Surface Ozone and Total Reactive Nitrogen Concentrations

over the Chesapeake Bay during DISCOVER-AQ

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Abstract

Air quality models, such as the Community Multiscale Air Quality (CMAQ) model, indicate decidedly higher ozone near the surface of large interior water bodies, such as the Great Lakes and Chesapeake Bay. In order to test the validity of the model output, we performed surface measurements of ozone (O_3) and total reactive nitrogen (NO_y) on the 26-m Delaware II NOAA Small Research Vessel experimental (SRVx), deployed in the Chesapeake Bay for 10 daytime cruises in July 2011 as part of NASA's GEO-CAPE CBODAQ oceanographic field campaign in conjunction with NASA's DISCOVER-AQ air quality field campaign. The EPA O_3 regulatory standard of 75 ppb averaged over an 8-hour period was exceeded three times during the 10-day period while ground stations in the area only exceeded the standard at most once. This suggests that there are days when the Baltimore/Washington region is in compliance with the EPA standard, but air quality over the Chesapeake Bay is exceeding the EPA standard. Further data analysis has shown that ozone observations over the bay during the afternoon were consistently 10% - 20% higher than the closest upwind ground sites during the 10-day campaign; this pattern persisted during good and poor air quality days. We suggest that a combination of complex boundary layer dynamics, reduced cloud cover, and slow deposition rates, among other lesser mechanisms are playing an integral role in the local maximum of ozone over the Chesapeake Bay. Observations from this campaign were compared to a CMAQ simulation at 1.33 km resolution. The model is able to accurately predict the regional maximum of ozone over the Chesapeake Bay, but simulations of NO_y are significantly overestimated. Explanations for the overestimation of NO_y in the model simulations are also explored.

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1. Introduction

Surface ozone, in high enough concentrations, is a hazardous secondary air pollutant regulated by the United States Environmental Protection Agency (U.S. EPA). As of 2013, the U.S. EPA has set an ambient 8-hour daily maximum concentration of 75 parts per billion by volume (ppbv) as the threshold for compliance under a set of regulations known as the National Ambient Air Quality Standards (NAAQS). This standard has been set based on several health studies {Anenberg et al., 2010} {Bell et al., 2004} {Fann et al., 2011} that show inhaling ozone can lead to premature aging of the lungs, difficulty breathing, increased risk of asthma attacks, and in rare cases death.
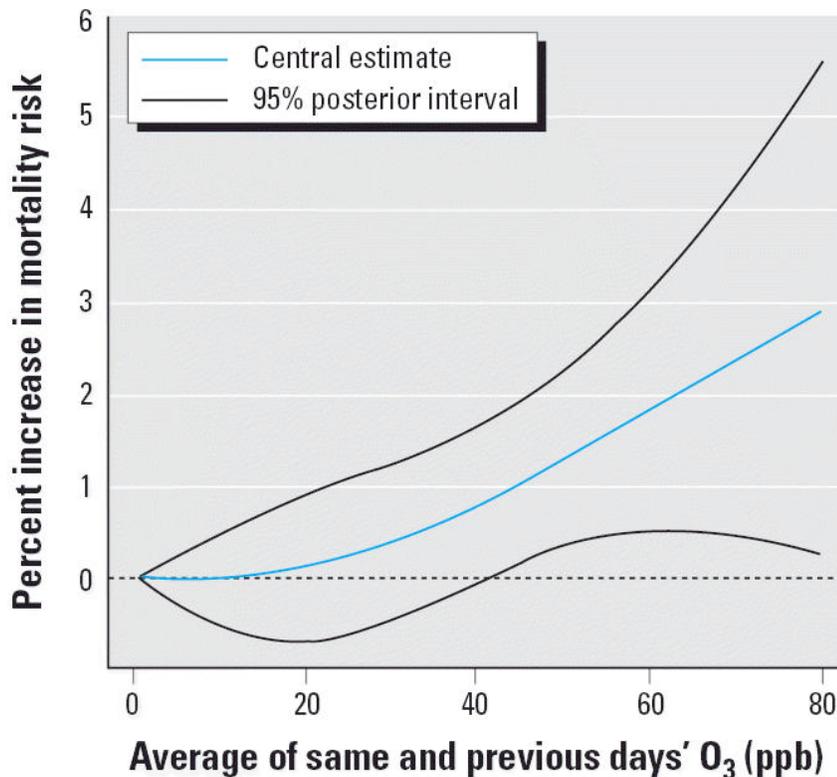
Figure 1. Percentage increase in daily nonaccidental mortality at various O_3 concentrations. Adapted from Bell et al. (2006)

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Air quality models such as the Community Multiscale Air Quality (CMAQ) model indicate decidedly higher ozone near the surface of large interior waters bodies such as the Great Lakes and Chesapeake Bay {e. g., Godowitch et al., 2008}.
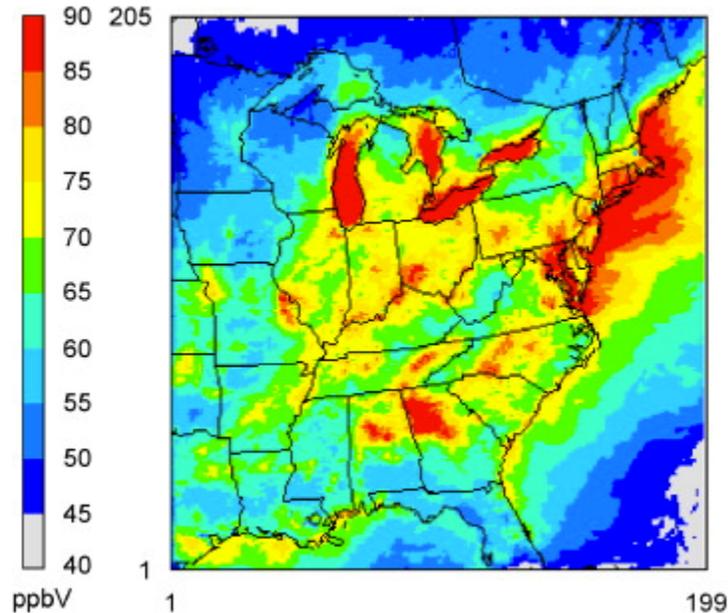
Figure 2. Maximum 8-hour O_3 concentration fields at the 95th percentile from base case results from the Summer 2002. Adapted from Godowitch et al. (2008)

In order to test the validity of the model output, we performed surface measurements of ozone (O_3) and total reactive nitrogen (NO_y) on 26-m Delaware II NOAA Small Research Vessel experimental (SRVx), deployed in the Chesapeake Bay for 10 daytime cruises in July 2011. The objectives of this paper are to:

- Compare ozone observations over the Bay to nearby land areas
- Determine if ozone concentrations are indeed higher over the Bay
- Determine if known meteorological and chemical processes can explain the observed differences
- Investigate whether model resolution plays a role in determining the simulated surface ozone concentrations over the Bay
- Investigate NO_y observations to determine if this group of precursors is accurately predicted by the model simulations

1.1 Current EPA Regulations and Designations

The U. S. EPA has shown a "moderate" non-attainment region in the counties surrounding Baltimore, MD and a "marginal" non-attainment region throughout the New York City-Philadelphia-Washington, D.C. metropolitan corridor {U.S. EPA 2008}. A "moderate" attainment region is an area that has a ground station that exceeds an 8-hour maximum concentration of 85 ppbv O_3 in its 3rd highest day, while a marginal attainment region has a threshold of 75 ppbv.

The Baltimore/Washington metro region currently exceeds the EPA threshold for O_3 between 20 and 40 days per year as seen data from the Maryland Department of the Environment in Figure 3. This is in stark contrast to 30 years ago, when exceedance of the EPA threshold routinely occurred between 60 and 80 days per year.
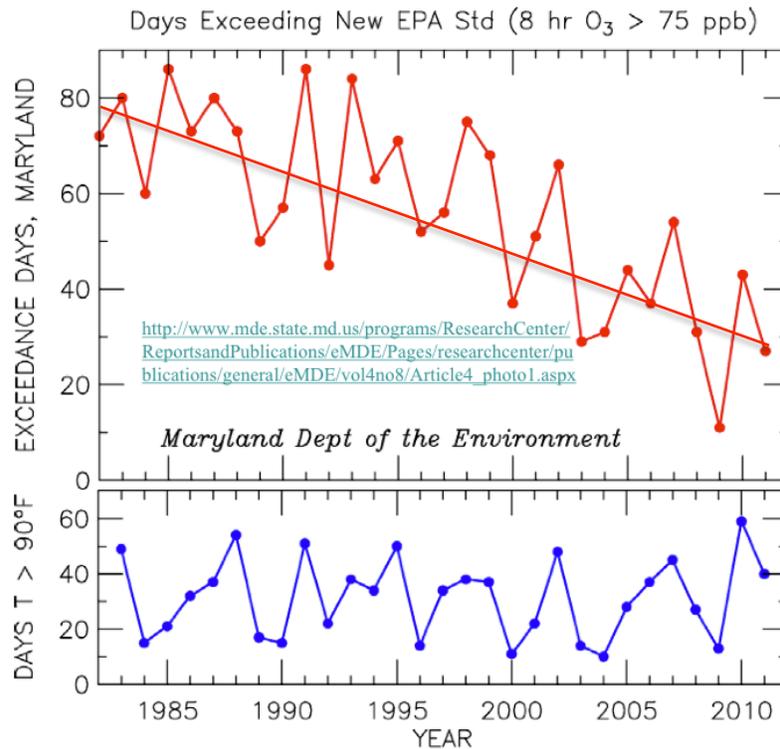
Figure 3. Data from the Maryland Department of the Environment (MDE) showing the number of O_3 exceedance days per year and temperature at the BWI airport above 90° F. Adapted from Ross J. Salawitch

The exceedances occur due to ideal meteorological conditions for ozone production during the summer months and substantial ozone precursor emissions, generated locally as well as advected to the region during strong westerly transport conditions {Ryan et al., 1998}{He et al., 2012}.

