

Figure 2-2. Close-up map of coastal sites with bay breeze wind directions. Defined wind directions for each site with onshore directions in red and offshore directions in black. Arrows show examples of flow for offshore and onshore directions with wind degree cutoffs labeled on dashed lines. Wind directions are reported to the nearest 10 degrees.
Hourly surface ozone data (EPA RSIG; http://badger.epa.gov/rsig/rsigserver) from the EPA monitor locations were available to 1981 at all sites studied; however a climatological analysis from 1986-2010 will be performed for reasons discussed below. Ozone and meteorological data from this period were analyzed. The EPA sites used for this analysis along with their Federal Information Processing Standard (FIPS) codes, which identifies the specific instrument site in the cases of more than one station per city, are shown in Table 2-2. The Hampton, VA ozone monitor was moved 10 km NE in 2009 and 1 km N again in 2010 for the CAPABLE field project, but these movements are not considered to have had an effect on the measured ozone values during bay breeze days. Study periods from each year were limited to May-September for this paper, when the sun provides sufficient radiation for photochemical production of ozone.

Table 2-1. Airport ASOS Locations. (Sites used in this study for determination of bay breeze and day type)

<table>
<thead>
<tr>
<th>Hourly ASOS Station</th>
<th>ICAO Code</th>
<th>Latitude($)</th>
<th>Longitude($)</th>
<th>Elevation (m)</th>
<th>Dist. Inland (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bait. Wash. Intl Airport</td>
<td>KBWI</td>
<td>39.18</td>
<td>-76.67</td>
<td>44.5</td>
<td>13</td>
</tr>
<tr>
<td>Dulles Intl Airport</td>
<td>KIAD</td>
<td>38.95</td>
<td>-77.46</td>
<td>95.0</td>
<td>85</td>
</tr>
<tr>
<td>Langley Air Force Base</td>
<td>KLFI</td>
<td>37.08</td>
<td>-76.36</td>
<td>3.4</td>
<td>6</td>
</tr>
<tr>
<td>Richmond Intl Airport</td>
<td>KRIC</td>
<td>37.51</td>
<td>-77.32</td>
<td>50.9</td>
<td>94</td>
</tr>
</tbody>
</table>

The determination of a bay breeze day depended on several criteria and checks, all of which must be satisfied in this study. The criteria were adapted from Sikora and Young (2010), who performed a climatological analysis of the Chesapeake Bay breeze at airport locations from 2001-2005. If all criteria were not met, the day was either grouped with “non-bay breeze” or “rainy/cloudy” days.
Rainy/cloudy days were separated from the non-bay breeze days to provide the best comparison with bay breeze days. Inclusion of rainy or cloudy days in the comparison would have led to a low ozone bias in the non-bay breeze days. Cloud cover greatly reduces the photochemical production of ozone, lowering mixing ratios. Additionally, rainfall will quickly wash out many pollutants including ozone through wet deposition. The goal of separating days into these three day types was to have the occurrence of a bay breeze circulation be the only discernable meteorological difference between non-bay breeze and bay breeze days.

