OZONESONDE CLIMATOLOGY AND SATELLITE PRODUCT EVALUATION: TROPOSPHERIC OZONE IN THE MID-ATLANTIC FROM 2005-2010

A Thesis in
Meteorology
by
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Abstract

Geostationary satellite missions are proposed to remotely assess regional air quality over large swaths, although the precise capability of the current set of satellite instruments to accurately resolve urban scale pollution remains unverified. We use the Trajectory Enhanced Tropospheric Ozone Residual product derived from Aura’s Ozone Monitoring Instrument/Microwave Limb Sounder satellite data to examine the regional climatology of ozone pollution in the mid-Atlantic, focusing on the Washington, D.C. area and downwind Delmarva. We use the North American Regional Reanalysis to determine the synoptic scale flow patterns in the lower troposphere. In addition, a set of proxies (OMI NO$_2$, surface ozone, cloud cover, and air mass classification) are employed to understand TTOR performance and interacting meteorological and chemical effects in the region. We find that the TTOR product accuracy varies substantially temporally, improving during summer months (0.22% monthly mean bias in May compared to 11% bias in October) for example, and during earlier years in the record more than later ones (0.3% annual mean bias in 2007 compared to 7.5% bias in 2009). TTOR product accuracy is influenced by air mass effects on advection and on planetary boundary layer ozone concentrations. Conditions conducive to ozone production yield a higher near-surface proportion of the tropospheric column as measured by Wallops Island ozonesondes. We identify synoptic-scale flow regimes that strengthen correlations between urban tropospheric ozone density and column density off the coast of the mid-Atlantic. These results indicate that remotely sensed measurements may indeed be able to discriminate urban influences on regional ozone and their effects in more remote areas and have implications for air quality assessment and model validation.
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Chapter 1. Introduction

Tropospheric ozone is an air pollutant that occurs near the surface and is a major component of photochemical smog. Ozone damages the living tissue of plants and animals, causing eye irritation, respiratory problems (Jacobson, 2002; Wang & Mauzerall, 2004; Ashmore, 2005), and manifests its harmful effects within five minutes for high concentrations of about 100 ppbv. These effects become worse as exposure is prolonged (WHO, 1999). Elevated ozone days often result in increased rates of hospitalization and emergency room visits owing to respiratory ailments (Cody et al., 1992; Thurston et al., 1992, 1994). The evidence of negative health effects owing to ambient ozone exposure demonstrates a need for further examination of its formation and transport using innovative methodologies.

A secondary pollutant, tropospheric ozone primarily forms in the presence of volatile organic compounds, nitrogen oxides (NOx), and sunlight. Day-to-day surface ozone variations at a given location thus are influenced by a variety of meteorological factors, such as actinic radiation levels, temperature, and humidity (e.g., Comrie, 1990; Comrie and Yarnal, 1992; Liu et al., 1994; Poissant et al., 1996; Xu et al., 1997; Seinfeld and Pandis, 1998). Changing emission levels generally vary little from one day to the next, with the exception of the predictable weekend effects, and so variability in surface ozone is attributable mostly to meteorological conditions (Qin et al., 2004).

More than ever, tropospheric ozone is a regional pollutant, with elevated levels of ozone observed in rural locations downwind of urban centers by as far as several hundred kilometers (Logan 1989; Fishman et al., 2003; Lawrence et al., 2007; West et al., 2009). Horizontal transport of pollution within the mixed layer as well as vertical diffusion of pollution from cities both significantly impact concentrations on the regional scale. In recent decades, trends show that global ozone concentrations may be increasing due to anthropogenic activity such as emissions from fossil fuel and biomass burning, and current estimates show a near doubling of ozone concentrations in the lower atmosphere of the Northern hemisphere (Ziemke et al., 2005; Sitch et al., 2007). Regional ozone estimates, however, appear inconsistent with this global trend and make localized estimation of ozone and its precursors necessary (Martins et al., 2011; Cooper et al., 2011).

Tropospheric ozone has been studied using various measurement networks. Global ozonesonde networks provide high vertical resolution measurements, although data density is limited spatially and temporally. Surface monitors, in contrast, yield a more dense spatial and temporal resolution, but these measurements are limited vertically. Satellite data are useful in that
they provide a broad swath of data over a given region at a given time, allowing for a more comprehensive understanding of regional ozone development, transport, and distribution. Doughty et al. (2011) explored the accuracy of satellite products for a location in the North American northwest over four weeks. Fishman et al. (2003) examined the comparison globally and for multiple decades. Although regional assessments of ozone variability have been conducted (Fishman et al., 2010; Kar et al., 2010) these studies were conducted based on monthly means and regional analyses remain imperfect. The present research expands upon this previous work by evaluating a long term record of daily ozonesonde profiles in conjunction with coincident satellite product measurements.
Chapter 2. Data and Methods

Ozonesonde profiles provide a comprehensive record of the atmospheric column, enabling an improved understanding of mixing, stratification, transport and distribution of ozone within atmosphere and are therefore tremendously useful. Ozonesonde data were downloaded from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) for the Wallops Island, Virginia location for 2005-2010 (data available from ftp://ftp.tor.ec.gc.ca/Archive-NewFormat/OzoneSonde_1.0_1/STN107/). Wallops Island (37.94°N 75.47°W) is located on the eastern shore of Virginia on the Delmarva (Delaware-Maryland-Virginia) Peninsula. Balloon-borne ozonesondes with electrochemical concentration cell (ECC) measurement instruments have been used at Wallops since 1970, although the past two decades have seen improvement in measurement reliability. The updated devices used for this study are accurate and precise to within 5-10% (Smit et al., 2007; Thompson et al., 2007; Deshler et al., 2008). The ozonesondes collect measurements at two-second intervals and so profiles are vastly more informative than surface observations of ozone. Moreover, given this high vertical resolution, profiles are useful for determining those atmospheric levels of particular importance to ozone formation and transport.

One such key level, the tropopause, is defined as the transition layer between the troposphere and the stratosphere (Stull, 1988). Different calculations yield varying tropopause altitude when the transition is defined thermally (WMO, 1957), chemically (Hsu and Prather, 2005), or dynamically (Postel and Hitchman, 1999). In the present study, the altitude level of the tropopause was determined using an ozonopause calculation wherein the height at which the ozone mixing ratio first falls below 100 ppbv, as measured down from the top of a profile, is identified as the transition between the high ozone stratosphere and the lower ozone troposphere (Dougherty, 2008). The column ozone was then derived by integrating ozone volume mixing ratio through the depth of the troposphere and converting the resulting value to Dobson units (DU) or 2.69x10^{16} molecules per square centimeter. DU provide a measurement of the density of ozone in an atmospheric column. The following equation was applied to develop the integrated column values

\[ 26.93 \int_{z_t}^{z_s} \frac{p(z) \mu_z}{T(k)} \, dz \]
where $p(z)$ is the pressure (hPa) at height $z$ (m), $z_t$ is the altitude of the tropopause, $z_s$ is the surface height, $T(z)$ is the temperature (K), and $\mu_z$ is the ozone concentration (ppmv) (Dougherty, 2008).