Peaks in surface ozone are highest just downwind of major metropolitan areas due to the enhanced emissions from the metropolitan city centers {Kleinman et al., 2000}. This has been shown in many air quality model simulations {Yegorova et al., 2011} {Castellanos et al., 2011} and has been verified by ground monitoring stations {U.S. EPA, 2006} {Castellanos et al., 2009}. In the Baltimore-Washington region there are complex interactions that arise with the influence of the Chesapeake Bay breeze {Loughner et al., 2011; 2013} {Stauffer et al., 2012}, which have not been fully investigated.

1.2 Surface Ozone Chemistry

Reactive nitrogen species and volatile organic compounds (VOCs), emitted by natural and anthropogenic sources, photochemically react to create ozone {Seinfeld and Pandis 2006}. This classifies ozone at the surface as a secondary pollutant: a chemical that is produced in the atmosphere rather than emitted.

The first step of surface ozone formation is the oxidation of VOCs or CO by the hydroxyl radical (OH) to create the peroxy radical (HO_2). Once the HO_2 radical is formed, it must attack a NO molecule to oxidize it to NO_2. At wavelengths hv < 420 nm, NO_2 will photodissociate into NO and $O(^3P)$. The excited $O(^3P)$ atom will quickly combine with O_2 to create O_3. A summary of ozone formation reactions from CO and CH_4 are given below {Seinfeld and Pandis, 2006}:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
$$HCHO + hv \rightarrow H + HCO$$
$$CO + OH \rightarrow CO_2 + H \qquad\qquad HCO + O_2 \rightarrow HO_2 + CO$$
$$H + O_2 + M \rightarrow HO_2 + M \qquad\qquad H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow NO_2 + OH \qquad\qquad 3\ (HO_2 + NO \rightarrow NO_2 + OH)$$
$$NO_2 + hv \rightarrow NO + O(^3P) \qquad\qquad 4\ (NO_2 + hv \rightarrow NO + O(^3P))$$
$$O_2 + O(^3P) \rightarrow O_3 \qquad\qquad 4\ (O_2 + O(^3P) \rightarrow O_3)$$

Net: $\quad CO + 2O_2 + hv \rightarrow CO_2 + \boldsymbol{O_3} \qquad CH_4 + 8O_2 + hv \rightarrow CO + H_2O + 2OH + \boldsymbol{4O_3}$
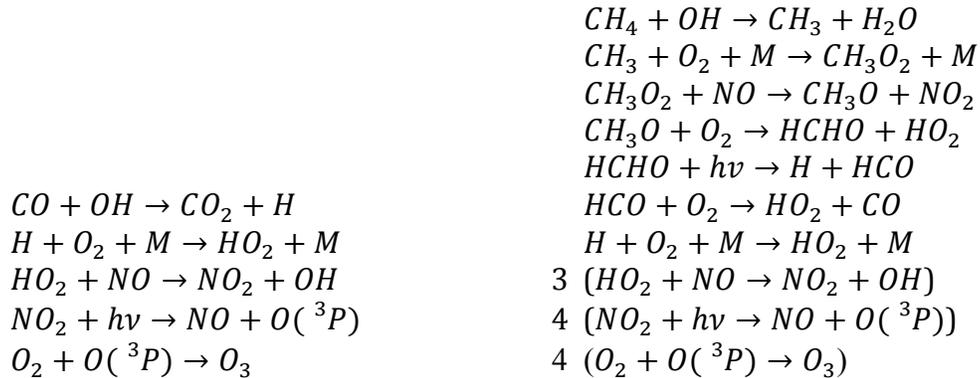
Warm temperatures, along with a capping inversion, associated with a strong summer anticyclone traps the ozone near the surface leading to rapid growth of ozone during the late morning and early afternoon.

1.3 Previous Field Campaigns over Interior Water Bodies

Measurements over the Great Lakes showed that the ozone was indeed higher over Lake Erie and this was leading to higher concentrations along the coastline of the lake {Levy et al., 2010}. An experiment in 2003 measured ozone at the Chesapeake Bay Lighthouse, located on an island 15 miles to the east of the entrance to the Chesapeake Bay, as a means to test ozone monitoring on ocean buoys and towers {Hintsa et al., 2004} and found ozone at the surface consistently exceeding 80 ppbv during an air quality episode from June 24 - 28, 2003.

1.4 DISCOVER-AQ Field campaign

During the month of July 2011, the National Aeronautics and Space Administration (NASA) conducted a comprehensive air quality field study, DISCOVER-AQ {Crawford & Pickering 2011}, in the states of Maryland, Delaware and Virginia to investigate air quality with the primary goal of providing data to better interpret observations from current and future satellites for air quality applications. In conjunction with DISCOVER-AQ, NASA conducted the oceanographic field campaign GEO-CAPE CBODAQ (Geostationary Coastal and Air Pollution Events-Chesapeake Bay Oceanographic Campaign with DISCOVER-AQ), to address questions related to both estuarine biogeochemical processes as well as atmospheric pollution over the Chesapeake Bay urban estuarine environment {Tzortziou et al., 2013}. A detailed description of the modes, locations, types, and days of observations is provided in Table 1. This paper focuses on observations from the 26-m Delaware II NOAA Small Research Vessel experimental (SRVx) deployed in the Chesapeake Bay as part of the CBODAQ campaign during from July 11 - 20, 2011.

2. Materials and Methods

2.1 Measurements description

The SRVx was equipped with a Thermo Environmental Model 49 UV photometric ozone (O_3) analyzer and a Thermo Environmental Model 42C chemiluminescence nitric oxide (NO) analyzer retrofitted with an external molybdenum catalyst to also measure total reactive nitrogen (NO_y).

The Model 49 O_3 Analyzer determines ambient concentration by measuring the attenuation of UV radiation emitted at 254 nm by a mercury (Hg) lamp. There are two optical benches in the analyzer: one measures the attenuation of the sample gas, while the other establishes a "zero" using a reference gas which is scrubbed of O_3. The solenoid switches every 10 seconds to rotate which optical bench is measuring the sample gas. Typical concentrations at the surface during the summer in the Baltimore / Washington region vary from 5 ppbv during pre-sunrise to 120 ppbv during the afternoons of the most polluted days. Typical 8-hour maximums can often exceed the 75 ppbv EPA standard.

The Model 42C NO Analyzer determines ambient concentration via a chemiluminescence technique. The NO in the sample gas reacts in a chamber with excess O_3 to form NO_2 in an excited state. The excited NO_2 releases a photon as it reverts to the ground state. A detector is able to identify the strength of the emission and correlates it to a concentration of excited NO_2 and via the stoichiometric 1:1 ratio, NO. An external molybdenum catalyst heated to 350° C reduces all reactive nitrogen species [NO_2, NO_3, HNO_3, 2 N_2O_5, HONO, peroxyacyl nitrates (PANs), organic nitrates ($RONO_2$) and particulate nitrate] into NO and non-reactive byproducts. Using a solenoid, sample air bypasses the molybdenum converter every 10 minutes measuring NO, while the

following 10 minutes it passes through the molybdenum converter measuring NO_y. To obtain a zero, the sample gas is diverted to a zeroing chamber, where the NO_2 releases a photon before being directed into the measuring chamber. The NO_y analyzer was zeroed for 10 minutes each hour during the campaign and measurements were adjusted based on the drift of the instrument. The NO_y analyzer was calibrated in-situ on July 19, 2011 of the campaign using a NO_2 standard reference material (SRM) from the National Institute of Standards and Technology (NIST). Typical concentrations of NO at the surface during the summer in the Baltimore / Washington region vary from 0.1 ppbv during the late afternoon to 1.5 ppb after the morning rush hour around 9 AM. Typical concentrations of NO_y vary from 1 ppbv during the late afternoon to 10 ppbv after the morning rush hour.

2.2 Model description

In this study, we use U. S. EPA's Community Multiscale Air Quality (CMAQ) {Byun and Schere, 2006} model Version 5.0, driven off-line by output from the Weather Research and Forecasting (WRF) {Skamarock et al., 2008} model Version 3.3 to simulate the state of the atmosphere covering the entire months of June and July 2011. The model simulations are at 36, 12, 4 & 1.33 km resolution in the area of interest and begin on 24 May 2011 to account for model spin-up time. Details of the model configuration and parameterization options used in the simulations are described in Loughner et al., 2013.

