Ozone and NO\textsubscript{x} chemistry in the eastern US: evaluation of CMAQ/CB05 with satellite (OMI) data

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Abstract

Regulatory air quality models, such as the Community Multiscale Air Quality model (CMAQ), are used by federal and state agencies to guide policy decisions that determine how to best achieve adherence with National Ambient Air Quality Standards for surface ozone. We use observations of ozone and its important precursor NO$_2$ to test the representation of the photochemistry and emission of ozone precursors within CMAQ. Observations of tropospheric column NO$_2$ from the Ozone Monitoring Instrument (OMI), retrieved by two independent groups, show that the model overestimates urban NO$_2$ and underestimates rural NO$_2$ under all conditions examined for July and August 2011 in the US Northeast. The overestimate of the urban to rural ratio of tropospheric column NO$_2$ for this baseline run of CMAQ (CB05 mechanism, mobile NO$_x$ emissions from the National Emissions Inventory; isoprene emissions from MEGAN v2.04) suggests this model may underestimate the importance of interstate transport of NO$_x$. This CMAQ simulation leads to a considerable overestimate of the 2 month average of 8 h daily maximum surface ozone in the US Northeast, as well as an overestimate of 8 h ozone at AQS sites during days when the state of Maryland experienced NAAQS exceedances. We have implemented three changes within CMAQ motivated by OMI NO$_2$ as well as aircraft observations obtained in July 2011 during the NASA DISCOVER-AQ campaign: (a) the modeled lifetime of organic nitrates within CB05 has been reduced by a factor of 10, (b) emissions of NO$_x$ from mobile sources has been reduced by a factor of 2, and (c) isoprene emissions have been reduced by using MEGAN v2.10 rather than v2.04. Compared to the baseline simulation, the CMAQ run using all three of these changes leads to a considerably better simulation of the ratio of urban to rural column NO$_2$, better agreement with the 2 month average of daily 8 h maximum ozone in the US Northeast, fewer number of false positives of an ozone exceedance throughout the domain, as well as an unbiased simulation of surface ozone at ground based AQS sites in Maryland that experienced an ozone exceedance during July and August 2007. These modifications to CMAQ may provide a framework for use in stud-
ies focused on achieving future adherence to specific air quality standards for surface ozone by reducing emission of NO\textsubscript{x} from various anthropogenic sectors.

1 Introduction

The spatial scale of tropospheric ozone production is of enormous consequence, especially for the eastern US where cross-state transport of air pollutants is a major policy concern (EPA vs. EME Homer City Generation, 2014). As early as the 1980's (Logan, 1989), analysis of measurements indicated that surface ozone episodes covered areas approaching 10\textsuperscript{6} km\textsuperscript{2}. Numerous observational studies have demonstrated the transport of ozone and its precursors from west to east and the impact of upwind emissions on high concentrations of pollution ozone (Brent et al., 2013; Hains et al., 2008; He et al., 2014, 2013a, b; Ryan et al., 1998; Taubman et al., 2004, 2006). Dramatic improvements in air quality have been observed due to reductions in the emission of ozone precursors (Butler et al., 2011; Fiore et al., 1998; Gego et al., 2007; He et al., 2013b; Marufu et al., 2004; Walsh et al., 2008). Numerical simulations of ozone show a dependence on NO\textsubscript{x} (NO + NO\textsubscript{2}) concentrations, but do not always capture the regional nature of photochemical smog events nor the strength of the response to NO\textsubscript{x} emissions controls (Fujita et al., 2013; Gilliland et al., 2008; Godowitch et al., 2008a, b; Hogrefe et al., 2011; Pollack et al., 2013; Wilson et al., 2012; Yegorova et al., 2011; Zhou et al., 2013).

The Community Multiscale Air Quality model (CMAQ) is used extensively for regulatory purposes (Byun et al., 2006). State Implementation Plans (SIPs) quantify future emission reductions that will bring nonattainment areas into compliance with the National Ambient Air Quality Standard (NAAQS) for surface ozone. The recommendations submitted in the SIPs are based on analysis of output from air quality models such as CMAQ that simulate meteorology and the nonlinearities inherent in tropospheric ozone chemistry. Oxides of nitrogen play a controlling role in ozone production in the eastern US and comparison of monitor records with CMAQ output suggest that this model
overestimates NO\textsubscript{x} concentrations in urban areas, but underestimates NO\textsubscript{x} in rural areas (Castellanos et al., 2011). The overestimate of NO\textsubscript{x} in urban areas, coupled with the underestimate in rural areas, means CMAQ may keep NO\textsubscript{x} too closely confined to source regions, thereby underestimating the interstate transport of ozone precursors. Such disagreement may stem from the complicated nature of NO\textsubscript{x} emissions, recycling, and removal. Organo-nitrate compounds can act as reservoirs or sinks for NO\textsubscript{x} and have received substantial attention for many years (Atlas et al., 1988; Beaver et al., 2012; Day et al., 2003; Lockwood et al., 2010; Neff et al., 2002; Perring et al., 2013, 2010, 2009; Xie et al., 2013). The production and loss mechanisms that govern the concentrations of organo-nitrate species are largely simplified in most air quality models. Ground based and aircraft measurements of ozone and its precursors provide important constraints on the concentrations of trace gases and can be used to validate model output. However, these data are geographically limited. In contrast, satellites provide a measure of the spatial variation of these species over a much larger domain.