The general method for picking each day type at both sites is outlined in Figure 2.3. For each day, the daytime (09 to 16 EST) wind directions were evaluated (Figure 2.3a). If the hourly wind direction measurement changed from either offshore (160° to 360° at KLFI; 190° to 50° at KBWI), calm, or light and variable, to onshore (10° to 150° at KLFI; 60° to 180° at KBWI) for two or more consecutive hours during the period, the next step was evaluated. If this wind shift to onshore directions did not occur (b), then the day was either marked “non-bay breeze,” without cloudy skies or rain, or “rainy/cloudy.” The latter category meant average daytime skies were greater than “broken” with 7/8 or more cloud fraction, or there was measurable rainfall during daytime. If the winds shifted to onshore during the day, the daytime cloud cover and rainfall were checked (c). If skies were less than broken and there was no measureable rainfall during the day, then the final check is performed (e). If an average of broken skies or rainfall was recorded with the bay breeze direction wind shift, radar and surface charts were manually analyzed (d; UCAR; Plymouth State). Days that exhibit bay breezes can often breed localized thunderstorm activity, so a closer inspection is warranted when rainfall is measured. If there was no evidence of a large-scale circulation causing the wind shift to onshore directions, then the final check for a bay breeze day could be evaluated, otherwise the day was placed in the “rainy/cloudy” day type. For the final criterion, the corresponding wind direction and speed were checked at the respective inland surface station (e; KRIC for Hampton; KIAD for Baltimore). This check was performed to
attempt to eliminate the possibility of synoptic winds that would be observed by both stations, indicating a larger-scale effect. If the corresponding inland wind directions were not from the same onshore wind directions for two or more hours or wind speeds were less than 3 ms\(^{-1}\) from any direction, then the day was grouped with “bay breeze” days. If the winds were from the same onshore directions at 3 ms\(^{-1}\) or more, the day was placed with “non-bay breeze” days. The 3 ms\(^{-1}\) speed was chosen to offset the chance that inland wind directions are random or light and variable during the day but still record hours of onshore wind directions, which is a much less likely coincidence at higher wind speeds.

![Bay Breeze criteria flow chart](image)

Figure 2-3. Bay Breeze criteria flow chart. Criteria checks begin at a) and continue as shown until a day type is determined. Full explanations for each criteria check are described in the text.

All available days from May through September, for the years 1986-2010 were placed into one of the three day types illustrated in Figure 2-3. These day types will be used to separate and analyze the behavior of surface ozone for each group of days.
Table 2-2. EPA Ozone Monitoring Sites. (Sites used in this study for analysis of surface ozone by day type)

<table>
<thead>
<tr>
<th>EPA Ozone Monitoring Site</th>
<th>FIPS Code</th>
<th>Latitude(°)</th>
<th>Longitude(°)</th>
<th>Dates Active</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baltimore, MD</td>
<td>240030014</td>
<td>38.9025</td>
<td>-76.6531</td>
<td>1981-Present</td>
</tr>
<tr>
<td>Hampton, VA</td>
<td>516500004</td>
<td>37.0033</td>
<td>-76.3992</td>
<td>1981-2008</td>
</tr>
<tr>
<td>Hampton, VA</td>
<td>517000013</td>
<td>37.0998</td>
<td>-76.4811</td>
<td>2009</td>
</tr>
<tr>
<td>Hampton, VA</td>
<td>516500008</td>
<td>37.1037</td>
<td>-76.3870</td>
<td>2010-Present</td>
</tr>
</tbody>
</table>

**O_3** Measurements

The surface ozone monitors used in this study all followed the Federal Reference Method (FRM) for measuring ambient ozone (Ray, 1986), up until the adoption of a Federal Equivalent Method (FEM) of ultra-violet absorption that is widely used today. The earlier FRM measurement technique involved a chemiluminescent reaction between O_3 gas and ethylene glycol solutions. The reaction produces photons which are then measured by a photo-multiplier tube (PMT) and converted into an ozone mixing ratio. This FRM method was implemented at the Hampton site and several others in the region by 1986 (personal communication, Szykman), thus 1986 is the start of the analyses for this thesis. The FEM measurement technique is now more widespread in use and is the current method utilized at the stations considered in this study.

The current FEM directs a beam of UV light (λ = 254 nm) through a gas sample. This wavelength of light is strongly absorbed by ozone, so the measurement is based on the Beer-Lambert Law, where ozone mixing ratio is directly related to the amount of light absorbed through:
Here, $I$ is the measured intensity of the UV light, $I_o$ is the reference UV intensity, $K$ is the molecular absorption coefficient (308 cm$^{-1}$), $L$ is the length of the sample gas cell, and $C$ is the ozone mixing ratio in parts per million by volume (ppmv; Thermo Electron Corporation).

The ozone monitors at both sites must pass routine bi-weekly quality checks as well as quarterly audits against an ozone mixing ratio standard to ensure the instruments are working within acceptable limits (Hains, 2012; VA-Department of Environmental Quality, http://www.deq.state.va.us/airquality/). The UV-photometry method and instruments are quite robust, with typical measurement uncertainties below 3% (Parrish and Fehsenfeld, 2000).