3. Results

3.1 Observational comparisons: Ozone

The SRVx was deployed in the Chesapeake Bay for 10 daytime cruises during the DISCOVER-AQ Maryland campaign, July 11, 2011 through July 20, 2011. This overlapped with four flights of the NASA P3-B (a four-engine turboprop capable of long duration flights of 8-12 hours) three flight days (2 flights per day) of the UC-12B King Air (a twin-engine turboprop capable of 6 hour flights) and three flight days (2 flights per day) of the University of Maryland (UMD) Cessna 402B (a twin-piston engine, unpressurized aircraft) (Table 1).

Mode of Measurement	Trace Gases Measured	Location	Days in which Active during July 11, 2011 through July 20, 2011
NASA P3-B	O3, NO, NO2, PNs, ANs, HNO3, NOy, CO, CH4, CH2O, CO2, VOCs		July 11, July 14, July 16, July 20
UC-12 King Air	Column O3, NO2, CH2O		July 11, July 14. July 20
Cessna 402B	O3, SO2, CO, NO2		July 11, July 18, July 20
MDE Ground Stations	O3, NO, NOy, PM2.5, CO, SO2	Aldino, MD, Beltsville, MD, Edgewood, MD, Essex, MD, Fairhill, MD, Padonia, MD	Every day
Pandora	Column NO2	Aldino, MD, Beltsville, MD, Edgewood, MD, Essex, MD, Fairhill, MD, Padonia, MD, College Park, MD, Catonsville, MD, SRVx NOAA Vessel	Every day
Ozonesondes	O3	Edgewood, MD	Every day
SRVx NOAA Research Vessel	O3, NO, total NOy	see Figure 1	Every day

Table 1: Modes of measurement during Phase I of the DISOVER-AQ campaign in the Baltimore-Washington region

The SRVx docked each night in Annapolis, MD and had different cruise route each day (Figure 4). The instruments were running while the SRVx was in port overnight in Annapolis, MD, but the data are subject to frequent local emissions.

Figure 4. Map of NOAA Delaware II SRVx routes from July, 11, 2011 through July 20, 2011

A plot of O_3 for the 10-day period can be seen in Figure 5. On three days ozone exceeded the 8-hour maximum 75 ppbv NAAQS threshold on the moving vessel in the Chesapeake Bay: July 13, July 19 and July 20. During this same time period, ground stations in the Maryland region exceeded the 75 ppbv threshold an average of 0.71 times per ground station. This alone is an indicator that the ozone may be higher near the surface of the Chesapeake Bay than nearby ground stations.

Figure 5. Ozone concentration (ppbv) as a function of time from July 11, 2011 through July 20, 2011. Map routes for each specific day can be seen in Figure 4. From 7 PM until 6 AM local time, the boat was docked at the US Naval Academy in Annapolis, MD.

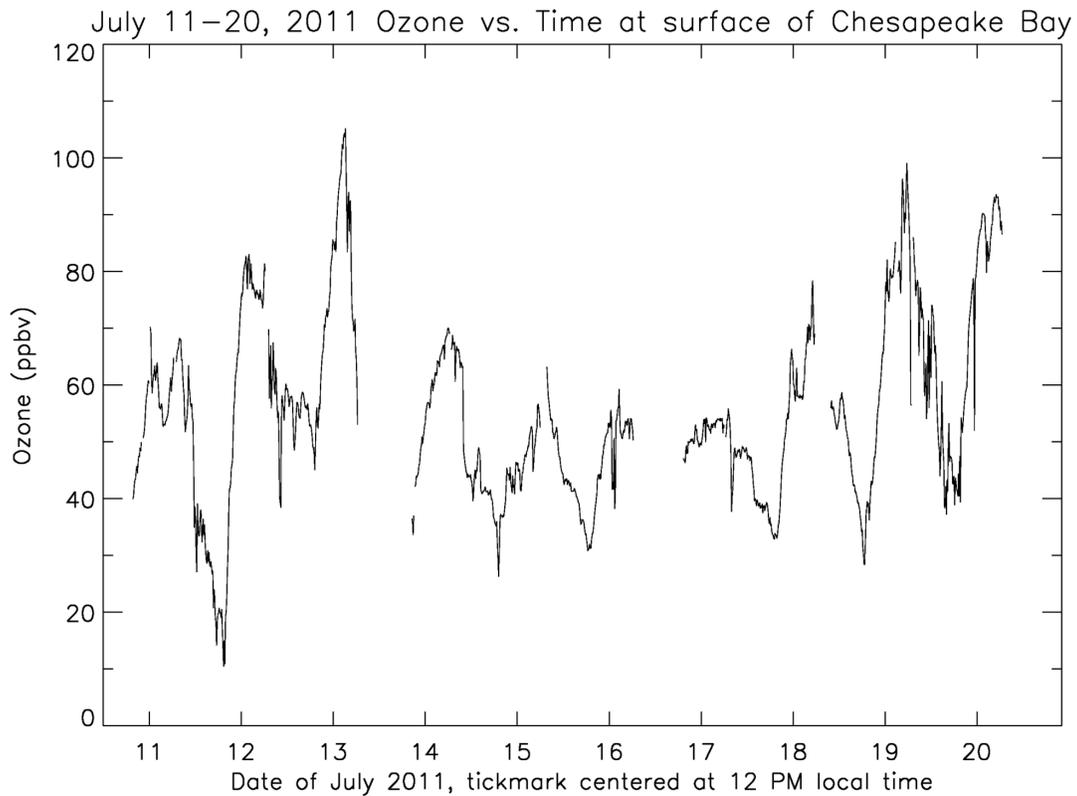Comparing the hourly ozone at the SRVx's location and closest upwind ground station using the HYSPLIT model reinforces the existence of higher ozone concentrations over the Bay. Eight-hour maximum ozone from all relevant ground sites and the SRVx can be seen in Table 2. The closest upwind ground station was often only 20 to 30 km away and was chosen to ensure that comparisons were made following a parcel of air.

Site Name	Max 8 hour ozone									
	7/11/11	7/12/11	7/13/11	7/14/11	7/15/11	7/16/11	7/17/11	7/18/11	7/19/11	7/20/11
Aldino	69	66	56	51	70	59	61	88	73	77
Calvert Co.	58	71	67	49	38	37	40	57	66	59
Davidsonville	53	67	61	50	45	41	41	81	76	63
Edgewood	61	61	52	49	66	55	53	82	59	74
Essex	58	61	53	51	58	47	51	71	72	68
Fairhill	68	65	49	48	69	51	55	86	68	66
HU-Beltsville	75	63	59	61	52	49	54	75	60	80
Millington	59	68	58	54	59	46	47	62	68	68
Padonia	73	64	54	52	62	60	53	67	65	86
PG Equestrian Ctr	54	72	62	51	44	42	41	80	75	61
South Maryland	55	70	63	46	40	38	42	54	64	71
Lums Pond, DE	59	65	53	49	58	N/A	49	76	61	57
Seaford, DE	53	76	62	44	46	N/A	41	52	63	65
NOAA SRVx	58	77	85	60	50	51	52	66	80	86
Closest Ground site	58	67	62	49	38	37	40	54	64	68
Name of Closest Ground site	Calvert	Davidsonville	PG Equestrian	Lums Pond	Calvert	Calvert	Calvert	S Maryland	S Maryland	Millington

Table 2: Maximum 8 hour ozone at various sites in the Maryland & Delaware region

Figures 6a and 6b show that during an exceedance day (July 13) and non-exceedance day (July 14), the ozone near the surface of the Chesapeake Bay is uniformly higher. During the afternoon of July 13 the ozone measurement on the SRVx was 10 – 40 ppbv greater than at the Calvert County MDE site. Ozone was consistently 10 – 20 ppbv greater over the Bay than at the Essex MDE site throughout the day on July 14. The 8-hour maximum ozone concentration over the Bay during each day of the 10-day cruise averaged 12.7 ± 6.1 ppbv higher than the closest upwind ground site.
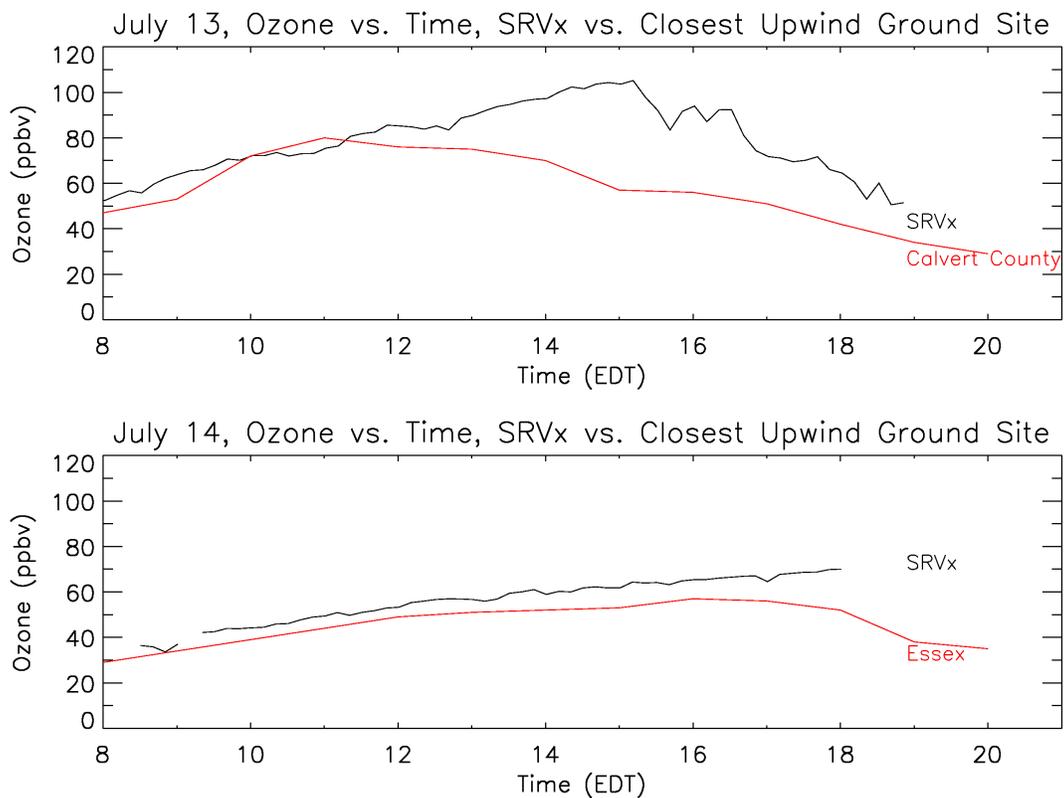
Figure 6a. Ozone concentration on July 13, 2011 (ppbv) as a function of time at the SRVx's location and the Calvert County ground monitoring station, the closest upwind monitoring station
Figure 6b. Same as Figure 6a but on July 14, 2011 Essex was the closest upwind monitoring station