In this study, we investigate the regional representation of NO\textsubscript{2} in CMAQ by comparing model output to satellite observations from the Ozone Monitoring Instrument (OMI) (e.g., Boersma et al., 2011; Buscela et al., 2013) during July and August 2007. Modifications to the chemical mechanism and emissions inventories considered by the model are suggested to improve agreement between model and observations. More relevant to policy makers is the ability of air quality models to reproduce surface ozone. We extend our analysis to include comparisons between model output and ozone observed at ground based stations throughout the domain (i.e. most of the United States eastward of the Mississippi river).

2 Data description: OMI satellite

OMI is one of four instruments onboard the NASA Aura satellite, now in its tenth year. The satellite is in a sun synchronous orbit, providing OMI a daytime overpass at \(\sim 13:40\) LT. NO\textsubscript{2} columns are retrieved using differential optical absorption spectroscopy...
(DOAS) in the 405–465 nm range. There are two operational retrievals of tropospheric column NO$_2$ based on radiances measured by OMI; the Derivation of OMI tropospheric NO$_2$ (DOMINO) product (Boersma et al., 2007, 2011) provided by the Royal Netherlands Meteorological Institute (KNMI) and the NASA Goddard Space Flight Center (GSFC) product (Buscela et al., 2013). The differences between the two data products are primarily due how the stratospheric component of the signal is removed from the total column observation.

Retrievals of tropospheric column NO$_2$ (hereafter, column NO$_2$) from OMI are available for the width of the atmosphere observed along the viewing track (or swath) of the instrument. These level 2 (L2) observations do not occur on a regularly spaced grid. For more meaningful comparison between satellite retrievals and model output, we generate level 3 (L3) products on a 0.25° × 0.25° (latitude, longitude) grid for both observed and calculated column NO$_2$. Column NO$_2$ from OMI is weighted based on satellite viewing angle using the formulation of Buscela et al. (2013). These same weights are applied to column NO$_2$ from CMAQ to assure a meaningful comparison.

Column NO$_2$ measurements are only considered for the gridding procedure when solar zenith angle is less than 85° and cloud fraction is less than 30%. Observations are also screened for a quality flag provided in the data files, called xtrackqualityflag for both retrievals. This flag allows OMI data products to be used in a manner than minimizes the influence of the row anomaly along the observing swath (see http://www.knmi.nl/omi/research/product/rowanomaly-background.php for more information). We only include retrievals where xtrackqualityflag equals zero. Summary quality flags provide quality assurance that at least 50% of the tropospheric column is determined by observed information. In our study, retrievals are only used when this flag also equals zero.

The production of ozone in our region of study is NO$_x$-limited for nearly all of the domain. An analysis of satellite observations acquired in 2005 to 2007 shows that ozone production is VOC-limited for only a small part of New York City, with the rest of the domain being NO$_x$-limited (Duncan et al., 2010). Hence the general focus of
this manuscript on model representation of nitrogen oxides. The results of this study may not be applicable to regions where production of ozone is VOC dominated, which occurs primarily in rural regions such as the so-called isoprene volcano of the Ozarks (Carlton and Baker, 2011) or regions of intense hydrocarbon processing such as Houston, Texas (Li et al., 2007).

3 Model description

For this analysis we use the Community Multiscale Air Quality (CMAQ) modeling system version 4.7.1 (https://www.cmascenter.org/cmaq/). This model has been used extensively by states that are members of the Ozone Transport Commission (OTC) in preparation for the 2015 ozone SIP call. For this analysis, CMAQ simulations were performed for the Eastern US with a 12 km × 12 km horizontal resolution and a 34 layer (σ coordinate) vertical grid from the surface to ~ 20 km with hourly output. Simulated meteorology is driven by output from the Weather Research Forecasting (WRF v3.1.1) model for year 2007 and processed for use in CMAQ by the Meteorological Chemistry Interface Processor (MCIP).