Although data throughout the depth of the troposphere are necessary for comparison with satellite products, urban emissions of atmospheric pollutants occur within the planetary boundary layer (PBL), and so this layer is especially critical in understanding ozone formation and distribution (Baird and Cann, 1995). In addition to the observations of meteorological parameters, ozonesonde profiles also provide in situ measurements of pollutant variability within the turbulent mixed layer. Although previous studies have classified ozone profiles in the free troposphere (Yorks et al., 2009), ozone in the PBL has received less attention in the literature. PBL ozone is subject to a multitude of confounding surface influences including land-sea breeze interactions that involve onshore flow of marine air that dilutes polluted continental air, as well as deposition of ozone on the water surface. Downward mixing of free tropospheric ozone under certain meteorological conditions may significantly impact PBL concentrations, and so lower tropospheric ozone observations must be considered in the present study. Diurnal development and decay of the PBL additionally complicates the production, mixing and transport of ozone in this layer. The relationship between mixing height and PBL ozone concentrations remains unclear (Rappengluck et al., 2008; Banta et al., 2011).

Equivalent potential temperature ($\theta_e$) profiles are calculated for each profile from the basic meteorological parameters of pressure, altitude, temperature and relative humidity. $\theta_e$ is a proxy for specific humidity, $q$, and is used to determine the top of the marine moist layer for this coastal location, thereby identifying the top of the mixed layer. The height of the most negative value of the second derivative of $\theta_e$ is calculated for all profiles to determine the top of the mixed layer using the method outlined by Stull (1988). Integrated columns of ozone are then calculated to the top of the PBL in the same way tropospheric columns are developed and these columns are also converted to DU.

The diurnal variability of the PBL requires careful consideration of launch time; profiles are therefore classified as morning, midday, afternoon or night according to launch time. Because daylight duration varies with time of year, the day is partitioned as follows: morning is defined as sunrise through the first third of daylight; midday is delineated from the end of the first third of daylight to two-thirds daylight; afternoon is defined as two-thirds daylight to sunset; night is defined as sunset to sunrise. This method accounts for the seasonal variation in sunlight amount, and the resulting variation in PBL depth for different times of day throughout the year. Launched at approximately 1:30 pm LST (1730 UTC) and with a nearly two hour ascent, these balloon-
borne instruments pass through the tropospheric altitudes of interest to the present study around 2 pm LST.

Coinciding with the 1730 UTC launch time of the ozonesondes is the 1800 UTC Aura satellite overpass. Sun-synchronous, the NASA Aura satellite carries the nadir-pointing Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS), which points in the direction of orbital motion (Chandra et al., 2003; Levelt et al., 2006). The OMI provides a total ozone column (TOC) from the top of the atmosphere and the MLS yields a stratospheric column ozone (SCO) measurement. Subtracting the MLS product from that of the OMI provides the tropospheric ozone residual (TOR) (Fishman et al., 2008). This residual value is approximately 10% of the TCO (typically ~300 DU), containing roughly 30 DU.

The Trajectory-Enhanced Tropospheric Ozone Residual (TTOR), developed in 2007 by Schoeberl et al., has an improved horizontal resolution of the SCO, in turn providing an improved TOR estimate. The Microwave Limb Sounder (MLS) aboard Aura scans in the plane of the orbital track, providing profiles every 165 km along its path at a vertical resolution of 3 km and horizontal resolution of 300 km in the upper troposphere-lower stratosphere (UTLS) region (Doughty et al., 2011). The precision of this record varies from about 20% at the 215 hPa level to 3-5% in the stratosphere (Boyd et al., 2007; Froidevaux et al., 2008).

Using forward-trajectory computations to improve the horizontal resolution of the SCO, Schoeberl et al. (2007) developed a more accurate TOR. Data from the MLS provided at the position of the satellite maps is assimilated in a three-dimensional chemical model (Schoeberl et al., 2007; Stajner et al., 2008). The trajectory mapping technique moves the measurement collected at a particular time to another time using the trajectory model and assimilated meteorological data. Version 1.6 (V1.6) of the TTOR product was used in the present study. For V1.6, two-day forward and two-day backward isentropic trajectories from GEOS-4 were incorporated to map V2.2 MLS measurements over the globe followed by interpolation of these values to 1.25°-by-1.0° grid (Schoeberl et al., 2007; Doughty et al., 2011). Although the resolution of the TTOR product is coarse, points within ~50 km of key locations are selected as proxies for these sites (Figure 1). Such points on this map are point 6, which represents for this analysis Wallops Island, VA; points 2 and 3 represent offshore points; point 15 serves as the proxy for Washington, D.C.
Figure 1. Spatial resolution of the TTOR product over the Washington, D.C. metropolitan area. Small red circle indicate the position of the satellite measurements. Large red circle indicate key locations to this study. The red star marks the location of Wallops Island, VA.

The tropospheric ozone budget for a given location, or virtual box, is defined as the balance between photochemical production, in situ chemical destruction, surface deposition, and advection of ozone into and out of the box (Figure 2). In turn, the individual budget terms are determined by in situ emission rates of ozone precursors, including reactive gases like nitrogen oxides (NOx) and volatile organize compounds (VOCs), by in situ meteorological parameters including temperature, humidity, radiation, wind speed and direction and cloud cover, as well as by advection of precursors and ozone into the study location (Figure 3) (Seinfeld and Pandis, 1998; Sillman, 1999). The advection term itself is governed not only by prevailing wind speed and direction, but also by the emissions upwind and the meteorological conditions relevant to photochemical production upwind. The abundance of ozone precursors upwind allows for significant in situ ozone production.
Wallop Island is a coastal town with approximately 400 residents and owing to this small population, it is reasonable to figure that transportation, industrial and commercial sources of \textit{in situ} NO\textsubscript{x} emissions will be comparably low. Uniquely situated downwind of Washington, D.C. and the urbanized I-95 corridor, however, Wallops Island is significantly impacted by the upwind production of ozone, and by the advection of this ozone and ozone precursors. This is important because peak local values of ozone are generally detected downwind of cities due to the photochemical time scales of ozone production and because of the relative concentrations of precursors required (Ryan, 2002). The lifetime of ozone depends on deposition and titration among other factors, although it can be estimated to be approximately 2-5 days in the PBL during the peak season. Given a typical upper PBL wind speed of 8 m/s, ozone could travel from Washington, D.C. to Wallops Island in a few hours.

The virtual box for developing the ozone budget in this study is defined as the troposphere over the Washington, D.C.-Wallops Island region. Within the box, the dependent variables include: i) ozonesonde integrated column ozone and ii) satellite-provided integrated column ozone. Ozone mixing ratios are known to vary with meteorological parameters such as temperature (indirectly impacted through incoming solar radiation), and cloud cover, and they have been shown to increase with biogenic and anthropogenic emissions. The major influencers of tropospheric ozone are therefore identified as follows: i) synoptic scale wind flow, which serves as a proxy for the advection term, and is provided as the mean wind flow over the region from North American Regional Reanalysis (NARR) wind data; ii) cloud cover, which serves as a proxy for incoming solar radiation, and is also provided by NARR; iii) prevailing meteorological conditions, provided via the Spatial Synoptic Classification (SSC) system to identity daily air

\textbf{Figure 2.} Schematic of the ozone budget for a virtual box.
mass regime; iv) precursor emissions, which are provided as nitrogen dioxide (NO$_2$) column density from OMI aboard the NASA AURA platform.