The systematic high anomaly over the Chesapeake Bay can be seen in Figure 7.

The closest upwind ground site never had a higher 8-hour maximum ozone and only

during three days did any ground station in the region have an 8-hour maximum ozone

concentration that was 10 ppbv higher than the SRVx's location. This was especially

pronounced on July 13 when the SRVx saw an 8-hour maximum of 85 ppbv and none of

the ground stations in the region exceeded the NAAQS standard. When compared to 8-

hour maximum ozone at the ground stations in the "moderate" non-attainment area, the 8-

hour ozone at the SRVx's location was 4.6 ± 14.3 ppbv higher suggesting that the

Chesapeake Bay area has just as poor if not worse air quality than the surrounding

"moderate" non-attainment area.

Figure 7. 8-hour maximum ozone concentrations (ppbv) at the SRVx's location and the
closest upwind ground monitoring station from July 11, 2011 through July 20, 2011

The ozone concentration remained higher over the Chesapeake Bay later into the afternoon than over the ground stations, suggesting that there must be a mechanism to maintain high O_3 concentrations later into the day. A plot of the median hourly ozone concentrations at the SRVx's location and closest upwind ground station (Figure 8) suggests a late afternoon high anomaly.
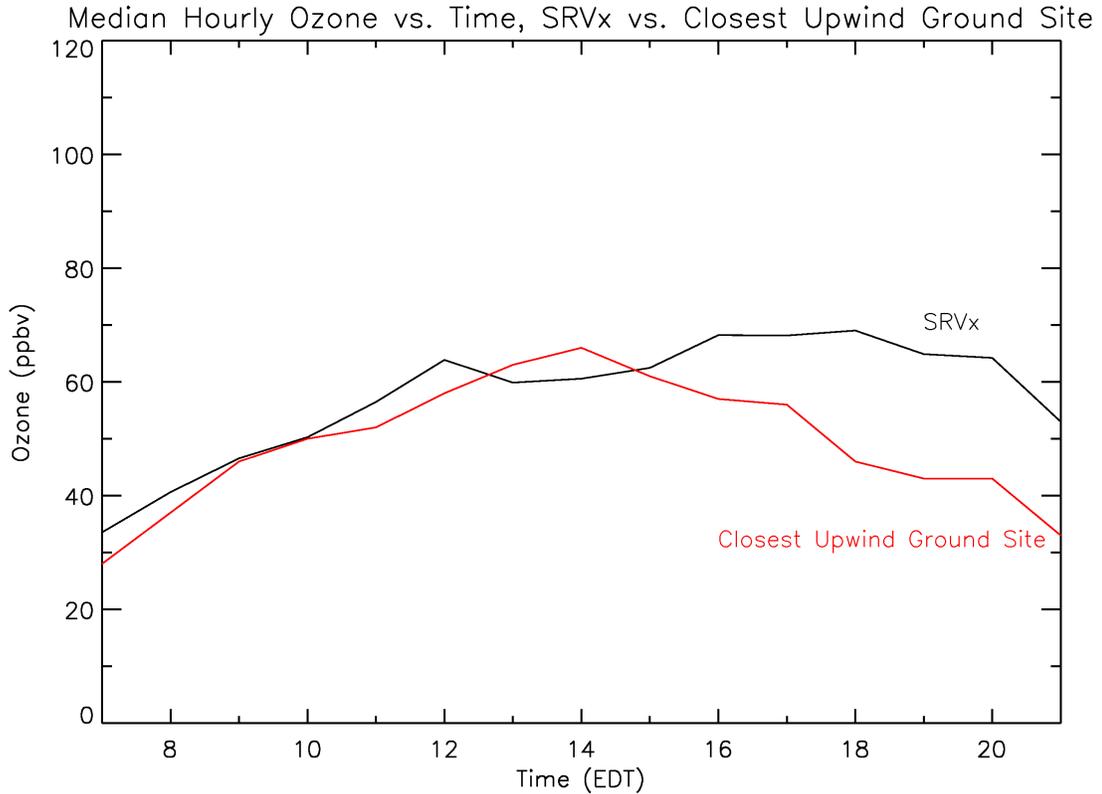
Figure 8. Median hourly ozone concentrations (ppbv) at the SRVx's location and the closest upwind ground monitoring station from July 11, 2011 through July 20, 2011 as a function of time

Ozone over the Bay is greater and of longer duration than over upwind land area due to several potential causes:

(1) A difference in ozone deposition rates over land and water;

(2) A shallower PBL depth over the Chesapeake Bay than the nearby land;

(3) Fewer fair-weather cumulus clouds over the Chesapeake Bay allowing for increased photolysis and;

(4) Decreased boundary layer venting caused by a meso-high pressure that develops over the Bay due to the bay-breeze circulation trapping pollutants; and

(5) Emissions from shipping on the Chesapeake Bay.

Furthermore, when meteorological conditions are conducive, a low-level jet can form overnight transporting polluted air over the Chesapeake Bay from the Norfolk/Virginia Beach, VA metropolitan region bypassing ground stations allowing for increased ozone production over the Bay. This phenomenon, however, was not observed during this field campaign.

3.2 Model Comparisons: Ozone

The CMAQ model simulations typically reproduce the systematically higher ozone concentrations over the Chesapeake Bay than in the Baltimore-Washington region. As shown in Figure 9, median ozone concentrations for the 10-day period output by both the 1.33 km and 4 km resolution CMAQ model simulations closely match the observations from the SRVx throughout the day, indicating that model bias is small. Once the grid cell size transitioned to 12 km, the surface ozone output by the model began to lose correlation and once the grid cell size transitioned to 36 km, there was very little correlation throughout the day; both the 12 km and 36 km models runs show a high model bias. Model resolution seems to play an integral role in predicting ozone concentrations.
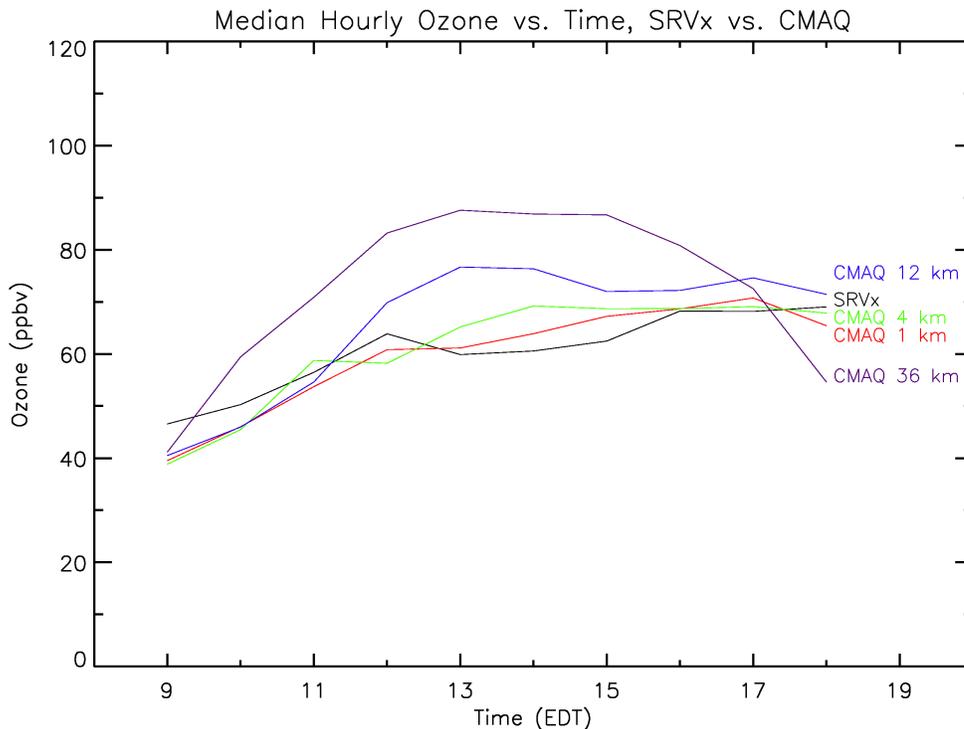
Figure 9. Median ozone concentrations (ppbv) at the SRVx's location and at the closest CMAQ (1.33 km) grid point for each hour from July 11, 2011 through July 20, 2011 as a function of time