Emissions inventories for year 2007 were developed by the Mid-Atlantic Regional Air Management Association, Inc. (MARAMA) specifically for use in OTC modeling efforts. Biogenic emissions were estimated using the Model of Emissions of Gases and Aerosols in Nature (MEGAN v2.04) (Guenther et al., 2006). Emissions from on-road mobile sources were developed using the Motor Vehicle Emission Simulator (MOVES) while off-road emissions were supplied by the National Mobile Inventory Model (NMIM). Emissions due to aircraft are included in the inventories based on take-off and landing data for individual airports. Emission inventories and WRF/MCIP meteorology are merged and gridded using the Sparse Operator Kernel Emissions (SMOKE v3.1, https://www.cmascenter.org/smoke/) model to generate time-varying, three dimensional CMAQ ready emission fields. CMAQv4.7.1 uses the 2005 Carbon Bond (CB05) chemical mechanism (Yarwood et al., 2005). Though there is a more re-
cent version of the Carbon Bond chemical mechanism (CB6) it is not available for use in publically available versions of CMAQ as of the submission of this manuscript.

We have added lightning generated NO$_x$ ($L_{NO_x}$), assuming a NO$_x$ production rate of 500 moles/flash, to the merged emissions files following the parameterization described in Allen et al. (2012). The production of $L_{NO_x}$ is correlated to lightning flashes observed by the National Lightning Detection network (NLDN), which records cloud to ground flashes (CG). The amount of intercloud lightning (IC) is calculated based on a climatological IC/CG ratio (Boccippio et al., 2001). In general, the amount of NO$_x$ supplied by lightning is much smaller than anthropogenic sources, especially in urban areas. This may not necessarily be true in the future as further pollution control measures are enacted to reduce the emissions of NO$_x$ from power plants, vehicles, etc. Neglecting $L_{NO_x}$ may result in modelled NO$_x$ being biased low, especially in rural regions where NO$_x$ levels are already much lower than in urban regions.

Modeled tropospheric column NO$_2$ is calculated by integrating the CMAQ NO$_2$ profiles from the surface to the level of the tropopause provided by either the DOMINO or GSFC retrieval teams. The model results are convolved with the air mass factors and averaging kernels (DOMINO) or scattering weights (GSFC) appropriate for the two satellite retrievals. We interpolate the CMAQ output to the pressure grid of the averaging kernel/scattering weight. The DOMINO tropospheric averaging kernel is calculated by taking the product of the averaging kernel and the ratio of the satellite air mass factor to the tropospheric air mass factor (Boersma et al., 2011). CMAQ output is multiplied by the tropospheric averaging kernel and then integrated over pressure. In a similar fashion, GSFC scattering weights are used with model profiles of NO$_2$ to generate CMAQ tropospheric column NO$_2$ for direct comparison with the GSFC tropospheric NO$_2$ product (Buscela et al., 2013; Lamsal et al., 2014).

Only those model grid points closest to the center of each pixel along the satellite swath are considered. To generate a model L3 gridded product, CMAQ output at each model grid cell is only used if the co-located satellite retrieval satisfies the quality flags and cloud fraction limits described above (i.e., we only use those CMAQ points where...
the closest satellite retrieval is also considered “valid”). CMAQ output is screened and gridded in an identical fashion as the respective OMI retrievals, to generate model L3 products (one for the DOMINO retrieval, the other for the GSFC retrieval) appropriate for comparison to the satellite data.

4 Analysis and results

4.1 Model/satellite comparisons

Gridded, L3 satellite retrievals of tropospheric column NO$_2$ over the Eastern US for the July/August 2007 period of study are shown in Fig. 1. Both the DOMINO and GSFC retrievals exhibit similar patterns of elevated NO$_2$ over urban centers and lower, but substantial and quantifiable NO$_2$ in rural regions. The two retrieval products are well correlated ($r^2 = 0.82$). Column NO$_2$ found by the DOMINO retrieval is $\sim 20\%$ higher than column NO$_2$ found using the GSFC retrieval. It is beyond the scope of this paper to probe the cause of this disagreement. As such, we will compare both satellite retrievals to model output separately. This difference between data sets may affect attempts to estimate emissions of NO$_x$ from satellite retrievals. Our focus is on the ratio of column NO$_2$ between urban and rural regions; both retrievals yield similar scientific conclusions.

Figure 2 shows comparisons of the baseline CMAQ model (MDL$_{BSE}$) value of column NO$_2$ to the satellite data product found by both retrievals. Regions of elevated column NO$_2$ are calculated over urban regions, roughly similar to observation, but the air quality model estimates significantly smaller levels of column NO$_2$ over rural areas than reported by OMI. The correlation between model and observed NO$_2$, shown for both retrievals in Fig. 2, is largely driven by the high density of points where column NO$_2$ is below $5 \times 10^{15}$ cm$^{-2}$ (Fig. 2, right panels). In this region of the distribution, observed NO$_2$ is larger than the baseline air quality model for both satellite retrievals. The mean ratio of model to observations across the domain, which is predominantly rural, is 0.34
and 0.37 for DOMINO and GSFC, respectively. In the predominantly urban regions (red points, right panels of Fig. 2) the opposite is true; the mean ratio of model to observed NO$_2$ rises to 1.56 and 1.62 for the two retrievals.