**Early 2000s NO$_x$ Reductions**

With such a large historical record of ozone data it is necessary to split the dataset into periods because of regulations of NO$_x$ emissions from power plants, a precursor for ozone production, implemented in the early 2000s. Levels of NO$_x$ across the United States dropped and ozone levels responded in kind (Kim et al., 2006). Frost et al. (2006) also found that by 2003, NO$_x$ emissions from 53 eastern U.S. power plants had been reduced by 50% from 1999 levels. For these reasons, 2002 is often used as a cut off between previous years and the current “low-NO$_x$” regime when analyzing historical ozone records (i.e. Bloomer et al. 2009). The ozone dataset is then split into three roughly equal length periods: 1986-1994, 1995-2002, and 2003-2010. While the NO$_x$ emissions from year to year within each period are not exactly constant,
this method of splitting the data ensures that ozone measurements within each period are comparable and can be analyzed together.

The effects of the transition in NO\textsubscript{x} regimes on surface ozone can be seen in Figure 2.4. The total number of exceedances in the most recent study period at Baltimore and Hampton decreased dramatically from the period before 2003. For uniformity, exceedance in this paper is defined by the current EPA definition of greater than 75 ppbv for an eight hour average.

Figure 2-4. Exceedances by Year. Total number of exceedances of the eight hour EPA standard of 75 ppbv from May through September for each year from 1986-2010. A vertical dashed line separates 2002 and 2003, the cutoff for the most recent study period, and the effect on the number of exceedances is readily seen owing to reductions in NO\textsubscript{x} emissions.
Chapter 3

Results

Day Type Meteorology

As mentioned, a goal of the bay breeze day identification process was to have the occurrence of the bay breeze be the only discernable meteorological difference versus the non-bay breeze days. Following analyses by Camalier et al. (2007), who determined that maximum daily temperature and average midday relative humidity were the two dominant meteorological variables controlling surface ozone variability in the Mid-Atlantic U.S., a statistical analysis was performed on the hourly meteorological measurements at both sites to evaluate differences between bay breeze days and non-bay breeze days. Along with maximum daily temperature and midday (10-16 EST) relative humidity, average daytime (06-18 EST) cloud cover was added to assess possible differences in incoming solar radiation for each day type. Statistical significance was determined from the 95% confidence interval acquired from a statistical bootstrap method (Efron 1979; Efron and Tibshirani, 1993). Bootstrapping is a method of resampling an observational dataset. The algorithm randomly picks data points from the original data to obtain a distribution of the same size. The mean is then calculated for each of the 10,000 performed “bootstraps,” with the distribution of means representing uncertainty in the observed average. The results of this process are shown in Table 3-1.

The only variable that showed a statistically significant difference was the average midday relative humidity at the Baltimore site. Camalier et al. (2007) estimated less than a 1%
decrease in surface $O_3$ per 1% increase in relative humidity, whereas surface $O_3$ was found to increase by approximately 4% per 1°C increase in maximum temperature. With a small statistical difference in relative humidity between bay breeze days and non-bay breeze days at Baltimore, the impact on surface ozone mixing ratios amongst the day types is expected to be minimal.

Table 3-1. Meteorological data by day type. (Pertinent meteorological variables averaged and separated into day type and checked for statistical significance. Cloud cover is converted from reported oktas to percentages.)

<table>
<thead>
<tr>
<th></th>
<th>Max Temperature (°C)</th>
<th>Cloud Cover (%)</th>
<th>Daytime RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLFI (Hampton, VA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bay Breeze</td>
<td>28.7</td>
<td>44.5</td>
<td>56.3</td>
</tr>
<tr>
<td>Non-Bay Breeze</td>
<td>28.3</td>
<td>46.9</td>
<td>56.1</td>
</tr>
<tr>
<td>Statistically Significant? NO NO NO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBWI (Baltimore, MD)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bay Breeze</td>
<td>28.9</td>
<td>50.0</td>
<td>49.3</td>
</tr>
<tr>
<td>Non-Bay Breeze</td>
<td>28.7</td>
<td>50.2</td>
<td>47.4</td>
</tr>
<tr>
<td>Statistically Significant? NO NO YES</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Day Type Ozone