Despite the 1.33 km resolution CMAQ model simulation closely matching the median for the 10-day period there were specific days when the model was unable to predict ozone accurately with both a high bias shown in Figure 10a and a low bias shown in Figure 10b. During an exceedance day (July 13), the model had a consistent 10 – 15 ppbv high bias and on a non-exceedance day (July 12), the model had a 10 -15 ppbv low bias.
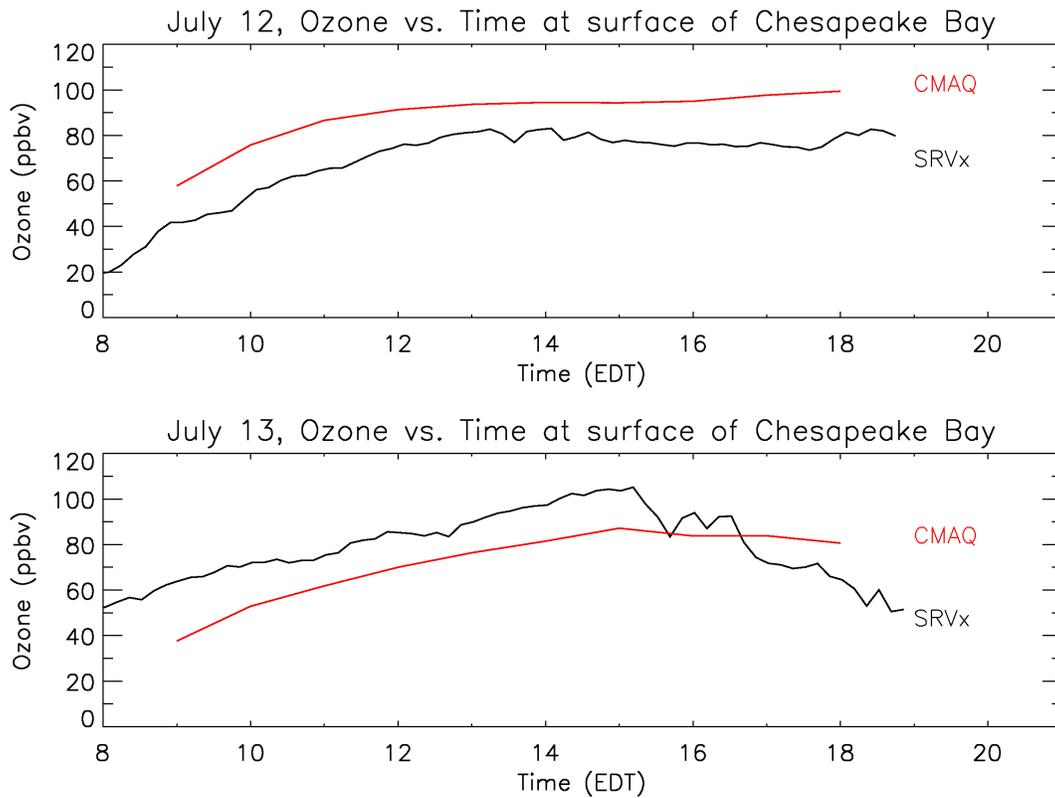
Figure 10. Ozone concentration (ppbv) as a function of time at the SRVx's location and at the closest CMAQ grid point on a) July 12, 2011 and b) July 13, 2011

This high bias of the model can likely be attributed to the boundary layer depths calculated by WRF and input into CMAQ. The modeled boundary layer is often substantially lower over the Chesapeake Bay than observed by the High Spectral Resolution Lidar (HSRL) aboard the UC-12B aircraft (Figure 11). The low bias of the model may be related to a lower temperature at the surface or perhaps a more stratified PBL inhibiting downward mixing.
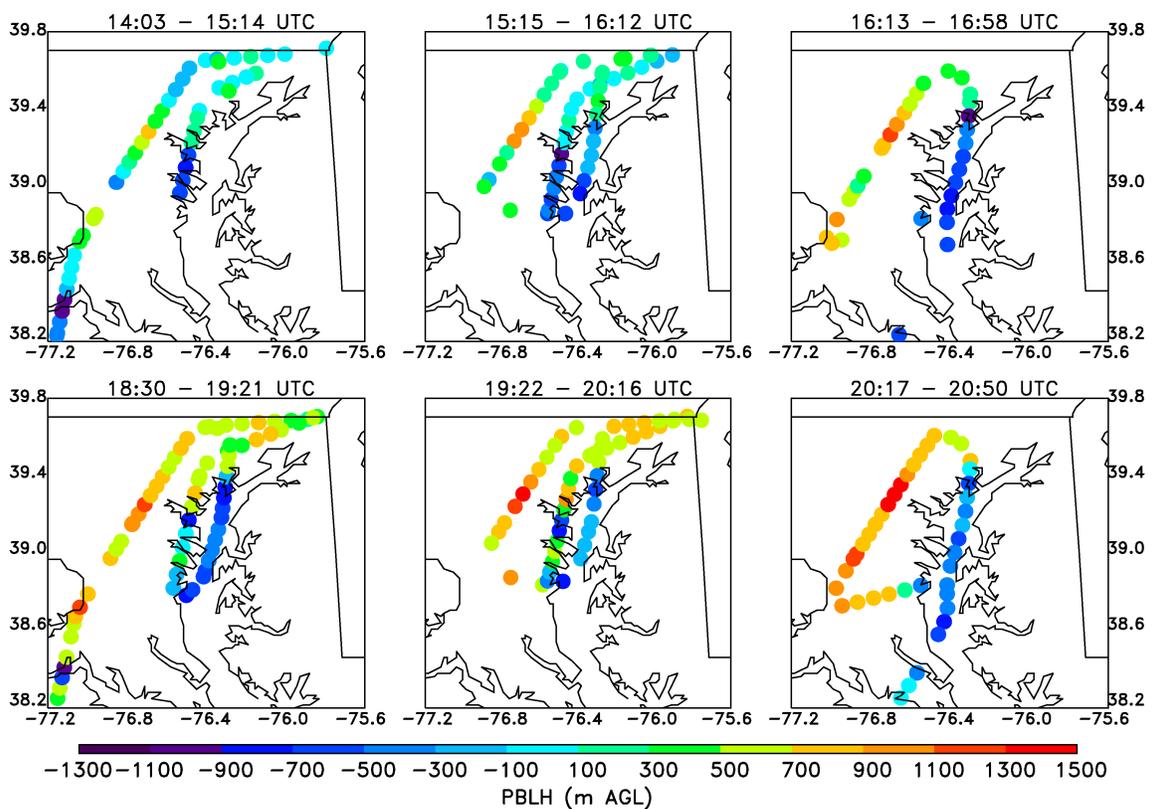
Figure 11. Difference between the PBL depth output by WRF and measurements of boundary layer height using a high spectral resolution lidar (HSRL) aboard the UC-12 aircraft on July 20, 2011

3.3 Model Comparisons: Total Reactive Nitrogen

Observations of reactive nitrogen species are critical since the eastern United States lies in the NO_x-limited regime of ozone production {Chameides et al., 1992} {Trainer et al., 1993} {Frost et al., 2006} due to the excess of isoprene from oak trees. Accurate model output of NO_y species is especially important due to reactive nitrogen's critical role in ozone formation in the NO_x-limited regime found in eastern United States during the summer. Observations of NO_y from the SRVx were compared to 1.33 km model results from CMAQ over the Bay. On each day of the 10 daytime cruises, with the exception of July 19 when the instrument was taken off-line for calibration, NO_y observations were consistently lower than the output from the nearest grid point in CMAQ. The model regularly overestimated NO_y by 50% and on July 13, it was overestimated by 250% in the early-afternoon as shown in Figure 12.
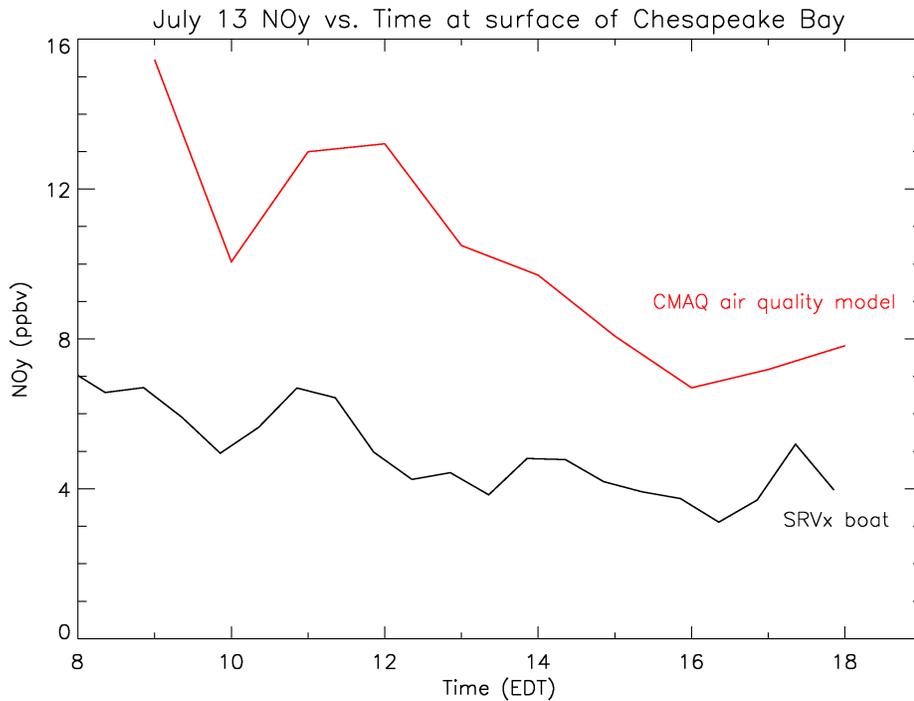
Figure 12. Total NO_y concentration measured on the SRVx compared to total NO_y from the closest grid point in CMAQ on July 13, 2011 as a function of time