Figure 3. Schematic of the factors influencing ozone concentrations in a given location.

Given the dominant influences on ozone at Wallops Island, the research questions for this analysis are four-fold and each builds upon the one prior:

I. How has tropospheric ozone changed over the Washington, D.C. region during recent years and to what extent have these changes been accurately detected by satellites?

II. How does the prevailing air mass type impact the ozonesonde-satellite product comparison?

III. How does the prevailing air mass type impact PBL ozone concentrations and what portion of the ozonesonde-satellite difference is attributable to the PBL?

IV. How can statistics be used to better understand the major ozone influencers and their interacting effects on tropospheric ozone in the region?
Chapter 3. Results

3.1 Ozonesonde – TTOR Product Comparison Climatology

The ozonesonde measurements and TTOR product display comparable annual time series for mean monthly integrated column values between 2005 and 2010 (Figure 4). Both peak in the summer months when tropospheric ozone production is enhanced. As described by Schoeberl et al. (2007), the TTOR exhibits a low bias by several DU throughout the year, although the difference is maximized in the winter months. This seasonal influence is attributable to the southward progression of the jet stream during winter months. This positioning increases the strength of the westerlies, resulting in greater advection of continental air and also in increased occurrence of stratospheric intrusions that bring high-ozone air into the troposphere. Given the increased accuracy of the TTOR product to the ozonesonde during the warmer months, the remainder of the study focuses on May through August.

A second feature of note in Figure 4 is that on for the 2005-2010 average, the TTOR product exceeds that of the ozonesonde during May. The mean ozonesonde value for this spring month displays nearly identical integrated ozone column value to that of April, whereas the TTOR product appears to follow a distinct seasonal trend upwards between January and May, leveling off in June. The reversal of the low TTOR bias in May might be caused by a seasonal shift in ozone production that is not accounted for by the TTOR product. It is important to note that the TTOR is not a chemical model but a stratospheric transport model yielding an improved estimate of the remaining tropospheric ozone component of the total column. Between April and May, the synoptic-scale patterns shift as the jet stream retreats northward, and the prevailing westerlies lessen. This factor may be poorly represented in the TTOR model and may account for these differences in the annual time series. The May anomaly appears to be inconsistent with previous ozonesonde-TTOR comparisons (Doughty et al., 2011). For this analysis, the difference between the datasets is computed as follows:

\[
\text{Ozonesonde integrated column ozone (DU)} - \text{TTOR integrated column ozone product (DU)} = \text{Column difference (DU)}.
\]
A striking third element in Figure 4 is the exaggerated low bias of TTOR in July. Given that these estimates represent the average monthly mean from 2005 to 2010, this deviation from the predominant pattern is unexpected and highlights the non-uniform bias of the TTOR product relative to the ozonesonde. The percent error between the ozonesonde and TTOR product ranges from 0.22% monthly mean bias in May to 11% bias in October, with a summer maximum of 7.9% bias in July.

The ozonesonde-TTOR product difference varies substantially between the years (Figure 5). The percent error between the mean annual values is lower during the earlier years examined with a minimum in 2007 of 0.3% annual mean bias. During 2009 and 2010, the bias increased to 7.5% and 5.6%, respectively, although the TTOR product biased low in 2009 and biased high in 2010. Studies have shown that excessive pollution during the summer of 2010 accounted for four National Ambient Air Quality Standard (NAAQS) exceedance days (defined as greater than 75 ppbv at the surface) versus zero exceedance days in 2009 for the region (Yorks et al., 2009). Despite this increased pollution, during 2010, the TTOR product overestimated the integrated column ozone value relative to the ozonesonde on average. That this difference is maintained

**Figure 4.** The annual variability in mean monthly integrating column ozone from the ozonesonde and from the TTOR product (DU). Error bars represent the 95% confidence interval.
even for a six-year average motivates further analysis of the specific layers that contribute to ozonesonde-TTOR differences.

Ozonesonde profiles for which the TTOR product was biased low or high are shown in Figure 6a and 6b, respectively. Notably, when the TTOR product yielded a negative bias relative to the ozonesonde truth, the concurrent profiles display on average a volume mixing ratio enhancement in the lowest 5 km of the troposphere relative to the sample mean for all profiles. Conversely, when the TTOR product yielded a positive bias relative to the ozonesonde, there exists a group of profiles with ozone volume mixing ratios in the PBL lower than average and lower than one standard deviation below average for the entire troposphere. Analysis of the *in situ* profiles reveals that the ozone column below 5 km often dominates the profile column density.

![Figure 5](image)

**Figure 5.** Time series of yearly mean ozonesonde and tropospheric ozone residual integrated column ozone (DU) for Wallops Island for May through August. Error bars represent the 95% confidence interval.
Figure 6. Ozonesonde profiles for May through August as grouped by (a.) negative TTOR bias relative to the ozonesonde or (b.) positive TTOR bias relative to the ozonesonde. The red line represents the mean for all summer profiles between 2005 and 2010; the green lines represent the standard deviations for the summer profiles. The difference between the mean and standard deviation is highlighted by grey shading.

3.2 Ozonesonde – TTOR Product Comparison by Air Mass Influence

Ozone production is significantly influenced by meteorological factors including temperature, humidity, actinic radiation levels, and cloud cover (Comrie, 1990; Comrie and Yarnal, 1992; Poissant et al., 1996; Seinfeld and Pandis, 1998), and an air mass-based analysis is therefore useful for understanding seasonal and interannual variations in ozone concentrations. Air mass types were derived using the Spatial Synoptic Classification (SSC) system (Sheridan 2002; 2003). Within this scheme, surface observations (e.g. temperature, dew point temperature, barometric pressure, wind speed, wind direction and cloud cover) collected four times daily are used to generate an air mass classification unique to each station across the U.S. each day. The air mass type is assigned based on proximity of observations to the prototype air mass type for a given station and time of year. Similar to the classic system developed by Bergeron (1930), the SSC method described above identifies six mutually distinct air mass types:

Dry Polar (DP) - this cold, dry air mass is generally associated with a polar anticyclone that has moved into the region from the north. DP has seasonably cool and sunny conditions in the mid-Atlantic in summer.
Dry Moderate (DM) – this group identifies air linked with near-normal temperatures that typically arrives in the region from the west. For some days, DM air represents Pacific air that has descended on the eastern side of the Rockies and therefore adiabatically dried and warmed.

Dry Tropical (DT) – for the Virginia and mid-Atlantic region this classification is typically associated with air that originates from the west or south that has undergone significant anticyclonic subsidence and has developed the hot and dry characteristics typical of desert air masses.

Moist Polar (MP) – this is a cool, humid air mass generally linked to overcast skies and often to precipitation. In the mid-Atlantic, MP frequently occurs simultaneously with frontal overrunning and the movement of marine air from the northeast or east to the north of the frontal boundary.

Moist Moderate (MM) – this classification includes humid air that is warmer than MP air. MM encompasses a variety of synoptic patterns that lead to moderate temperatures and elevated humidity.

Moist Tropical (MT) – this air mass includes warm, humid air that is usually advected from source regions in the Gulf of Mexico or the Atlantic Ocean. During summer, as warm, humid conditions prevail over much of the southeastern United States and frontal passages are infrequent, MT air becomes the primary weather type in this region.