The density distribution of all maximum one hour averages by day type for each site is shown in Figure 3-1. Densities were calculated within each day type as there are much fewer bay breeze days than the other two day types. Before calculating the maximum one hour average for each, 75% error-free hourly averages for the whole day (18 of 24 quality measurements) are required to ensure a true representative maximum is reported for that day.
The one hour ozone maxima for each day type at both sites exhibit a skewed distribution that is typically seen with surface ozone values. A small number of extremely high averages are seen in exceptional cases, and for the entire study period the mean maximum one hour average was higher on bay breeze days than non-bay breeze days at both locations (69.1 vs. 63.4 ppbv at Hampton; 78.0 vs. 73.3 ppbv at Baltimore). A larger spread in values is seen in the analysis of Baltimore, MD one hour ozone maxima, as that location sees many more elevated ozone days than Hampton, VA, the latter evidenced by a narrower distribution.
Figure 3-1. Maximum one hour averages in density by day type for May-September, 1986-2010. A histogram of maximum one hour averages of surface ozone for non-bay breeze (black), rainy/cloudy (green), and bay breeze (red) days. The day types were separated and densities calculated within each group. Data are binned every 5 ppbv.
The density distribution of all maximum eight hour averages by day type for each site is shown in Figure 3-2. In addition to the requirements for calculating a one hour ozone average, 75% valid hourly averages from 09 – 20 EST (8 of 12 quality measurements) are also required to calculate an eight hour ozone maximum. This is to keep from reporting eight hour maxima on days with only nighttime data, which are likely too low and not representative of the actual ozone levels on that day.

The distributions of the maximum eight hour averages for each day type at both locations show similar behavior to the maximum one hour averages. Again, the bay breeze days exhibit the highest mean maximum eight hour ozone averages, followed by the non-bay breeze days and the rainy/cloudy days. Bay breeze days at Hampton had a mean eight hour maximum of 60.4 versus 56.9 ppbv on non-bay breeze days, while bay breeze days at Baltimore had a mean eight hour maximum of 69.2 versus 65.1 ppbv on non-bay breeze days. The higher eight hour averages on bay breeze days have regulation implications since the EPA standard of greater than 75 ppbv is evaluated as an eight hour running average. Ozone averages and diurnal behavior by day type, as well as exceedances of the EPA standard by day type will be further discussed below.
Figure 3-2. Eight hour maximum averages in density by day type for May-September, 1986-2010. A histogram of maximum eight hour averages of surface ozone for non-bay breeze (black), rainy/cloudy (green), and bay breeze (red) days. The day types were separated and densities calculated within each group. Data are binned every 5 ppbv.
A breakdown of ozone averages is provided in Table 3-2. The data are separated into the three study periods of 1986-1994, 1995-2002, and 2003-2010 with number of each day type, number of exceedances and mean ozone averages at Hampton and Baltimore. Fewer bay breeze days are recorded at Baltimore (13 km inland) than Hampton (6 km inland). This is to be expected as the further from the coast a site is, the less chance a bay breeze front will propagate that far. The sharp decrease in total number of exceedances, as well as the average ozone values, after 2002 can also be seen in Table 3-2. This shows how the reduction in NO\textsubscript{x} emissions has reduced regional pollution episodes, potentially increasing the pertinence of bay breeze events to air quality violations.
Table 3-2. Surface ozone averages and exceedances. (Breakdown of surface ozone maximum averages, exceedances, and day types for both sites by study period from May to September)