The data from the TD-LIF instrument {Day et al 2002} on the P3-B aircraft during a spiral on July 20 also indicate a significant overestimation of NO_y species by CMAQ, as shown in Figures 13a and 13b. While NO_2 matches to within 50%, peroxy nitrates (PNs), alkyl nitrates (ANs), and nitric acid (HNO_3) are overestimated by factors of 3, 5, and 2 respectively. This overestimation of reactive nitrogen species has also been seen in other modeling studies {Brioude et al., 2013} {Yu et al., 2012}.

July 20, P3-B NOy species over Chesapeake Bay, at 16:30z
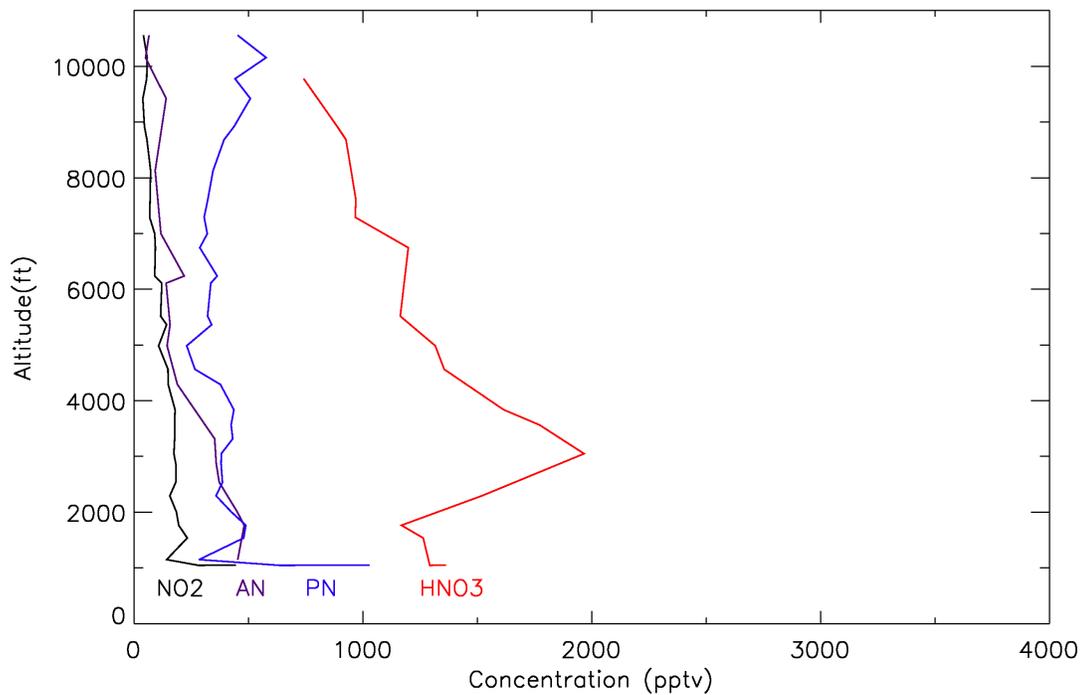
Figure 13a. Total NO_y concentration (minus NO) split by compound (NO_2, peroxy nitrates (PN), alkyl nitrates (AN), and HNO_3 measured on the P3-B as function of altitude during the 1630Z spiral on July 20, 2011 over the Chesapeake Bay

July 20, CMAQ NOy species over Chesapeake Bay, at 17z
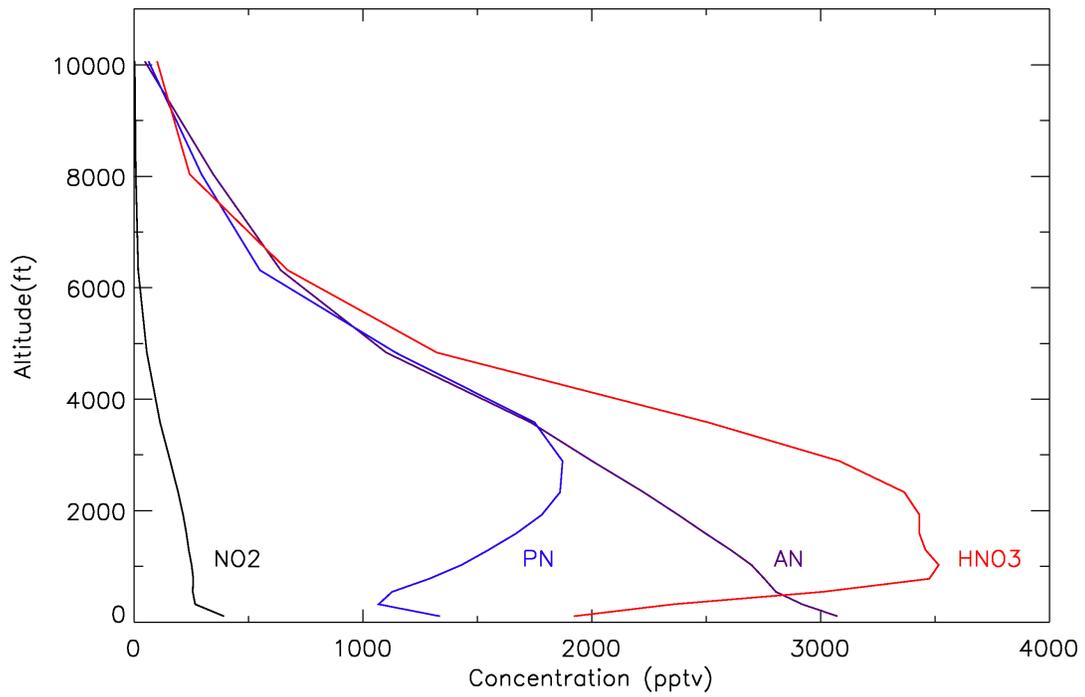
Figure 13b. Same as Figure 13a but using data from the closest grid point in CMAQ at 1700Z (1 PM local time)

To understand whether the overestimate is an emissions issues, chemistry issue, or both, we looked at whether the partitioning of the species is correct. If partitioning of NO_y species is correct, then this issue is likely high emissions or low dispersion rates. To gain insight on this issue, we took the ratio of NO/NO_y during the morning hours when the two species are positively correlated and the NO measurement is above the detection limit. As seen in Figure 14, the NO/NO_y ratios between the model simulation and observations often lie below the 1-to-1 line. A mean of the data shows NO concentrations are 10.0% of total NO_y in the observations, while NO concentrations are 7.6% of total NO_y in the CMAQ simulation.