Transition (TR) – this final grouping encompasses days for which a frontal passage has occurred and thus they cannot be classified into a single air mass type. Transitions are identified based upon the change in dew point temperature, wind direction, and pressure over the course of a day, regardless of the direction of these changes.

The standard air mass conditions described above vary over the course of the year, and so the SSC allows for the distinction of MT air in winter and DP air in summer, for example. It is therefore an air mass classification scheme that identifies relative synoptic types based upon the expected distribution at that time of year. Regardless, MT is still more common in Virginia in the summer than DP (Sheridan, 2002; 2003). The SSC was calculated from archived weather observations taken at the weather station in Norfolk, VA from 1948 to present, and this study incorporated the daily SSC for 2005-2010 from the online SSC database at http://sheridan.geog.kent.edu/ssc.html. Norfolk was selected for this thesis to be representative of the predominant air mass in the region for a given day as this site is closest to Wallops Island at a distance of 145 km to the south.

Mid-Atlantic summers are typically dominated mostly by DM and MT, and, to a lesser extent, MM. Less frequent during the summer are DP, DT and MP air masses.
Norfolk, VA experienced a high frequency of MT days, with slightly lower frequencies of DM and MM days (Figure 7). Years 2009 and 2010 display the greatest deviation from the climatological norm, in that 2009 experienced anomalously frequent MM air masses and less frequent DM conditions. In contrast, the summer of 2010 experienced the most MT days of the six-year record with relatively few MM and DM days. DT frequency was also high in 2010. Notably, the years that most closely adhere to the climatological standard for the mid-Atlantic, 2007 and 2008, also resulted in the lowest percent error between the ozonesonde the TTOR product. This result indicates that TTOR inaccuracy may be exacerbated by atypical air mass conditions, a question that is examined next.

![Air Mass Frequency by Year](http://sheridan.geog.kent.edu/ssc/clusters/3c.jpg)

**Figure 7.** Air mass frequency by year for May through August.

The SSC identifies predominant daily air mass characteristics for the Wallops Island region and is used in the present study to determine patterns in the meteorological conditions conducive to ozone formation. Moreover, the SSC provides a representation of the regional air mass type as opposed to the localized weather conditions recorded by the ozonesonde and launch site, and the SSC is determined independent of those ozonesonde measurements.
Figure 8. Mean integrated column ozone from the ozonesonde and the TTOR product (DU) by air mass type for May through August. Error bars represent the 95% confidence interval.

Given the photochemical nature of ozone formation and the known influences of various meteorological variables, it is expected that DT conditions will yield the highest ozone, MP the lowest, and the moderate air masses, DM, DP, MM, and MT, will result in average ozone values. For the data collected at Wallops, the ozonesonde-TTOR product comparison varies substantially by air mass type (Figure 8). DT air does result in the greatest integrated column ozone values as reported by the ozonesonde, but with a large difference (11% error) between the ozonesonde and TTOR. The TTOR product biases low relative to the ozonesonde for all air mass conditions excluding DM and MP air. For DM air mass days, the TTOR exceeds the ozonesonde on average, although only slightly, yielding a percent error of 2.0%. For MP days, in contrast, the difference is much greater with 25% error. This major discrepancy is attributable to the infrequent occurrence of MP conditions in the region between May and August. The lowest percent error occurred for MM days at 1.1%.
The mean difference between the ozonesonde and the TTOR product ranges from -10 DU for MP days to 4 DU for DT days (Figure 9). With the exception of MP air mass days, the mean difference falls between -1 and 4 DU. The air mass types that result in the greatest absolute differences between the TTOR product and the ozonesonde are those air masses yielding the greatest ozonesonde or TTOR integrated column ozone values. These air masses, DT and MP, are also the “extreme” classification types, resulting in the largest (ozonesonde for DT; TTOR for MP) and smallest (ozonesonde for MP) measurements. It follows, therefore, that the TTOR product performs least effectively for the air mass classification extremes, when tropospheric conditions are conducive to very high or low ozone values.

As noted, 2009 and 2010 differed dramatically in the frequency of severe ozone episodes, in air mass frequencies, and in the relative accuracy of the TTOR product. To examine these correlations for possible relationships, the air mass frequencies and climatological conditions of June 2009 and June 2010 are compared. Recall that in 2010, the TTOR biased high relative to the
ozone sondes by 5.0 DU, and in 2009 the TTOR biased low by 4.0 DU. During the month of June alone, the TTOR product biased low by 10.0 DU in 2009 compared to a high bias of about 5.0 DU in 2010 (Figure 10). Additionally, the monthly air mass frequencies exhibit significant differences between June 2009 and June 2010. In 2009, June is approximately 55% MT, 25% MM, 8% DM, 8% DT, and 4% DP. In 2010, 67% of days are MT, roughly 14% are DT, 10% MM, 6% TR, and 3% DM (Figure 11).

![Figure 10](image)

**Figure 10.** Ozone sondes minus TTOR product difference during June by year. Error bars represent the 95% confidence interval.

The June 2009 SSC frequencies indicate that mean winds in the lower troposphere arrive into the region from the west, northwest, northeast, and that source regions are moderate to cooler. Given the relative frequencies, it is expected that air is moist on average, contributing to conditions not conducive to ozone formation. During 2010, however, the high occurrence of MT and DT days indicates a persistent westerly and southwesterly flow regime of Gulf of Mexico air that has circulated over the southeastern U.S. and has modified during that time. The lack of
either DP or MP days suggests that air temperatures are warmer than average. The relatively high DT frequency indicates a drier lower troposphere on average, as well.

![Pie charts showing air mass types for June 2009 and 2010.](image)

**Figure 11.** Frequency of air mass types for June (a) 2009 and (b) 2010.

During June 2009, the lowest layers of the atmosphere experienced the following flow anomalies relative to the 1981-2010 mean: easterly flow south of the mid-Atlantic region, northerly flow off the coast, and westerly flow north and northeast of the study region (Figures 12 and 13). Although these vector winds (m/s) at 925 mb and 850 mb were anomalies relative to the 20-year mean and not actual winds, they point to differences in prevailing wind and synoptic conditions between June 2009 and June 2010. In particular, the flow anomalies indicate a higher occurrence of low pressure systems over the mid-Atlantic were more common during the summer of 2009, and that the subtropical high was more frequently located farther northeast in the Atlantic. This flow regime typically brings clean and cool marine air into the mid-Atlantic region, thereby reducing ozone concentrations. Air temperatures during this time were approximately 0.5°C above the 1981-2010 average, and the relative humidity was 2 to 4% greater (Figures 14 and 15).

In contrast, during June 2010, the lowest layers experienced flow anomalies indicative of a subtropical high consistently situated nearer to the coast and farther south than in 2009. Specifically, the flow anomaly was westerly south of the mid-Atlantic and easterly north of the study region relative to the 1981-2010 climatological mean, bringing MT air from the Gulf and modifying it over the southeast. This air passed over the region west of the mid-Atlantic which
was notably 2 to 2.5 °C warmer than the 1981-2010 average, with a relative humidity up to 3% lower.

![Figure 12](image1.png)

**Figure 12.** Vector wind (m/s) composite anomaly at 925 mb for June (a) 2009 and (b) 2010.

![Figure 13](image2.png)

**Figure 13.** Vector wind (m/s) composite anomaly relative to the 1981-2010 climatological mean at 850 mb for June (a) 2009 and (b) 2010.
Figure 14. Air temperature (°C) composite anomaly at 850 mb for June (a) 2009 and (b) 2010.