<table>
<thead>
<tr>
<th>Location</th>
<th>Period</th>
<th># of Days</th>
<th># of Exceedances</th>
<th>Exceedance %</th>
<th>Average 1hr max (ppbv)</th>
<th>Average 8hr max (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hampton, VA</td>
<td>1986-1994</td>
<td>Bay Breeze</td>
<td>215</td>
<td>48</td>
<td>22.3</td>
<td>73.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>756</td>
<td>121</td>
<td>16.0</td>
<td>66.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>375</td>
<td>19</td>
<td>5.1</td>
<td>53.0</td>
</tr>
<tr>
<td></td>
<td>1995-2002</td>
<td>Bay Breeze</td>
<td>184</td>
<td>41</td>
<td>22.3</td>
<td>71.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>646</td>
<td>112</td>
<td>17.3</td>
<td>66.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>362</td>
<td>11</td>
<td>3.0</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td>2003-2010</td>
<td>Bay Breeze</td>
<td>244</td>
<td>16</td>
<td>6.6</td>
<td>63.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>637</td>
<td>18</td>
<td>2.8</td>
<td>56.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>310</td>
<td>3</td>
<td>1.0</td>
<td>46.0</td>
</tr>
<tr>
<td></td>
<td>All Years</td>
<td>Bay Breeze</td>
<td>643</td>
<td>105</td>
<td>16.3</td>
<td>69.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>2039</td>
<td>251</td>
<td>12.3</td>
<td>63.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>1047</td>
<td>33</td>
<td>3.2</td>
<td>50.6</td>
</tr>
<tr>
<td>Baltimore, MD</td>
<td>1986-1994</td>
<td>Bay Breeze</td>
<td>120</td>
<td>47</td>
<td>39.4</td>
<td>80.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>721</td>
<td>226</td>
<td>31.4</td>
<td>76.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>329</td>
<td>13</td>
<td>4.0</td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>1995-2002</td>
<td>Bay Breeze</td>
<td>132</td>
<td>56</td>
<td>42.4</td>
<td>81.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>607</td>
<td>195</td>
<td>32.1</td>
<td>75.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>459</td>
<td>32</td>
<td>7.0</td>
<td>57.9</td>
</tr>
<tr>
<td></td>
<td>2003-2010</td>
<td>Bay Breeze</td>
<td>91</td>
<td>17</td>
<td>18.7</td>
<td>60.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>524</td>
<td>64</td>
<td>12.2</td>
<td>65.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>575</td>
<td>22</td>
<td>3.8</td>
<td>54.2</td>
</tr>
<tr>
<td></td>
<td>All Years</td>
<td>Bay Breeze</td>
<td>343</td>
<td>120</td>
<td>35.0</td>
<td>78.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No Bay Breeze</td>
<td>1852</td>
<td>485</td>
<td>26.2</td>
<td>73.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rainy/Cloudy</td>
<td>1563</td>
<td>67</td>
<td>4.9</td>
<td>55.6</td>
</tr>
</tbody>
</table>
Baltimore/Hampton Ozone Diurnal Differences

To examine the behavior of ozone on each day type throughout the day, ozone values are placed into bins for each hour and averaged to obtain a typical diurnal cycle of ozone. The day types are separated and shown by study period at each site in Figure 3-3. A statistical bootstrap method was again performed 10,000 times to assess significance of the diurnal means for each hour. The 95% confidence intervals at which statistical significance is determined are marked in Figure 3-3, revealing differences among the bay breeze’s effect at the two sites.

At Hampton, on average the bay breeze provides statistically significantly higher afternoon ozone than on non-bay breeze days for all three study periods. At Baltimore, the days with a bay breeze on average exhibit statistically significantly higher ozone only in the mid-afternoon hours of the 2003-2010 period (excluding the late evening hours of the 1995-2002 period). This result, along with the much greater separation in ozone amongst the day types in 2003-2010 at Hampton, gives evidence that bay breeze circulations may be causing higher ozone anomalies on average since the inception of the recent NOx regulations. The diurnal cycles of ozone also shows intriguing results related to the early morning meteorological conditions of each day type, with statistically significant different ozone during those hours as well. This will be examined in detail below.
Figure 3-3. Diurnal cycles of ozone at Hampton (left panels) and Baltimore (right panels). Shown are average hourly surface ozone for each site by study period from May to September. Day types are separated into bay breeze (red), non-bay breeze (black), and rainy/cloudy (green) days. The dashed lines represent the 95% confidence interval for each mean, with statistical significance represented by separation between the dashes for each day type.
Normalized Ozone

In addition to the comparison of the average diurnal cycles of ozone for each day type, a direct comparison of normalized data is also performed. This will eliminate the seasonality of surface ozone within each year and give a measure of the anomalies displayed from the three day types throughout the ozone season.