Hourly NO/NOy ratios during the AM hours from CMAQ & the SRVx
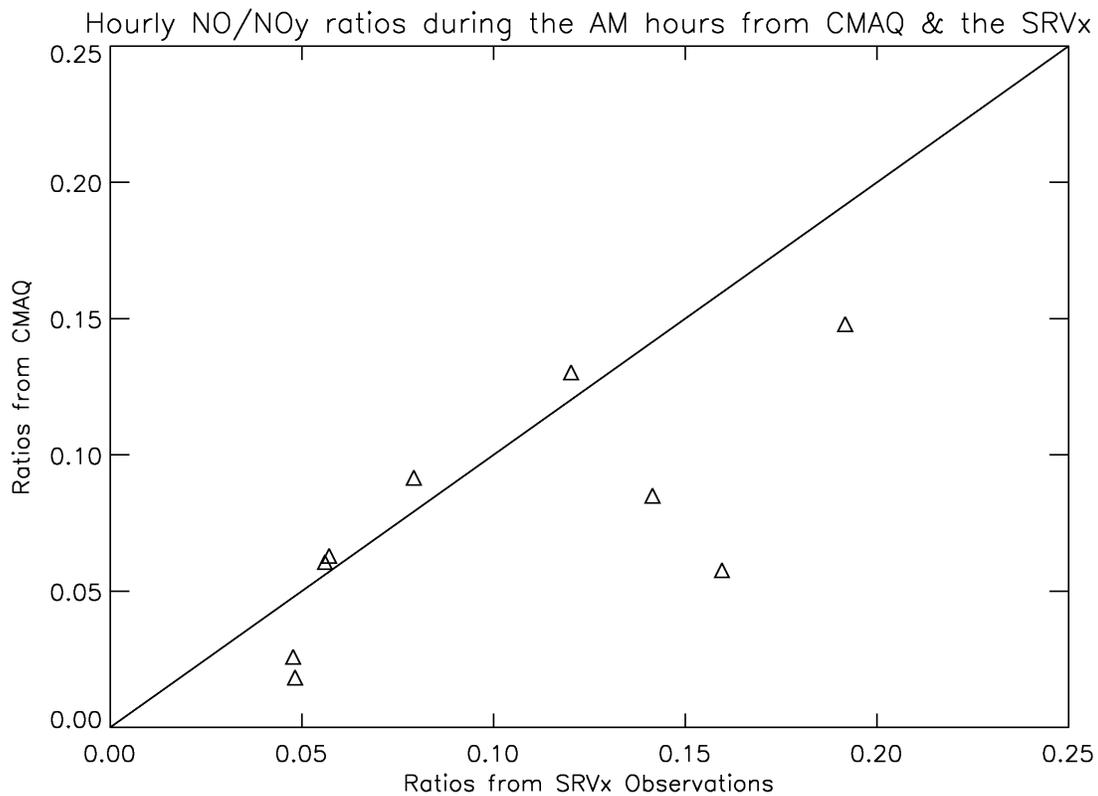
Figure 14. NO/NO_y ratios from 1.33 km CMAQ run and the during the morning hours when NO and NO_y are positively correlated and NO is above the instrument's detection limit

This indicates that CB05, as employed, partitions more NO_y species as higher oxides (i.e., ANs, PNs, HNO_3) than is observed. This suggests that gas-phase chemistry scheme (CB05) is overestimating the lifetimes of higher order NO_y species such as ANs and PNs, removal rates are too slow, or conversion rates of NO_y to NO_2 are slower than observed.

To minimize computing time, the CB05 chemical mechanism simplifies the alkyl nitrates by grouping all alkyl nitrates in a single chemical species (NTR). The lifetime of NTR calculated during a simulation of CMAQ using 2007 summer conditions, yields a lifetime of 10 days. It has been shown that isopropyl nitrate has a lifetime that is 10 days {Luke et al., 1989}, but higher-order alkyl nitrates have a much shorter lifetime (1-2 days) {Horowitz et al., 2007} {Perring et al., 2009}, due to a lack of electronegativity holding the gas phase species together. The shorter lifetimes of the high-order alkyl nitrates species are not accounted for in the CB05 gas-phase chemistry scheme. After decomposition, the alkyl nitrates split into an alkyl chain and NO_2. If the lifetime of NTR in CB05 were to be shorter, then this would yield lower concentrations of alkyl nitrates, which would be more in line with observations.

To represent peroxy nitrates in the model, the CB05 mechanism simplifies the species into peroxyacyl nitrates (PAN), all other higher order peroxyacyl nitrates (PANX) and peroxynitric acid (PNA), with the latter being a very small fraction of the first two at high temperatures. The summation of peroxy nitrate concentrations (PNs) in the model is higher than observed. The primary destruction of peroxyacyl nitrates is via thermal dissociation. At higher temperatures, PAN and PANX dissociate more rapidly into acetylperoxy radicals (C2O3) and higher order acylperoxy radicals (CXO3) respectively.

The concentration of PAN and PANX is therefore governed by the equilibrium constant, which is a function of temperature, and the concentrations of the products, C2O3/CXO3 and NO_2. To account for the high bias in the model, either the temperature consistently has a low bias, or the concentrations of the products are too high. Both need to be further investigated, with the latter being a more reasonable explanation.

Observations from the SRVx were compared to the UC-Berkeley thermal dissociation laser-induced fluorescence (TD-LIF) instrument {Day et al., 2002} used on the P3-B when it flew spirals over the Chesapeake Bay. The TD-LIF does not measure NO, so all comparisons are NOy – NO. The observations of NO_y – NO from the SRVx using a chemiluminescence instrument with external molybdenum converter are higher than the data the TD-LIF. This is an expected outcome since NO_y concentrations decrease exponentially with height {Brent et al., 2013} due to emissions that come from the surface and relatively short lifetimes compared to other trace gases. There were no other ground observations of NO_y during this campaign, as MDE does not maintain research grade NO_y analyzers at its ground stations.

4. Discussion

The observations from the SRVx show, with a 2-sigma level certainty, that ozone concentrations are elevated over the Bay when compared to upwind ground sites. The extended period of high ozone makes a higher number of days exceed the U.S. EPA 8-hour 75 ppbv NAAQS threshold than over nearby land areas. Here we discuss potential reasons for this phenomenon and attempt to apportion a relative importance for each mechanism.

During a day that lacks precipitation, which is the case for most ozone exceedance days in the Baltimore-Washington metropolitan region, ozone is primarily destroyed by the following mechanisms {The Royal Society 2008}:

- Dry deposition to vegetation or water   (1)

- $O_3 + NO \rightarrow O_2 + NO_2$ (2)

- $O_3 + OH \rightarrow O_2 + HO_2$ (3)

- $O_3 + HO_2 \rightarrow OH + 2O_2$ (4)

- $O_3 + h\upsilon \rightarrow O_2 + O\left(^1D\right)$ $at\ h\upsilon < 320\ nm$ (5)
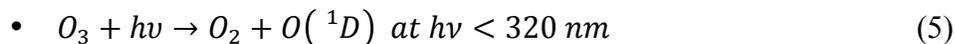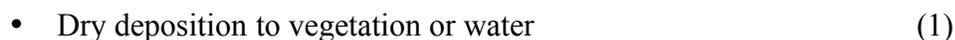
Dry deposition (mechanism 1) is the primary mode of destruction of ozone near the surface. Titration due to NO (mechanism 2) also occurs near the surface, but this serves as a reservoir to O_3 as NO_2 is re-generated. Mechanisms 3 – 5 are most prominent in the upper troposphere and isolated ocean regions where dry deposition rates are minimal.

Deposition is the primary mode of destruction in the boundary layer and occurs fastest in heavily forested areas {Fowler et al., 2001} {Nowak et al., 2006}. Differences in ozone dry deposition rates have been widely studied. A list of 24-hour-averaged dry deposition velocities from the literature is given in Table 3 {Wesely & Hicks 2000} {Chang et al., 2004} {Nowak et al., 2006}.

	Table 1: Ozone dry deposition velocities		
	Forest	Coastal	Ocean
Nowak (2006)	0.5 cm/s	-	-
Wesely (2000)	0.8 cm/s	-	-
Chang (2004)	-	-	0.05 cm/s
Gallagher (2001)	-	0.148 cm/s	-

Table 3. Ozone deposition velocities for various land types

For a mix of 50% deciduous forest, 25% grass, and 25% pavement, the 24-hour averaged dry deposition velocity for ozone is 0.50 cm/s. However, estimates for dry deposition of ozone in a coastal environment are 0.15 cm/s. The slower deposition velocity is due to a lack of vegetation and surface roughness in coastal areas {Gallagher et al., 2001}. To calculate the difference in ozone deposition over an hour, we can use the following formula:

$$\frac{v_{d(land)}}{PBL_{depth}} - \frac{v_{d(bay)}}{PBL_{depth}}$$

For a boundary layer depth of 800 m, which typical over the Chesapeake Bay during the mid-afternoon, an the ozone concentrations would be approximately 1.6% higher after an hour than an air parcel of similar concentration over land due to slower deposition velocities over water, assuming all other environmental conditions are the same.

$$\frac{18\,\frac{m}{hr}}{800\,m} - \frac{5.328\,\frac{m}{hr}}{800\,m} = 1.58\,hr^{-1}$$

If winds are from the southwest, maximizing residence time over the Bay, an air parcel that entered the southwest portion of Chesapeake Bay may have been over the Bay for approximately 5 hours. By the time an air parcel leaves the Bay, its ozone concentration theoretically could be up to 8% higher.

Boundary layer height also plays a major role in determining concentrations of ozone near the surface {Rao et al., 2003}. Pollutants are primarily confined within the boundary layer due to a strong subsidence inversion during anticyclonic events. The only mechanism by which pollutants can be vented out of the boundary layer during strong anticyclonic setups is through fair-weather cumulus clouds {Dacre et al., 2007}. However, cumulus clouds are largely non-existent over the Chesapeake Bay during strong subsidence events {Loughner et al., 2011}.