To highlight areas where the model is higher than observations we restrict our maps to only show those places where model calculations are at least 25% higher than observed by satellite (Fig. 3). The regions that meet the 25% criteria are generally large urban centers, for which CMAQ NO$_2$ is usually biased high by 50 to 60% (DOMINO and GSFC retrievals, respectively). This overestimate of column NO$_2$ is not true for all highly populated urban centers, such as the I-95 corridor from Washington, DC through Philadelphia, PA. Over the entire domain shown in Fig. 2, NO$_2$ found using MDL$_{BSE}$ is $\sim$ 60% lower than observed. Overall, the ratio of urban NO$_2$ (those areas shown in Fig. 3) to rural NO$_2$ (all other areas) in the model is at least a factor of 2 larger than in the same ratio calculated from space-based observations. Use of the BEHR (Russell et al., 2011) retrieval of column NO$_2$ (not shown) gives similar results. These results are similar to documented discrepancies based on comparison of CMAQ output to observations of column NO$_2$ from SCIAMACHY (Napelenok et al., 2008) as well as surface NO$_2$ (Castellanos et al., 2009).

### 4.2 Long-lived NO$_x$ precursors

The CB05 chemical mechanism represents all organic nitrate species, such as alkyl nitrates (e.g., isopropyl nitrate, n-propyl nitrate, isobutyl nitrate, isoprene nitrates), as a single species called NTR (Yarwood et al., 2005). In CB05, NTR is created by the breakdown of isoprene and isoprene products such as methacrolein (MACR) and methyl vinyl ketone (MVK) and is lost through photolytic and oxidation processes. The photolysis of NTR is calculated in the model using the cross section of isopropyl nitrate to represent all organic nitrate species and produces NO$_2$ and HO$_2$, important precursors to surface O$_3$ formation (Yu et al., 2010).

We have diagnosed the lifetime of NTR due to photolysis to be $\sim$ 10 days in CMAQ during summer, in agreement with the lifetime of C$_2$ to C$_4$ alkyl nitrates in the mixed
The CMAQ lifetime for NTR is based on photolysis frequencies calculated by the photolysis rates preprocessor module (jproc). Within CMAQ, NTR often constitutes 20 to 40% of the total NO$_y$ budget. The long lifetime of NTR results in sequestration of nitrogen compounds far from the emission source, perhaps accounting for the low bias of CMAQ NO$_2$ in rural areas. Analysis of aircraft observations, however, indicates the speciation of NTR is not well described in CMAQ using CB05, with the most abundant species in this family being hydroxynitrates with lifetimes on order $\sim$ 1 day or less (Horowitz et al., 2007; Perring et al., 2009; Beaver et al., 2012). Furthermore, a recent analysis of laboratory studies that evaluated absorption cross sections and photolysis frequencies indicates that the photolysis of carbonyl nitrates may be 3 and 20 times faster than previously reported (Müller et al., 2014).

A comparison of NTR from a baseline CMAQ run to measurements obtained during the 2011 NASA DISCOVER-AQ field mission shows modeled NTR to be 2–4 times greater than observed (Fig. 4, top). This version of the model uses emissions inventories and meteorological fields appropriate for 2011 (Loughner et al., 2013; Anderson et al., 2014; Goldberg et al., 2014; Flynn et al., 2014; He et al., 2014). To investigate the source of this discrepancy we have increased the photolysis frequency of NTR by a factor of 10, reducing the lifetime to $\sim$ 1 day. This model scenario will be referred to as MDL$_{NTR}$ for the remainder of this study. Values of NTR found using a shorter lifetime are in much better agreement with observed NTR, indicating a significant improvement in the model representation of alkyl nitrate chemistry (Fig. 4, bottom). We recognize that decreasing the lifetime of NTR with respect to photolysis by a factor of 10 may be too simplistic, but this calculation is meant to illustrate how a thorough representation of the NTR family of gases may lead to overall improvements to the model framework. A full revision of alkyl nitrate is being undertaken by the EPA (Leuckcen and Schwede, 2014).

The breakdown of NTR, having a lifetime of $\sim$ 1 day, increases local NO$_2$ both by direct production of NO$_2$ and by shifting the partitioning of NO$_x$ toward NO$_2$ via the HO$_2$ + NO reaction. A comparison of CMAQ tropospheric column NO$_2$ (convolved with
the averaging kernels) found for the MDL\textsubscript{NTR} simulation and OMI column NO\textsubscript{2} is shown in Fig. 5. There is slightly better agreement between modeled and column NO\textsubscript{2} and both satellite retrievals for the entire domain compared to the baseline simulation, generally due to increased NO\textsubscript{2} in rural areas for MDL\textsubscript{NTR}. However, for MDL\textsubscript{NTR}, modeled column NO\textsubscript{2} in urban regions (red points, Fig. 5) lies further from observed NO\textsubscript{2} than found for the baseline simulations.