Figure 15. Relative humidity (%) composite anomaly at 850 mb for June (a) 2009 and (b) 2010.

In addition to the dissimilarity between climatological anomalies in flow patterns, air temperature and moisture content, ozonesonde profiles from Wallops Island also differ substantially between June 2009 and June 2010. Profiles collected for June 2009 exhibit decreased ozone volume mixing ratios below 5 km relative to the mean profile for May through August, for 2005 through 2010 (Figure 16a). In contrast, this average is exceeded by most of the profiles collected during June 2010 below 5 km, indicating enhanced ozone concentrations in the PBL during 2010 versus reduced concentrations in the PBL during 2009 (Figure 16b). The
middle and upper profiles layers of the profiles for both years are close to the average, suggesting that lower tropospheric ozone content significantly impacts tropospheric column values. The contribution of PBL ozone to the total tropospheric integrated column is explored in the next section.

![Ozone Change with Height: 2009](image1) ![Ozone Change with Height: 2010](image2)

**Figure 16.** Ozonesonde profiles during June (a) 2009 and (b) 2010. The red line represents the mean for all summer profiles between 2005 and 2010; the green lines represent the standard deviations for the summer profiles. The difference between the mean and standard deviation is highlighted by grey shading.

Given the disparities in prevailing flow patterns, air temperature and relative humidity over the mid-Atlantic between 2009 and 2010, different signals of coastal air pollution transport are also expected. This is because the urban centers of Washington, D.C., Baltimore and Philadelphia are upwind of Wallops Island for westerly winds and will therefore impact the air quality offshore for this flow regime. Urban pollution will substantially replace cleaner marine air off the coast for flow from the west, but flow from the east cannot significantly counteract and diminish urban signatures. Correlations between the TTOR sample points along the coastline and offshore are examined for 2009 and 2010. For both years, the correlation is strongest for Wallops and the closest offshore point 2 (R² = 0.78 in 2009, R² = 0.90 in 2010), and weakest for Washington, D.C. and point 2 (R² = 0.27 in 2009, R² = 0.38 in 2010). This is expected as Wallops and point 2 are 110 km apart; Wallops and point 3 are 156 km apart; Wallops and Washington, D.C. are 245 km apart; Washington, D.C. and point 2 are 345 km apart. The regional correlations between Wallops and points offshore as well as between Washington, D.C. and points offshore are stronger for all points during the summer of 2010 versus during the summer of 2009. Notably,
the correlation between Wallops and point 2 during 2010 is greater than the correlation for the data from 2005 through 2010, meaning that this year experienced significantly increased production of ozone along the coast, and that this enhanced ozone formation substantially diluted the cleaner marine air off the coast via advection eastward.

\[ R^2 = 0.78 \]

\[ R^2 = 0.34 \]

\[ R^2 = 0.54 \]

\[ R^2 = 0.27 \]

**Figure 17.** Correlations between TTOR points for the summer of 2009.
Figure 18. Correlations between TTOR points for the summer of 2010.

The dissimilar airmass frequencies that characterize summer 2009 versus summer 2010 point to variations in the prevailing flow patterns, air temperatures, and moisture levels, and these differences relate to disparities in offshore transport of ozone. Air mass frequencies therefore help identify major differences in synoptic-scale meteorological conditions that favor or impede ozone production in the lower troposphere. Furthermore, the cool, moist conditions and onshore vector wind anomaly of June 2009 in the mid-Atlantic are related to a negative (low) TTOR bias,
whereas the warm, dry conditions and largely offshore vector wind anomaly of June 2010 correspond to a positive (high) TTOR bias. A study of tropospheric columns over Beltsville, Maryland during the summers of 2004-2007 showed that nearly 60% of the columns are influenced by advection into the region. Thus, the substantial differences in flow regime may significantly influence the tropospheric ozone column (Yorks et al., 2009). This addition or removal of tropospheric ozone from the climatological norm will result in greater differences between the ozonesonde and the TTOR product; varying meteorological conditions significantly impact satellite retrieval accuracy and may account for changing accuracy among air mass types, seasons, and years.

3.3 Planetary Boundary Layer Impacts

Emissions of ozone precursors occur in the planetary boundary layer (PBL) and accurate detection of this near-surface layer remains a challenge for remote sensing of regional air quality (Godish, 2003; Martin, 2008). Vertical profiles of ozone exhibit a strong influence of ozone enrichment or deficiency in the lowest 5 km on average. This near-surface layer appears to dominate the tropospheric integrated column and contributes to disagreement with the TTOR product. This section addresses the following science questions: i) Is PBL integrated column ozone consistent among seasons and among years? ii) Which layers of the lower troposphere exhibit the greatest transport influence of ozone? iii) How do fraction of tropospheric height and tropospheric ozone in the PBL vary with air mass type?

Integrated column ozone in the PBL will vary directly with PBL depth, that is, a deeper PBL will encompass a larger amount of ozone, and the conditions conducive to enhanced PBL growth are similarly favorable to ozone production (Rappenglueck et al., 2008; Banta et al., 2011). The PBL column ozone increases during the warmer months due to both increased photochemical production and due to greater mixing layer depths (Figure 19). PBL ozone reaches a maximum in August, with the highest column ozone values occurring during July through September. This maximum is slightly offset from that of the troposphere which displays an integrated column ozone peak in July and three-month maximum between June and August. The PBL ozone delay relative to the troposphere may be attributed to the increased usage of NO\textsubscript{x}-emitting air conditioners during the later summer months, as well as the thermal lag in tropospheric heating during increased solar insolation (Jacobson, 2002).

As in the tropospheric time series, the PBL time series displays a departure from the increasing spring to summer upward trend during May. This decline may be due to the seasonal
shift from a winter VOC-limited to a summer NOx-limited regime in the mid-Atlantic. Reduced transport from the west during the spring also impacts the eastern coast ozone concentration especially at the near surface.

![Mean integrated column ozone in the PBL at Wallops Island as reported by the ozonesondes by month for all years. Error bars represent the 95% confidence interval.](image)

**Figure 19.** Mean column ozone in the PBL at Wallops Island as reported by the ozonesondes by month for all years. Error bars represent the 95% confidence interval.

To examine the distribution and magnitude of ozone in the PBL, 11 layers of integrated column ozone are evaluated, each 25-mb deep, from 725 mb up to 975 mb. These layers will be referred to as Integrated Lower Tropospheric Columns, or ILTCs, for the remainder of this thesis. During summer in the mid-Atlantic, 725 mb corresponds roughly to 3 km; 850 mb corresponds approximately to 1600 m; 975 mb corresponded roughly to 500 m. Polar graphs illustrate the wind speed, direction, and integrated column ozone at 750 mb (Figure 20a), 800 mb (20b), and 925 mb (20c).

Moving down through the troposphere the wind speed decreases because of increasing friction near the surface and because of decreasing thermal wind effects. Within the 750 mb ILTC, westerly winds occur 21% of the time and account for 18% of the ILTC ozone; NE winds occur 21% of the time and account for 17% of ozone; NW winds occur only 9% of the time but account for 17% of ozone. Within the 800 mb ILTC, NE, W and NW winds occur 21%, 20%, and
9% of the time, respectively, and account for 17%, 17% and 18% of the ILTC ozone. The ILTC encompassing 925 mb experiences flow from all directions; each direction contributes approximately 11 to 13% of the resulting total ozone in the layer.