The boundary layer over land tends to be deeper because the temperature is higher over land during clear-sky conditions in the mid-afternoon. As the boundary layer depth decreases, the precursors to ozone, such as NO_x compounds, accumulate in a smaller volume of atmosphere leading to higher concentrations. On July 20 between 20Z – 21Z or 4 PM – 5 PM local time, the HSRL aboard the UC-12B aircraft measured the aerosol-based boundary layer depth to be 1000 - 1200 m over land and 400 - 600 m over the Chesapeake Bay within 10 minutes as seen in Figure 15.
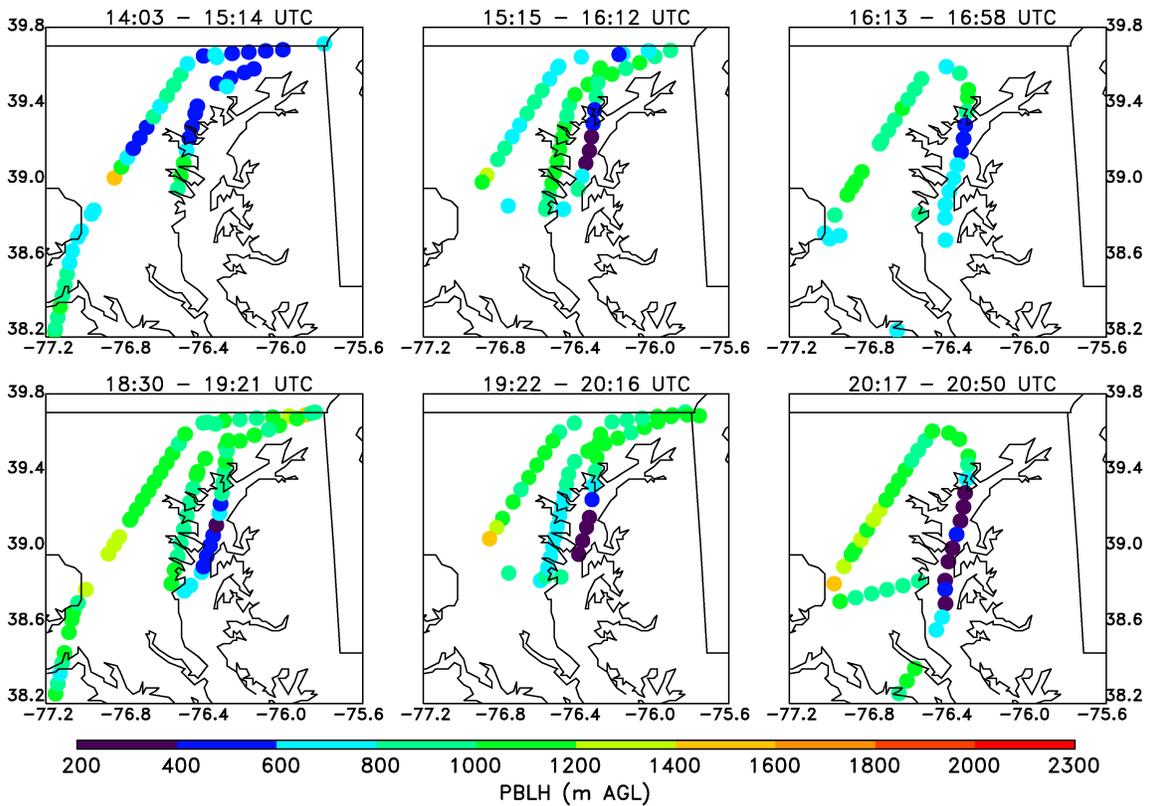

Figure 15. Measurements of boundary layer height using a high spectral resolution lidar (HSRL) aboard the UC-12 aircraft on July 20, 2011

If there were no boundary layer venting and environmental conditions and emissions were identical, the concentrations of NO_2 could be up to a factor 2 higher over the Bay leading to a substantial increase in O_3, since the mid-Atlantic region is in the NO_x-limited regime. However, there is likely some vertical mixing and emissions are likely lower over the Bay. Although there were no direct measurements of NO_2 at the surface of the bay during this particular campaign, data on the P3-B shows that at 0.3 km, the lowest altitude of the flight spirals, NO_2 is higher by as much as 0.5 ppbv over water than land. Using ozone efficiency rates from the DISCOVER-AQ campaign, for every 1 ppbv increase in NO_x, ozone production will increase by average of 8.26 ppbv with a 90% confidence interval of 4.93 to 19.4 ppbv {He et al 2013}; this is slightly higher than a urban study in Houston, which showed an average ozone production efficiency of 5.9{Neuman et al., 2009}.

A bay-breeze circulation often develops over the Chesapeake Bay during the late spring and early summer {Ryan et al., 1998} {Stauffer et al., 2012} impacting the coastal temperature structure and associated meteorological conditions. The bay-breeze yields a meso-high pressure directly over the Chesapeake Bay, and a meso-low pressure just inland from the Bay. This creates stagnation and clear skies directly over the Bay. Fewer cumulus clouds develop over the Chesapeake Bay because of the lower surface temperature, shallower boundary layer depth and relative lack of thermals over the Bay. Decreased cloud cover increases photolysis rates by allowing more UV radiation to reach the lowest levels of the atmosphere creating an environment more favorable for ozone production.

On July 20, visible satellite imagery, Figure 16, shows an expanse of low level fair cumulus clouds over the Baltimore-Washington region, while there are no clouds over the Bay. Cloud coverage is estimated to be 10-30% over land and 0% over the Bay leading to a j(NO_2) value that will be higher over the Bay.


Figure 16. Visible image from the MODIS satellite at 1610Z (2:10 PM local time) on July 20, 2011 showing the presence of low-level cumulus clouds only over the land

During the DISCOVER-AQ campaign, the P3-B aircraft measured $j(NO_2)$ throughout its flights. In the mid-afternoon, 3:30 PM local time, on July 20, 2011 when the P3-B flew at an altitude of 390 m over land in an absence of clouds, the $j(NO_2)$ rate constant was 0.0082 s^{-1}, while 30 seconds later underneath a fair-weather cumulus cloud, which was confirmed by looking at the forward camera on the P3-B, the $j(NO_2)$ rate constant dropped to 0.0043 s^{-1}. If we assume the sky is filled with 20% cumulus clouds and the Bay has none, the average $j(NO_2)$ would be 0.0074 s^{-1} over land and 0.0082 s^{-1} over the Bay. Therefore, dissociation of NO_2 into NO and odd oxygen may be up to 10.5% faster during the mid-afternoon of a summer day.

NO_x emissions from barges that travel the Chesapeake Bay account for 10% of all mobile emission sources {U.S. EPA, 2010}. In March 2010, the U.S. EPA adopted a regulation designating that large barges must burn cleaner fuel that releases less NO_x when they are within 200 nautical miles of the North American coastline {U.S. EPA 2010}. However, this regulation was not enforceable by the U.S. EPA until August 2012, which is after the Maryland DISCOVER-AQ field study. Many large transport tankers burn bottom-of-the-barrel bunker fuel, which releases a higher proportion of NO_x than diesel fuel {Eyring et al., 2005}. There has been little quantification of barge emissions {Mason et al., 2008}. Using the 8.26 ppbv O_3 per ppbv NO_x ozone production efficiency calculated during the DISCOVER-AQ campaign {He et al., 2013}, we estimate that 0.1 ppbv increase in NO_x concentrations over the Chesapeake Bay could yield a 0.8 ppbv increase in ozone, since the mid-Atlantic region is characterized by the NO_x-limited regime of ozone production.

One factor inhibiting ozone production over the Bay is the lower tropospheric temperature profile. Coastal areas in extratropical latitudes heat up more slowly than nearby inland locations during the summer due to the influence of the cooler waters. During the 10-day campaign, temperatures on the SRVx at 3 PM local time were on average 3.3°C cooler than the Baltimore-Washington International (BWI) airport which is located 30 km inland from the Chesapeake Bay. The dissociation of PAN into NO_2 has a strong temperature dependence; the kinetics equation is given below:

$$PAN \rightarrow CH_3C(O)OO + NO_2$$

$$k = 1.95 * 10^{16} * exp\left(\frac{-13543}{T}\right)$$
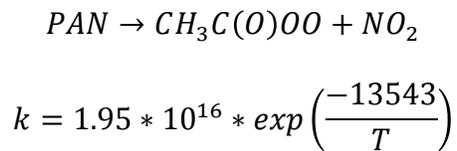
A quick calculation of the rate constant at the two temperatures shows that PAN dissociates 1.63 times quicker at 305.8 K than 301.5 K. The quicker dissociation of PAN at higher temperatures over land shifts the equilibrium reaction towards NO_2, the primary precursor to ozone in the NO_x-limited regime over the Mid-Atlantic. However, the dissociation of PAN is slower over the Bay, keeping more NO_2 tied up as PAN, and thereby decreasing O_3 production.

5. Conclusions

Observations from the SRVx during the DISCOVER-AQ campaign show with a certainty exceeding the 2-sigma level, that ozone concentrations are elevated over the Bay when compared to the closest upwind ground station. We posit that this high anomaly is influenced by a number of mechanisms including:

- Slower deposition velocity over the Bay
- Shallower boundary layers
- Higher photolysis rates due to clear skies over the bay
- Decreased boundary layer venting due to a lack of fair-weather cumulus clouds
- Emissions from shipping

The ozone concentrations exhibit a high anomaly over the Bay even though temperatures are cooler and allow precursors to ozone such as PAN to remain up to twice as stable. The observed high anomaly over the Chesapeake Bay is of primary importance since many citizens spend their leisure time on or near the Chesapeake Bay during the summertime and are exposed to the unhealthy air quality conditions. Furthermore, when the winds are onshore, these harmful conditions are advected to local communities several miles inland. Expanded monitoring of ozone directly over the Chesapeake Bay is needed to more precisely quantify the extent of this high anomaly.

Acknowledgements

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