In CB05, 100 % of the NO\textsubscript{x} from photolysis of NTR or its products is recycled. Loss through OH attack, also fast for isoprene nitrates, yields HNO\textsubscript{3}, a NO\textsubscript{x} sink in the troposphere. The model output presented here can be considered a bounding scenario since this treatment of NO\textsubscript{x} is an over-simplification. If NO\textsubscript{x} recycling were not 100 % efficient, we would expect a decrease in column NO\textsubscript{2} throughout the domain, and a corresponding reduction in O\textsubscript{3}. It is beyond the scope of this study to assess the sensitivity of NO\textsubscript{2} and O\textsubscript{3} to this level of detail of the CB05 mechanism.

Emissions from airplanes en route are not considered in the emissions inventories. However, the overall contribution from aircraft aloft to the tropospheric column is relatively minor (i.e. less than 1 % of tropospheric column) and would not explain the urban/rural discrepancy between satellite observations and model output (Jacobson et al., 2013).

4.3 Emissions of NO\textsubscript{x} from mobile sources

A comparison of NO\textsubscript{x} from emission inventories for 2011 to observations taken during DISCOVER-AQ (July 2011) has quantified a potential overestimation of mobile NO\textsubscript{x} (Anderson et al., 2014). The ratio of CO/NO\textsubscript{y} from observations was roughly a factor of 2 greater than the ratio based on the National Emissions Inventory data used in CMAQ. Model CO is only \sim 15 % greater than observed for this time period, indicative of a large overestimate of mobile NO\textsubscript{x} emissions (Anderson et al., 2014). This conclusion is in agreement with a study by Yu et al. (2012), who compared aircraft data from the TexAQS/GoMACCS campaign to CMAQ simulations that considered 2001 NEI point and source emissions projected to 2006, mobile emissions generated from the EPA
MOBILE6 model, and used the CB4.2 chemical mechanism. Though Yu et al. report good agreement between modeled and observed CO, the ratio of observed CO/NO$_y$ is roughly a factor of 2 higher than the calculated ratio of these species from CMAQ. A separate study of 2011 DISCOVER-AQ observations has shown that CMAQ consistently overestimated NO$_y$ by a factor of 2 from the surface to 3000 m altitude (Goldberg et al., 2014).

Airborne observations analogous to those taken during DISCOVER-AQ in summer 2011 do not exist for summer 2007. We have examined observations of CO and NO$_x$ from 6 surface air quality monitoring sites in the Maryland, Northern Virginia, and the District of Columbia acquired during summer 2007. The chemiluminescence method of detecting NO$_x$ suffers from known interferences (Castellanos et al., 2011). It is reasonable to assume that the surface sites are actually reporting NO$_x^* = NO_y - HNO_3$. For the summer of 2007, CO observations also seem to have calibration issues. Nonetheless, we have compared the observed ratio of CO/NO$_x^*$ from these 6 sites to the CMAQ value of CO/NO$_x^*$, where CMAQ is sampled at the time and location of each surface observation. The mean and 1-sigma standard deviation of the observed divided by modeled value of CO/NO$_x^*$ is 1.97 ± 1.5 for summer 2007; the large SD reflects a great deal of noise in the surface observations. The fact that observed CO/NO$_x^*$ exceeds the modeled value of this quantity supports the notion that mobile emissions in the 2007 inventory exceed the actual emissions from this source by an amount comparable to that reported by Anderson et al. (2014).

Following Anderson et al. (2014), we assume that there is a similar overestimation of NO$_x$ in the 2007 emissions inventories used in our analysis and we test for this discrepancy by reducing mobile NO$_x$ emissions by 50%. Results from a CMAQ model run that considers this change as well as the reduction in NTR lifetime in the CB05 chemical mechanism, termed MDL$_{N50}$, are shown in Fig. 6. The most noticeable difference between these results and those presented in Figs. 2 and 5 is the reduction in column NO$_2$ over urban regions, which is now in much better agreement with satellite observations (ratios between model and observations of 1.20 and 1.24 for DOMINO...
and GSFC, respectively). While the modifications to the CB05 chemical mechanism and emissions inventories have somewhat reconciled the differences between modeled and remotely sensed urban tropospheric column NO₂, rural NO₂ is still under estimated by the model. Mean ratios for the domain (0.34 and 0.38) are similar to results from the baseline model. Essentially, these modifications to the model have improved the urban disagreement, but overall model performance is unchanged.