To remove the seasonality of ozone, the May through September time period is broken down into eight sequential subsets. Seven groups contain 19 consecutive days each, with the last group containing the remaining 20 days. The entire ozone dataset is now in 24 separate groups at both sites when considering the three study periods. The sets of 19-20 days are meant to avoid comparing September ozone data with June for example, when the sun’s zenith angle is much higher and more ozone can be photochemically produced by more intense radiation. Within each of the 24 groups of ozone data, the average ($\bar{x}$) ozone and standard deviation ($\sigma$) for each hour of the day is calculated, and the original data ($x$) in the group are normalized via the equation:

$$A = \frac{x - \bar{x}}{\sigma}$$

Here, $A$ is the surface ozone anomaly in standard deviations from the mean. Every ozone data point is now in terms of anomaly from the mean for their respective hour of the day. This method of normalizing the data will allow for a direct comparison of each day type with the mean ozone in that group.

Figure 3-4 displays the ozone anomalies by hour of the day at both sites by day type. A number of interesting features that could be implied previously are now spelled out. Rainy/cloudy days consistently have higher ozone in the morning hours compared with the mean.
This is likely a result of a disturbed boundary layer on days with rain or cloud cover. Under these conditions, a stable nocturnal layer cannot form, and early morning emissions of NO\textsubscript{x} do not titrate O\textsubscript{3} as quickly and lower mixing ratios to near zero (see eqn. 5). The opposite is true for bay breeze days. One would expect stagnant conditions to rule before a bay breeze forms, leading to radiational cooling at night and a well defined stable layer. In this well defined stable layer, emissions of NO\textsubscript{x} are trapped and will titrate any O\textsubscript{3} relatively quickly. Ozone will also readily deposit to the surface in the stable layer, leading to the lower morning ozone mixing ratios on bay breeze days. The non-bay breeze days fall in between those two results. Once the sun begins photochemically producing ozone on bay breeze and non-bay breeze days, the rainy/cloudy days fall below the mean as rain and clouds inhibit the sun’s ability to form O\textsubscript{3}.

Baltimore and Hampton show different qualities in the diurnal variability of ozone anomalies, especially late in the day. With respect to the mean, the high ozone on bay breeze days at Hampton subsides more quickly than at Baltimore, which remains elevated through the evening hours. At both sites however, the 2003-2010 bay breeze days represent the highest average anomalies during the daytime, again giving evidence that localized meteorology plays a larger role in the current “low NO\textsubscript{x}” regime. It is also interesting to note that at Baltimore, the 2003-2010 rainy/cloudy days represent less of a negative anomaly in ozone than previous study periods, a testament to the overall lowering of typical ozone mixing ratios in that region.
Figure 3-4. Ozone anomalies by day type for Hampton (top) and Baltimore (bottom). Average anomaly in standard deviations from the mean by hour of day for each day type are shown. Day types are separated into bay breeze (red), non-bay breeze (black), and rainy/cloudy (green) days. Study periods are also separated by 1986-1994 (solid line), 1995-2002 (stars), and 2003-2010 (open circles). The zero line, representing mean ozone, is marked with a dashed blue line. Note the different y-axes for each plot.
The Increasing Role of the Bay Breeze

The goal of this study is to determine whether the bay breeze has an increased role in the percentage of exceedances in a given area. With the decline of NOx emissions by U.S. power plants in the early 2000s, we have hypothesized that bay breeze events are becoming an important meteorological scenario that can cause an exceedance, with the combination of stagnation, hot weather and convergence of pollutants creating an environment that is extremely favorable for ozone formation.