The ILTC ozone varies by pressure level and by wind direction, and the mean of each 25-mb layer of ozone by wind direction is presented in Figure 21. Because the layers are shallow, the ILTC ozone values are small, on the order of 0.5 to 2.0 DU. Enhanced ozone values occur for SE winds at several levels: the greatest occurs for 850 mb, and slightly smaller for 900 mb, 925 mb, 825 mb, 750 mb. ILTC ozone ranges from 1.1 to 1.3 DU for all 25-mb layers for winds from the SE.
SW, W, NW and N. Winds from the E, SE, S and NE display the greatest variability of ILTC ozone by pressure layer, although easterly flow results in reduced ozone at all levels except 800 mb relative to other directions.

The greatest ozone values occur for the 850 mb and 900 mb ILTCs when wind flows from the SE, although all ILTCs display ozone peaks for NE and W winds. As shown in the polar graphs, lower ILTCs display a more even spatial distribution of winds; high ILTCs show flow more concentrated from the W, NW and N. By wind direction, the lower ILTCs also display slightly different ozone patterns relative to those of higher ILTCs (Figure 21). The variation of ILTC ozone by wind direction is stratified by ILTC height, indicating that lower tropospheric concentrations do not significantly impact layers above. This is consistent with PBL depths observed for summers in the mid-latitudes (<2500 m) as the PBL does not frequently penetrate the highest ILTCs. Increased wind speeds may allow these layers to avoid stagnation, thereby facilitating ozone production, although this only matters if these layers occur within the PBL.

In contrast to these upper ILTCs, lower layers experience greater frictional drag from the surface, causing increased ozone deposition, and titration from higher NOx concentrations (Ryan, 2002). Moreover, 850 mb typically occurs at 1,500 m during the summer in the mid-Atlantic, and so this pressure level indicates the layer just above the PBL top, or the residual layer. These interactions ultimately yield the greatest ozone values for the middle 25 mb ILTCs, 850 mb and 900 mb.

Figure 21. Integrated column ozone (DU) (y-axis) by wind direction bin (x-axis) and pressure level (mb) (colored lines).
The relative contributions of each direction to the lower tropospheric integrated layer ozone are shown in Figure 22. By frequency, the majority of cases involve flow from the NE, NW, W and SW, with less from the N and S. Very few cases display flow from the E and SE. By percentage, the W and NW wind regimes are largely observed at the upper levels, whereas N, NE, SW and S are evenly divided between layers. Flow from the E and SE is dominated by winds in the lowest layers.
Winds from the SE occur infrequently, yet account for the largest 25-mb integrated columns of ozone in the lower troposphere. Examination of the specific dates during which SE flow occurred shows that two distinct synoptic regimes yield southeasterly flow into the study region and explain the elevated ozone values. The first synoptic pattern entails anticyclonic flow from the Gulf of Mexico over the southeastern U.S. and into the mid-Atlantic (Figure 23). Such flow is characteristic when the subtropical high is positioned off the southeastern coast of the U.S. This regime brings modified marine air into the region and the heavily urbanized and industrialized SE account for enhanced ozone concentrations. This air is moist, with relative humidity values near 90%. Notably, the long-range back-trajectories arrive from the SW and not from the SE, indicating that small-scale circulation of the air over the region accounts for the detection of SE flow into Wallops Island.

Figure 22. Instances observed for each wind sector and for each pressure level by (a) number frequency, and (b) percentage of total for that direction bin.
Figure 23. Backward trajectories ending at 0000 UTC on May 3, 2010. The lines represent flows ending at altitudes of 500 m (red), 1500 m (blue) and 3000 m (green) at Wallops Island, VA.

The second dominant flow regime that accounts for southeasterly winds occurs when air originating from the N and NE moves into the mid-Atlantic and recirculates under stagnant conditions associated with a high pressure system located farther NW than for the previous flow regime (Figure 24). Because the long-range flow arrives from the NW, it is this recirculation in the study region that accounts for classification of SE flow as identified by NARR. The Canadian source region and high altitude of this air explains the very low relative humidity of the resulting SE winds: 27-30%. Notably for the May 10 2010 example shown, the 3000 m backward trajectory passes through altitudes greater than 6000 m, drying the air and increasing chances for mixing with higher-ozone air from a stratospheric intrusion before moving into the mid-Atlantic. Despite their differences in moisture content, temperature, and geographical location relative to the mid-Atlantic, both the Gulf of Mexico and Canadian source regions yield enhanced ozone concentrations for flow into Wallops Island. This finding negates the assumptions that polar air
masses and marine source regions will always yield “clean air” with reduced tropospheric ozone. In this way, examination of ozone values and flow regime into the study region at layers within the lower troposphere provides new insight into the synoptic patterns and meteorological conditions conducive to increased ozone.

![Figure 24](image.png)

**Figure 24.** Backward trajectories ending at 0000 UTC on May 10, 2010. The lines represent flows ending at altitudes of 500 m (red), 1500 m (blue) and 3000 m (green) at Wallops Island, VA.

Examination of the complete lower troposphere shows that integrated column ozone in the PBL varies between 2005 and 2010, ranging from 7.0 to 8.0 DU between 2005 and 2007 before falling to about 6.0 DU during 2008 and 2009 (Figure 25). The interannual peak in PBL ozone occurred in 2010 at 9.0 DU, coinciding with enhanced ozone pollution conditions as previously mentioned. This correlation indicates that a substantial portion of increased tropospheric ozone is attributable to the PBL. It is important to note, however, that the PBL depth was also greatest in 2010 relative to the previous five years. To account for this proportionate
variation in PBL ozone amount with PBL depth, the fractions of tropospheric ozone and tropospheric altitude encompassed in the PBL are developed and compared. These fractions are computed as follows:

Fraction of tropospheric ozone in the PBL = PBL ozone / ozonesonde tropospheric ozone;
Fraction of tropospheric depth in the PBL = PBL depth / ozonesonde tropospheric depth.

By comparing these fractions instead of the PBL ozone and height values directly, the errors introduced by diurnal and seasonal influences on depth are reduced.

![Figure 25](image.png)

**Figure 25.** Mean column ozone in the PBL (DU) at Wallops Island as reported by the ozonesondes by year for May through August. Error bars represent the 95% confidence interval.

It is expected that the fractions of troposphere depth and ozone in the PBL will vary proportionately. That is, a deeper mixed layer will encompass a greater fraction of both troposphere depth and tropospheric ozone. Instances in which the fractions are unequal indicate conditions when ozone in the PBL is disproportionately contributing to or detracting from the tropospheric column. Such conditions are represented by daily air mass classification or SSC. Comparing the relationship between SSC and tropospheric column ozone to the relationship between SSC and PBL ozone may illuminate the extent to which pollution in the lower troposphere influences total tropospheric pollution development and concentration.
Integrated column ozone in the PBL varies substantially by SSC (Figure 26). The greatest near-surface ozone amount results for dry conditions, with the maximum ozone occurring on average for DT days: 10.0 DU. This follows as dry, warm days are associated with increased sunlight and often with high pressure subsidence conditions favorable to photochemical ozone production. Moist air masses, associated with increased cloud cover and precipitation, yield lower PBL ozone, and MP days result in the minimum near-surface ozone, on average: 4.0 DU.