4.4 Biogenic emissions

As stated above, the original emissions inventories generated by MARAMA include biogenic sources from the Model of Emissions of Gases and Aerosols in Nature (MEGAN v2.04) (Guenther et al., 2006). Since the 2007 emissions inventories were made available, an updated version of MEGAN was released (v2.10, Guenther et al., 2012). One of the main differences in biogenic emissions between the two versions of MEGAN is that isoprene, the dominant VOC in the mid-Atlantic region, has decreased by about 25% in the latest version. Emissions of biogenic isoprene calculated using MEGAN v2.10 are significantly less sensitive to high levels of photochemically active radiation (PAR) compared to earlier versions of MEGAN, resulting in lower isoprene during midday near the time of OMI overpass. An in-depth analysis of the sensitivity of regulatory air quality models to simulation of biogenic emissions will be the subject of a forthcoming paper.

Fundamentally, isoprene oxidation is initiated by reaction with OH to generate isoprene peroxy radical intermediates, termed RO₂. In the presence of NOₓ, these RO₂ intermediates react with NO, producing MVK, MACR, HCHO, and a small amount of organic nitrates (Paulot et al., 2009). Overall, when output from the latest version of MEGAN is incorporated into the emissions inventories (MDL_MGN) there is an overall increase in column NO₂ across the model domain due to the reduction in NOₓ sinks (Fig. 7).

Combining the modifications to the CB05 chemical mechanism with the changes to mobile and biogenic emissions yields the best overall agreement between model and
observations (MDL\textsubscript{TOT}, Fig. 8). The correlation between measured and modeled NO\textsubscript{2} is larger for MDL\textsubscript{TOT} ($r^2 = 0.77, 0.64$ for DOMINO, GSFC) than for any other model scenario. While further work is needed, we have succeeded in decreasing the urban overestimate and rural underestimate of tropospheric column NO\textsubscript{2} compared to satellite data by: (a) using the latest version of MEGAN, (b) prescribing a factor of 2 reduction in mobile NO\textsubscript{x} emissions throughout the domain, and (c) reducing the lifetime of NTR within CB05 by a factor of 10. Future work will investigate the importance of soil emissions of HONO, which are not included in the current versions of MEGAN and the chemical kinetics of other species that are important precursors to surface ozone. Prior studies indicate that soil emissions may account for 7\% of column NO\textsubscript{2} during the summer ozone season (Choi et al., 2008) and that HONO could be an important morning source of OH in an urban, VOC rich environment (Ren et al., 2013).

5 Ozone

The focus of state implementation plans is attainment of the 8 h standard for surface ozone. It should be noted that CMAQ is most often used in a relative sense for this purpose. For instance, modifications to emissions inventories from a wide variety of sources, which represent future conditions based on possible proposed regulations, are run through CMAQ. Output from this model is compared to a base scenario to determine how much surface ozone is expected to decrease if these policy measures were to be enacted. For this study, we instead focus on the ability of CMAQ to reproduce observed surface ozone. In Fig. 9, we compare average maximum daily 8 h average ozone from the four modeling scenarios considered above (MDL\textsubscript{BSE}, MDL\textsubscript{NTR}, MDL\textsubscript{N50}, and MDL\textsubscript{TOT}) to measured surface ozone from ground based air quality observing sites (AQS). We have chosen to show the average of the daily maximum 8 h ozone for July and August 2007 at each mode grid point. While it may seem that there were no violations of the 75 ppb standard, based on the scatter plots of model and observed ozone (Fig. 9, bottom), this is certainly not the case. There were exceedances
of the 75 ppb ozone standard during this time; however, we have averaged these events with days having lower ozone. There were no locations where the 62 day average of daily maximum 8 h ozone exceeded 75 ppb for this time period. An additional comparison, shown at the end of this section, will focus on days when the surface ozone standard was exceeded in Maryland.

All of the CMAQ simulations presented in Fig. 9 generally over-estimate observed surface ozone. Ozone from MDL_{BSE} is 26% greater than observed (ratio of 1.26 denoted on Fig. 9), with 87 locations averaging higher than 75 ppb within the model. CMAQ results for MDL_{NTR} lead to a further increase (32%) in modeled ozone (an ozone dis-benefit from this model change). While the changes made to CB05 for MDL_{NTR} provide a much more realistic representation of NO\textsubscript{x} chemistry (see Fig. 4), comparison of ozone found using MDL_{NTR} and the baseline run suggests the presence of compensating errors in the chemistry and/or dynamics that control ozone. The inclusion of a 50% reduction of mobile NO\textsubscript{x} (MDL_{N50}) (Anderson et al., 2014) leads to a decrease in modeled ozone compared to results from the MDL_{NTR} run. Simulated ozone is still 24% greater than measured, although there is slight improvement compared to the baseline run. Improved agreement between model and AQS observations of ozone occurs when updated biogenic emissions are also included, together with the aforementioned changes to mobile NO\textsubscript{x} and the lifetime of NTR. In this scenario, MDL_{TOT}, the model/measurement discrepancy for ozone is reduced to 19% and there are only 40 false positives. The reason for this model behavior is that the reduction in isoprene emission upon use of MEGANv2.10 leads to decreases in HO\textsubscript{2} and RO\textsubscript{2}, important ozone precursors.