To quantify the part that the bay breeze plays in the total number of exceedances at each site studied and how that changes with each study period, the total number of days with an eight hour average above 75 ppbv was calculated. The exceedances were then grouped by day type, and by study period. The number of bay breeze day exceedances was then compared with the total number of exceedances by:

\[
\text{Bay Breeze Exceedance \%} = \frac{\text{# Bay Breeze Day Exceedances}}{\text{# Total Exceedances}}
\]

Figure 3-5 shows the results of splitting the number of exceedances at each site by study period and evaluating the bay breeze exceedance percentage for each. At Baltimore, the bay breeze exceedance rate holds steady throughout the three study periods, going from 16.4\%, to 19.8\%, to 16.5\% from past to present. This shows that at Baltimore, whereas the bay breeze is producing higher ozone anomalies in the 2003-2010 time period as shown previously, it does not appear to have an effect on the percentage of exceedances. Possible reasons will be discussed below. At Hampton, the bay breeze exceedance rate holds at 25.5\% and 25.0\% for the first two periods then leaps to 43.2\% for 2003-2010. This result shows that the bay breeze has become a
much larger factor leading to exceedances at Hampton, VA, consistent with the hypothesis put forth by Martins et al. (2012).

Since the reduction of NOx emissions in the early 2000s the bay breeze has contributed more to violating the EPA eight hour ozone standard at Hampton, VA than at Baltimore, MD. There are several possible reasons for this difference. Baltimore still saw an average of almost 13 exceedances per year from May through September 2003-2010, while Hampton averaged just 4.8 per year over the same period. This likely means that weather that is conducive to surface ozone violations is now more critical at Hampton than at Baltimore; bay breezes are providing those exceptional conditions. This leads to the higher percentage of total exceedances at the Hampton site. The fact that the Baltimore ozone monitor was further inland could also contribute to the differences in results at the two sites. As the bay breeze air mass moves inland, the sun is able to mix higher the shallow marine boundary layer through surface heating, which can dilute the elevated mixing ratios seen at the immediate coast. Lastly, the ozone monitor at Baltimore was not located as close to the KBWI hourly reporting station as the Hampton monitor was to the KLFI station. This will ultimately lead to a few days where a bay breeze was observed at the airport, but perhaps not at the ozone monitor, and vice versa. All of these reasons could have contributed to the lack of response in bay breeze exceedance percentage at Baltimore, with the overall higher frequency of ozone pollution events at Baltimore likely being the largest cause.
Figure 3-5. Bay breeze exceedance rate by study period. Total number of exceedances for each study period by day type with non-bay breeze days in black, bay breeze days in red and rainy/cloudy days in green. The dashed line with black markers represents the percentage of total exceedances occurring on bay breeze days for each study period, shown on the right y-axis. Note the different left y-axes for each site.
Chapter 4
Conclusions and Future Work

An analysis of surface ozone during bay breeze days at Hampton, Virginia and Baltimore, Maryland, two sites along the western shore of the Chesapeake Bay was performed from May through September, 1986-2010. Bay breeze days were separated from non-bay breeze days and rainy or cloudy days based on data from hourly airport ASOS reporting stations collocated with EPA ozone monitors. The analysis of ozone data was based on this separation of three different day types. The 1986-2010 climatology was also split into three periods of 1986-1994, 1995-2002, and 2003-2010 based on NOx regulations implemented in the early 2000s.

Previous work showed that bay breezes can provide both relief from and exacerbate poor air quality. This study finds that in general bay breezes in the Chesapeake Bay region enhance air quality problems, due to ubiquitous ozone precursors near these urbanized areas. Differences in the calculated eight hour means of ozone were typically 3 to 5 ppbv higher on bay breeze days at both sites compared to other days. In both locations, mean hourly surface ozone was highest on bay breeze days compared to non-bay breeze and rainy/cloudy days for all time periods. The difference was statistically significant at Hampton for afternoon hours during all three study periods, but was only statistically different during late afternoon hours for the 2003-2010 study period at Baltimore. This highlights a characteristic difference between the two sites, with Baltimore located further inland than Hampton, potentially allowing for dilution of higher ozone mixing ratios through vertical mixing as the bay breeze propagates onshore.
Surface ozone anomalies were also calculated at each site by hour of day. Both locations saw the highest ozone anomalies during bay breeze days for the years 2003-2010 during the afternoon period. The peak in high ozone anomalies at Hampton occurred several hours earlier than at Baltimore, another possible effect of Baltimore’s farther inland location.