![Figure 26](image.png)

**Figure 26.** Mean column ozone in the PBL (DU) by air mass type for May through August. Error bars represent the 95% confidence interval.

For all air mass types except MP, the fraction of tropospheric ozone in the PBL is greater than the fraction of troposphere depth in the PBL (Figure 27). This follows as ozone precursor emissions occur in the mixed layer, resulting in a substantial contribution to the tropospheric column from the near-surface. In contrast with the integrated column ozone amount in the PBL, the greatest ozone and depth fractions result for DP days; the second highest fractions occur during DT days. The synoptic-scale flow regime from the north that typically yields DP identification, however, is likely correlated with stronger westerly and northwesterly flow than DT air moving into the region from the west and south, and this lower tropospheric flow results in greater vertical mixing of horizontal wind speeds. Additionally, the cooler air aloft associated with a DP air mass allows for a deeper PBL via encroachment (Yanai, 1994).
Dry air mass types yield greater differences between ozone and depth fractions (~5%), on average, than moist air masses (~2%), although MT is an exception and also displays a substantial difference between ozone and depth fractions (~5%). On average, the fraction of tropospheric ozone in the PBL is 7% greater than the fraction of troposphere depth in the PBL for DT air mass days. In contrast, MP displays a reversal in the pattern: the fraction of tropospheric ozone in the PBL is outweighed by the fraction of troposphere depth in the PBL. The deviation from this pattern on MP days is indicative of significant reduction in ozone production due to cloud cover and increased specific humidity. Moreover, in the mid-Atlantic, MP air in particular is associated with frontal overrunning and the movement of marine air from the northeast or east to the north of the frontal boundary. This flow regime from the northeast, however, results generally from cyclonic circulation around a surface low pressure system, and such conditions are known to result in a deeper mixed layer (e.g. moist convection) (Jacobson, 2002). MP conditions are associated with reduced PBL ozone and increased depth of the mixed layer through the troposphere, thus yielding a reversal in the ratio of the ozone and depth fractions.

Figure 27. Mean fraction of tropospheric ozone and depth in the PBL and mean temperature (Celsius) within and at the top of the PBL at Wallops Island by air mass type for May through August. Error bars represent the 95% confidence interval.
As shown in Figure 26, the PBL column ozone is reduced for MM and MP air masses. Moist air mass types also result in the lower PBL depths during the summer months as they represent cool, humid conditions, often with precipitation, and are linked to increased cloud cover. This cloud coverage limits the amount of downward solar radiation reaching the ground, yielding reduced thermal eddy development, less turbulent mixing, and therefore lower PBL depths (Jacobson, 2002). Thus, since both PBL integrated column ozone and PBL depth are diminished for MM and MP air masses, the fractions of tropospheric values for each are more similar than for the other air mass types. In contrast, there exist large differences between the PBL fraction of tropospheric ozone and depth for DM, DP, DT and MP air mass types. The varying differences between ozone fraction and depth fraction by air mass type indicates that the PBL contribution to the total tropospheric ozone column is influenced by air mass conditions.

As shown in Figure 27, PBL integrated column ozone and depth relative to tropospheric ozone and depth are typically unequal. As noted in prior sections, the meteorological conditions represented by the SSC directly impact both the depth of the PBL and its constituent ozone. The variation in these ratios by air mass type supports the hypothesis that air mass type directly influences the contribution of near-surface ozone to the total tropospheric column. For DP and MP days (Figure 28, left) and for DT and MT days (Figure 28, right), the integrated column ozone in the PBL versus PBL depth are given along the upper row, and the fraction of tropospheric ozone in the PBL versus fraction of tropospheric altitude in the PBL are given along the lower row. For those air masses less advantageous for ozone formation (DP, MP), the rate of change of PBL ozone with PBL depth is lower (slope = 0.0038) than for air masses favorable for ozone production (slope = 0.0051). The same pattern holds for the relationship between the PBL ozone and PBL depth fractions. For DP and MP days, the fraction of tropospheric ozone in the PBL changes with the fraction of troposphere depth in the PBL with a ratio of 1.11; for DT and MT days this rate of change is quantified by a slope of 1.48.

Conditions conducive to ozone formation, as represented by DT and MT air mass types, exhibit a greater change in PBL ozone with change in PBL depth than those conditions unfavorable to ozone formation, as represented by DP and MP air mass types. This difference indicates that the tropospheric ozone column is disproportionately influenced by PBL ozone for ozone-favorable air mass conditions. Moreover, this enhanced PBL contribution of ozone may be a factor in the ozonesonde-TTOR differences described prior because satellite detection of near-surface ozone remains limited (Martin, 2008).
**Dry Polar and Moist Polar**

![Graph](image)

\[ y = 0.0038x - 0.2 \quad R^2 = .76 \]

**Dry Tropical and Moist Tropical**

![Graph](image)

\[ y = 0.0051x - 0.2 \quad R^2 = .88 \]

**Dry Polar and Moist Polar**

![Graph](image)

\[ y = 1.11x - 1.03 \quad R^2 = .84 \]

**Dry Tropical and Moist Tropical**

![Graph](image)

\[ y = 1.48x - 0.4 \quad R^2 = .90 \]

**Figure 28.** Change in PBL column ozone with PBL depth and change in PBL column ozone fraction of tropospheric column ozone with change in PBL depth fraction of troposphere depth for (a, b) Dry Polar and Moist Polar days and (c, d) Dry Tropical and Moist Tropical days.
3.4 Analysis of Variance (ANOVA)

Tropospheric ozone varies as a function of meteorological parameters such as temperature, cloud cover, wind speed and direction, and as a function of biogenic and anthropogenic emissions (e.g., Comrie, 1990; Comrie and Yarnal, 1992; Liu et al., 1994; Poissant et al., 1996; Xu et al., 1997; Seinfeld and Pandis, 1998; Sillman, 1999; Davis et al., 2010). Given the complexity of tropospheric ozone formation, examination of multiple factors together will yield new insight into its development and distribution in the mid-Atlantic. Analysis of variance (ANOVA) is a useful statistical tool for evaluating situations in which there exist multiple independent variables because it determines how these independent variables interact and what effects these interactions have on the dependent variable (Sokal and Rohlf, 1994). In ANOVA testing, an effect is applied to a dataset and the resulting groups are then evaluated for statistical differences in their means. ANOVA ultimately tests for significant differences between the means of groups.

The dependent variable for the present study is TTOR product integrated column ozone. The major influences on ozone values, the independent variables, are identified as follows: i) synoptic scale wind flow (advection term), provided by the North American Regional Reanalysis (NARR) wind data; ii) cloud cover (incoming solar radiation), that is also provided by NARR; iii) meteorological conditions, provided via the Spatial Synoptic Classification (SSC); iv) precursor emissions, which are provided as nitrogen dioxide (NO₂) column density from the Ozone Monitoring Instrument aboard the AURA platform. In using the ANOVA technique, this section addresses the following science questions: i.) how does measured ozone statistically significantly change with the major influencers? ii.) what combinations of factors yield statistically significant interaction effects on ozone? iii.) what combinations of conditions yield the greatest ozone values?