If a ground based ozone monitor reports 8 h average ozone exceeding the NAAQS standard, currently 75 ppb, it is considered to be in non-attainment. These sites are the subject of intense focus by state agencies to determine the fundamental causes of the ozone exceedance (e.g. local sources of pollution vs. out of state upwind sources). A comparison of ozone from non-attainment sites in the Maryland during July and August 2007 to CMAQ model output is shown in
Fig. 10. It should be noted that the ozone standard in 2007 was 80 ppb. However, the state of Maryland provides historic ozone data for the current, 75 ppb standard. These data can be found at https://data.maryland.gov/Energy-and-Environment/Maryland-Ozone-Exceedance-Days-in-2007/iyzm-8pqd. The model values of daily 8 h average ozone represent the closest points, spatially, to the monitor sites on the day that the exceedance occurred. For all model cases, CMAQ shows greater variability than the ground based monitors during times of ozone exceedance. The overall analysis of the model runs for these days/times leads to results similar to the analysis in Fig. 9. The decrease in the lifetime of NTR (13 % overestimate) leads to an increase in model ozone compared to baseline (6 % overestimate), while the model that considers both reduced NTR lifetime and a 50 % decrease in mobile NO\textsubscript{x} emission yields an improved representation (2 % overestimate) of ozone compared to the baseline. Best agreement between modeled and observed ozone, for the times and place of exceedance, occurs when MEGANv.2.10 is considered along with the other model modifications. While the comparison still exhibits significant scatter about the 1 : 1 line, CMAQ is now on average in agreement with observed surface ozone (ratio of 1.00). This represents significant progress for the modeling of surface ozone, since we have prescribed a scenario for which the CMAQ air quality model is unbiased during a period of air quality exceedance.

6 Conclusions

We examine the ability of CMAQ to simulate reactive nitrogen over the eastern US by comparing model output to column content NO\textsubscript{2} observed by the OMI instrument on the AURA satellite. For July and August 2007, CMAQ consistently overestimates NO\textsubscript{2} over urban areas and underestimates NO\textsubscript{2} over rural areas relative to OMI observations; this finding is insensitive to the choice of GSFC or DOMINO retrieval product. Neither inclusion of lightning NO\textsubscript{x} nor consideration of the averaging kernel/scattering weights for OMI alters this conclusion. While the absolute value of NO\textsubscript{2} column content is sub-
ject to errors from a variety of sources, the urban/rural ratio provides a rigorous test of CMAQ’s ability to simulate the photochemistry of NO$_2$ and the transport of this important, criteria air pollutant. Because CMAQ using the CB05 mechanism overestimates the urban to rural ratio of tropospheric column NO$_2$, this model may underestimate the interstate transport of NO$_x$ and/or NO$_x$ reservoirs.

The CB05 chemical mechanism represents all alkyl nitrates as isopropyl nitrate – a reasonable simplification given the state of knowledge at the time of creation. However, there is substantial evidence indicating an entire family of alkyl nitrates and substituted alkyl nitrates (Horowitz et al., 2007; Perring et al., 2009; Beaver et al., 2012). These can have lifetimes as short as hours and recycle NO$_x$ much faster than do short chain alkyl nitrates. Reducing the simulated lifetime of NTR in CB05 from ~10 days to ~1 day improves the agreement between measured and modeled tropospheric column NO$_2$ for the Baltimore–Washington area. This modification to CB05 reduces, but does not eliminate the urban/rural NO$_2$ bias within CMAQ. Implementation of a factor of 2 reduction in NO$_x$ emissions from mobile sources (Anderson et al., 2014) decreases NO$_2$ in urban regions that have a high density of vehicular traffic, which improves the CMAQ representation of the ratio of urban to rural NO$_2$. Use of the latest MEGAN emission scenario for VOCs, v2.10 (Guenther et al., 2012), reduces NO$_2$ throughout the domain and further improved the CMAQ representation of urban to rural NO$_2$, due to smaller levels of RO$_2$ that are driven by lower emission rates for isoprene.

We have also examined the effect of these various model runs on the CMAQ representation of surface ozone. Reducing the lifetime of NTR by a factor of 10 increases the average daily 8 h maximum ozone by ~5%; decreasing mobile source NO$_x$ emissions by a factor of 2 decreases ozone by about 6%. The use of MEGAN v2.10 causes surface ozone to fall by 2.5% relative to a simulation that is identical, except for use of MEGAN 2.04. Combining all three of these model changes (i.e., factor of 10 reduction in NTR lifetime, factor of 2 reduction in mobile NO$_x$, MEGAN v2.10) leads to the best simulation of surface ozone for the mid-Atlantic. This model run leads to agreement with the 2 month average of daily 8 h maximum ozone at the ±20% level, fewest num-
ber of false positives of an ozone exceedance throughout the domain, as well as an
unbiased simulation of surface ozone at ground based AQS sites that experienced an
ozone exceedance (8 h ozone greater than 75 ppb) within Maryland during July and
August 2007. The prescription of an unbiased simulation of ozone, coupled with a fairly
accurate simulation of the urban to rural ratio of column NO$_2$, may provide a frame-
work for use in studies focused on achieving future adherence to specific air quality
standards for surface ozone by reducing emission of NO$_x$ from various anthropogenic
sectors.