Lastly, the percentage of total exceedances occurring on bay breeze days was calculated. This was done to provide a measure of the relative importance of bay breeze days compared with other days in regards to exceeding the EPA eight hour ozone standard of 75 ppbv. The percentage of total exceedances during bay breeze days held steady at Baltimore for all three study periods, but jumped a total of 18% from 1995-2002 to 2003-2010 at Hampton, with 43% of exceedances occurring on bay breeze days in the latest period. This is telling of the overall higher levels of pollution at Baltimore, where exceptional meteorological conditions are not as necessary for elevated ozone as they are at Hampton. This also validates the idea put forth by Martins et al. (2012) that the bay breeze is becoming more important to exceedance probability, and will likely continue to be should ozone standards become more stringent and NOx emissions continue to decline.

Expansion of this study could be implemented through analysis of another local-scale event that has been shown to affect surface O₃, particularly at night. The nocturnal low level jet (LLJ) is an effective long-range transporter that can mix down high O₃ found within a shallow layer of enhanced winds in localized areas. The LLJ is brought about by nighttime meteorology similar to that which precedes the bay breeze on synoptic scales (Zhang et al., 2006), so a study of those compounding processes for elevated surface O₃ would be practical.

It should be noted that while it has been shown that bay breeze days exhibit higher average ozone than other days at these two sites, this will not hold in other locations where the occurrence of a water-body breeze results in cleaner marine air. The existence of ozone precursors over water is necessary for production of ozone that can then be transported inland, a
condition often met in the urban areas studied here. Without the emission of NOx and VOCs over the water surface, many locations may experience air quality relief from a non-polluted marine air mass.

While the bay breeze’s effect on exceedances has been evaluated in depth here, the detrimental health effects of O3 do not plateau at 75 ppbv. It would therefore be useful to provide a measure of the bay breeze’s influence on surface ozone beyond the eight hour EPA standard to assess the frequency and likelihood of dangerous mixing ratios of O3 approaching and beyond the less used EPA one hour standard of 120 ppbv. A comparison of the different day types using this one hour standard may be necessary for evaluating the more acute, short term effects of high levels of surface O3 during bay breeze events.

It would be interesting to perform this type of analysis in other locations around the United States with air quality issues that are also susceptible to water-body breezes. In addition to characterizing ozone during water-body breeze events, a more quantitative approach to connecting NOx reductions and the confinement of air quality events could be performed. Other candidates for this type of analysis include Wallops Island, VA, which has ozonesonde records to 1970 and would be useful for examining the vertical structure of ozone during sea breeze events. Metropolitan locations such as Houston, Texas have been intensely examined on a case-study basis, and will be the focus of the DISCOVER-AQ campaign in 2013. Thus a climatological analysis of gulf breeze events would give an expanded view of air quality events in that region. Other considerations include both urban and non-urban areas of New England, as more remote locations often experience the effects of transported pollutants downwind of major cities.

Other sites along the Chesapeake Bay routinely experience high ozone in the summer months, also thanks in part to the bay breeze. While unavailable for this particular analysis, another approach to determine the climatological occurrence of a bay breeze is desired as the DISCOVER-AQ campaign has shown similar results to this study during a much shorter time
period in July 2011. One possibility for those sites listed but unused in this study would be the use of a statistical model for the prediction of past bay breeze occurrences. Without the actual measurement of wind direction at the coastal site, surrounding meteorological variables could be used to obtain a probability that a bay breeze was observed given a sufficient set of data to train a model. This may be possible using ozone sites currently outfitted with meteorological measurements and a similar analysis could be performed at additional locations for a broader view into the connections between bay breezes and surface ozone.
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