One-way ANOVAs conducted for each independent variable individually produced distinct patterns of resulting ozone values (Table 1). The greatest tropospheric ozone resulted for limited cloud cover, for DT and MT air mass conditions, for winds from the N, NW, NE and SW, and for high and high moderate precursor emission levels. These patterns occur, however, only approximately 20% to 60% of the time for wind direction and cloud cover, respectively, indicating that anomalies from these norms also occur with relative frequency and are difficult to anticipate.
Table 1. Typical patterns for major ozone influencers. Statistical significance is determined as \( p < 0.05 \).

Building upon the ANOVAs conducted for one independent variable, ANOVAs with interaction effects are run for multiple independent variables. Evaluation of the TTOR product at Wallops Island as a function of SSC and \( \text{NO}_2 \) column density at Washington, D.C. exhibits results that would not be expected if only one independent forcing were considered. The greatest column ozone results for DP air mass days and for high moderate precursor concentration upwind in Washington, D.C., yielding nearly 55.0 DU. Recall that the maximum ozonesonde tropospheric integrated column ozone resulted for DT conditions for the ozone-SSC analysis. High ozone is also generated for moderate and low moderate precursor density for MP days, at about 48.0 DU. Low column ozone, between 34.0 and 38.0 DU, results for very low, high, and very high precursor conditions occurring in conjunction with DM, MM and MP air mass days, whereas moderate ozone, between 38.0 and 55.0 DU, is the outcome for DP, DT, and MT days for nearly all concentration types.

Because \( \text{NO}_x \) and ozone are not linearly related, greater column densities do not necessarily yield greater tropospheric ozone (Seinfeld & Pandis, 1998). For example, the influence of high and very high precursor values is countered by the MP air mass type, yielding a reduced column of ozone to less than 40 DU. Examination of SSC and \( \text{NO}_2 \) column density upwind together, however, provides new information about the conditions conducive to the highest ozone values. These results suggest that the relationships between ozone and SSC and between ozone and \( \text{NO}_2 \) are themselves dependent on additional ozone influences. These interactions therefore may obscure the true causes of tropospheric ozone variability in the mid-Atlantic.
Figure 29. Analysis of variance with interaction effects for the TTOR product of integrated column ozone (DU) at Wallops Island, Va. as a function of Spatial Synoptic Classification (SSC) and of NO₂ column density at Washington, D.C.
Chapter 4. Discussion and Conclusions

The comparison between the integrated tropospheric column of ozone provided by the ozonesonde and the Trajectory-Enhanced Tropospheric Ozone Residual (TTOR) product retrieved via the Ozone Monitoring Instrument (OMI) varies substantially by month, by year, and by air mass type. Interannual variations in the summer ozonesonde-TTOR comparison show an enhanced TTOR product high bias in 2010 relative to a low bias for most of the previous five years. The positive TTOR bias in 2010 is in sharp contrast to 2009 when the TTOR biased low relative to the ozonesonde. Ozonesonde profiles indicate that ozone concentrations below 5 km dominate the differences between the in situ and satellite measurements.

Daily air mass type significantly influences tropospheric ozone values, resulting in greater measurement differences between the ozonesonde and TTOR product for the extreme types of Dry Tropical (DT) and Moist Polar (MP). For DT and Moist Tropical (MT) conditions, the TTOR biases low relative to the ozonesonde with 11% error; for MP conditions, the TTOR biases high with 25% error. The TTOR bias also exhibits a strong relationship with differences in air mass frequencies, correlating with varying summertime conditions of temperature, moisture, and synoptic wind flow in the mid-Atlantic between June 2009 and June 2010. The differing flow regimes during the two summers in turn impact regional correlations between coastal and marine TTOR integrated column ozone values, pointing to enhanced urban outflow during 2010. Furthermore, the TTOR biased low relative to the ozonesonde by nearly 10.0 DU during June 2009 and high by 2.0 DU in 2010. Ozonesonde profiles collected during these months identify the lowest 5 km, including the planetary boundary layer (PBL) as the dominant influence on the resulting TTOR biases.

PBL ozone varies substantially by month and by year, ranging from 4.0 DU (December) to 8.0 DU (August), and exhibiting an interannual minimum in 2009 at 6.0 DU, and maximum in 2010 at 9.0 DU. Wind speed decreases and wind direction becomes less westerly and northwesterly moving down from 725 mb to 975 mb, and while only the lowest 25-mb layers experience easterly and southeasterly flow, the ozone values are greatest for flow from the SE at 850 mb, 900 mb, 925 mb, and 825 mb. Flow from the Gulf of Mexico over the urbanized southeast and from the interior of Canada over the Ohio River Valley yield moist and dry 25-mb layers, respectively, and account for the enhanced ozone values associated with SE winds.

The correlation between PBL ozone fraction of the tropospheric column and PBL depth fraction of the troposphere are significantly impacted by air mass type. As compared to Dry Polar (DP) and MP air mass days, DT and MT conditions yield a sharper increase in PBL ozone
relative to PBL depth, as well as a greater rate of change in the fraction of tropospheric ozone within the PBL with change in the fraction of tropospheric altitude within the PBL. This difference in slope indicates that the tropospheric ozone column is disproportionately influenced by PBL ozone for ozone-conducive (DT and MT) air mass conditions. This enhanced PBL contribution to the troposphere may also be a factor in the ozonesonde-TTOR differences.

Analyses of variance (ANOVA) show that each independent variable statistically significantly influences tropospheric ozone, although deviations from the typical resulting patterns occur regularly. Evaluation of multiple factors together, such as SSC and NO₂ column density, within an ANOVA conducted with interaction effects yields ozone value patterns that are different than those produced when SSC or NO₂ column density are considered alone. Specifically, the results suggest that when characterizing the ozone climatology of the mid-Atlantic, there is sufficient “value added” in considering both the meteorological conditions and the precursors conditions upwind. This result indicates that the relationships between tropospheric ozone and each independent variable are themselves significantly impacted by interactions with other primary ozone influencers. In this way, examining interaction effects provides more information than is obtained from a one-way ANOVA with a single independent factor. Further analyses of these interaction effects are necessary to improve our understanding of the conditions that govern high ozone days in the mid-Atlantic region.
Chapter 5. Future Work

Validation of satellite products remains an ongoing area of research. With the inclusion of additional years of ozonesonde and satellite records over a broader region, the work of this thesis may be expanded and advanced. The present study may prove illuminating, as well, in contrast to a similar analysis conducted for another type of location, such as an inland, urban, mountainous region, to evaluate the extent to which the Wallops Island coastal location relative to Washington, D.C. contributes to the patterns observed. Examination of the concurrent climatology of stratospheric column ozone for the mid-Atlantic provided by the Aura MLS will also serve to reduce error in this analysis, since the TTOR product is derived from the total column ozone minus the stratospheric contribution.

While the TTOR product exists only for recent years, the ozonesonde climatology can be extended to its earliest records collected in 1970 to evaluate multidecadal climatology for the ozone in this region. Moreover, SSC values are available since 1948, and can be included in this analysis. Incorporation of air quality models will also provide new insight (and a more temporally and spatially complete dataset) into the production, transport, and variability of mid-Atlantic tropospheric ozone, especially within the PBL.
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