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Figure 1. Average OMI tropospheric column NO$_2$ observations for July and August 2007 for both the DOMINO (left) and GSFC (middle) retrievals. The level 2 swath data for both retrievals has been screened, weighted based on viewing angle and gridded onto a 0.25° × 0.25° lat/lon grid. Only observations where cloud fraction is less than 30% are used in the gridding process. Both data sets indicate that the highest levels of tropospheric NO$_2$ occur over urban regions. A scatter plot of DOMINO vs. GSFC observations (right) indicates that the DOMINO retrieval is roughly 20% higher, on average, than the GSFC satellite product.
Figure 2. Comparison of satellite observations of tropospheric column NO$_2$ (left panels) to output from a baseline CMAQ model run (CMAQ$_{BSE}$) convolved with the satellite averaging kernels for the DOMINO retrieval (top middle) and GSFC retrieval (bottom middle). Model output is screened, weighted, and gridded in the same manner as the satellite retrievals. A scatter plot comparison of model to satellite (right panels) indicates the model can explain $\sim$ 50–70% of the satellite observations. Much of this correlation is driven by the large concentration of points below $5 \times 10^{15}$ cm$^{-2}$, where the model underpredicts the satellite. The red points represent areas where the model is at least 25% greater than observations.
Figure 3. The same model output as Fig. 2 except results are only shown for regions where the simulations are at least 25% greater than observations (left panels). This clearly shows that model is biased high over urban regions indicated by the red points in the scatter plots (right panels). The variance ($r^2$) in both panels is calculated using all model grid points. The mean ratio for all points within the domain ($\text{ratio}_{\text{domain}}$) and for the urban regions (red points, $\text{ratio}_{\text{urban}}$) is provided.
Figure 4. (Top Panel) Comparison of baseline CMAQ simulations of organic nitrates (NTR) (colored contours) to NTR observed during the DISCOVER–AQ field mission on 29 July 2011 (colored points). (Bottom Panel) As in the top panel, except the CB05 chemical mechanism in CMAQ has been modified such that the lifetime of NTR is reduced by a factor of 10 (colored contours).
Figure 5. Similar to Fig. 2 except the chemical mechanism in the CMAQ model has been modified such that the lifetime of NTR is reduced by a factor of 10 (CMAQ$_{NTR}$). Gray points on the scatter plots represent the results shown in Fig. 2 (right panels). As in Fig. 3, red points represent urban regions.
Figure 6. Same as Fig. 5 except model results include both changes to NTR chemistry and a 50% reduction in the emissions of NO\textsubscript{x} from mobile sources (CMAQ\textsubscript{N50}). Gray points on the scatter plots represent the results shown in Fig. 2 (right panels).
Figure 7. Same as Fig. 5 except model include updated biogenic emissions from MEGANv2.10 (CMAQ_{MGN}). Gray points on the scatter plots represent the results shown in Fig. 2 (right panels).
Figure 8. Same as Fig. 5 except model results include changes to NTR chemistry, a 50% reduction in the emissions of NO\textsubscript{x} from mobile sources, and updated biogenic emissions (CMAQ\textsubscript{TOT}). Gray points on the scatter plots represent the results shown in Fig. 2 (right panels).
Figure 9. Average daily maximum 8 h daily ozone for July and August 2007 for four model cases: MDL\textsubscript{BSE} (top left), MDL\textsubscript{NTR} (top middle left), MDL\textsubscript{N50} (top middle right), and MDL\textsubscript{TOT} (top right) and ground based observations. Colored contours represent the CMAQ model output. Colored points denote average daily maximum 8 h daily ozone from ground based AQS sites for the same time period. Scatter plots of each CMAQ model output vs. observations are shown (bottom panels). Gray horizontal and vertical lines indicate the 75 ppb ozone exceedance level. The number of times the model output is greater than 75 ppb while the observations are less than 75 ppb is shown (false positive). The mean ratio between CMAQ surface ozone and observations at air quality sites is indicated for each model simulation.
Figure 10. Comparison of average 8 h surface ozone calculated from baseline CMAQ model output (top left), MDL\textsubscript{NTR} model output (top right), MDL\textsubscript{N50} model output (bottom left panel), and MDL\textsubscript{TOT} (bottom right) to observations from ground based AQS sites for those days and locations in Maryland that experienced exceedances (8 h average ozone greater than 75 ppb) during July and August 2007.