



RESEARCH LETTER

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Key Points:

- Ozone is simulated well by CAMx, but there is an overestimate of NO_y and underestimate of HCHO
- Ozone production in the new model framework is more sensitive to NO_x emissions
- Point sources likely contribute more to surface ozone than commonly appreciated

Supporting Information:

- Supporting Information S1

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CAMx ozone source attribution in the eastern United States using guidance from observations during DISCOVER-AQ Maryland

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Abstract A Comprehensive Air-Quality Model with Extensions (CAMx) version 6.10 simulation was assessed through comparison with data acquired during NASA's 2011 Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) Maryland field campaign. Comparisons for the baseline simulation (Carbon Bond 2005 (CB05) chemistry, Environmental Protection Agency 2011 National Emissions Inventory) show a model overestimate of NO_y by +86.2% and an underestimate of HCHO by –28.3%. We present a new model framework (Carbon Bond 6 Revision 2 chemistry (CB6r2), Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 biogenic emissions, 50% reduction in mobile NO_x, enhanced representation of isoprene nitrates) that better matches observations. The new model framework attributes 31.4% more surface ozone in Maryland to electric generating units (EGUs) and 34.6% less ozone to on-road mobile sources. Surface ozone becomes more NO_x limited throughout the eastern United States compared to the baseline simulation. The baseline model therefore likely underestimates the effectiveness of anthropogenic NO_x reductions as well as the current contribution of EGUs to surface ozone.

1. Introduction

Policymakers and regulatory agencies use regional air quality models to predict how future air quality will respond to control strategies [U.S. Environmental Protection Agency (EPA), 2014a]. Many air quality models can skillfully simulate surface ozone in North America for focused studies of certain time periods [Hogrefe et al., 2004; Appel et al., 2007; Ferreira et al., 2011; Appel et al., 2012; Simon et al., 2012]. Global models can reflect changes in ozone resulting from control measures [e.g., Clifton et al., 2014; Rieder et al., 2015], especially for rural sites representative of regional atmospheric composition, but nonattainment is based on monitors with the highest readings. Urban-scale events, such as seen in Edgewood, MD, discussed below, require urban-scale resolution of 12 km or better [e.g., Loughner et al., 2011; Goldberg et al., 2014].

Even where regional air quality models accurately reproduce surface ozone concentrations, many have difficulty simulating the response of ozone to reductions in precursor emissions [Gilliland et al., 2008; Zhou et al., 2013; Foley et al., 2015]. This may be linked to the challenge of simulating ozone precursors: NO_x (NO_x = NO + NO₂) and volatile organic compounds (VOCs) [Castellanos et al., 2011; Zhou et al., 2013; Canty et al., 2015]. For any given ozone concentration, there can be many different production pathways; empirical kinetic modeling approach (EKMA) diagrams [Kinosian, 1982; Chameides et al., 1992; Sillman, 1999] highlight this nonlinear dependence of ozone production on NO_x and VOCs. Air quality models must be in the correct ozone production regime (i.e., NO_x limited versus VOC limited) if they are to accurately forecast how air quality regulations will improve ozone concentrations.

Many studies show an overestimate, by up to a factor of 2, of total reactive oxidized nitrogen (NO_y) in regional air quality models compared to observations [Doraiswamy et al., 2009; Castellanos et al., 2011; Yu et al., 2012; Brioude et al., 2013; Anderson et al., 2014; Goldberg et al., 2014]. Some link the calculation of too much NO_y to the overestimate of NO_x emissions from area sources [Doraiswamy et al., 2009], while others link it to an

overestimate of NO_x emissions from commercial marine vessels [Brioude *et al.*, 2013]. Anderson *et al.* [2014] examined airborne observations of CO, NO_x , and NO_y obtained in the Baltimore-Washington corridor and concluded that a substantial portion of the error must be due to an overestimate in NO_x emissions from mobile sources since this source accounts for the majority (62%) of NO_x emissions in the 2011 National Emissions Inventory (NEI). Fujita *et al.* [2012] also find an overestimate of NO_x mobile source emissions in Motor Vehicle Emission Simulator (MOVES) 2010a, which is used to develop the NEI.

A better representation of NO_y chemistry may resolve a portion of the overestimate of NO_y noted above. The Carbon Bond 6 Revision 2 (CB6r2) gas-phase chemistry has been released recently [Hildebrandt-Ruiz and Yarwood, 2013]. This updated mechanism more explicitly represents alkyl nitrates in regional air quality models and provides a significant improvement in the simulation of these compounds compared to CB05 [Hildebrandt-Ruiz and Yarwood, 2013; Canty *et al.*, 2015]. CB6r2 splits the alkyl nitrate grouping (NTR) into three families: alkyl nitrates that exist primarily in the gas phase (NTR1), larger multifunctional alkyl nitrates that partition to organic aerosol (NTR2), and isoprene nitrates (INTR) that react rapidly with OH. NTR1 and INTR can recycle back to NO_2 , but the only gas-phase sink for NTR2 is conversion to HNO_3 . The CB6r2 gas-phase mechanism calculates a shorter lifetime of alkyl nitrates and faster recycling of NO_x , which agrees better with laboratory studies [Perring *et al.*, 2013] than CB05. In addition to improving the representation of alkyl nitrates in the regional air quality models, this change may also improve the simulation of ozone attributed to sources beyond state borders. To further improve the representation of alkyl nitrates in air quality models, Horowitz *et al.* [2007] suggest increasing isoprene nitrate deposition velocities.

As anthropogenic sources of ozone precursors continue to decrease, biogenic emissions will play an even larger role in the ozone formation process. Two models are used to simulate biogenic emissions within regional air quality models: Biogenic Emissions Inventory System (BEIS) [Pouliot and Pierce, 2009] and Model of Emissions of Gases and Aerosols from Nature (MEGAN) [Guenther *et al.*, 2012]. Isoprene emissions are uniformly larger in the MEGAN model within North America than in BEIS [Warneke *et al.*, 2010; Carlton and Baker, 2011].

2. Methods

We use the Comprehensive Air-quality Model with Extensions (CAMx) version 6.10 to simulate trace gas mixing ratios in the eastern United States for July 2011; the model domain is shown in Figure S1 in the supporting information. Many previous studies have used CAMx to simulate ozone with reasonable fidelity [Emery *et al.*, 2012; Dolwick *et al.*, 2015; Koo *et al.*, 2015]. The Anthropogenic Precursor Culpability Assessment (APCA) probing tool in CAMx is used as a means to tag ozone source attribution from 12 source regions and 7 source sectors. The 12 source regions are shown in Figure S2. The seven source sectors are listed in Table S1. We also use the Ozone Source Apportionment Tool (OSAT) to calculate the ozone attributed to NO_x - and VOC limited production regimes. For a detailed description of CAMx version 6.10 and the APCA and OSAT probing tools, please refer to the CAMx User's Guide [Ramboll Environ, 2014]. CAMx was driven off-line by meteorological output [EPA, 2014b] from the WRF version 3.4 model [Skamarock *et al.*, 2008] at hourly intervals. Specific details about the meteorology simulation are in the EPA technical support document [EPA, 2014b]. Table S2 describes the CAMx options chosen for our baseline simulation.

For the baseline simulation, we use version 2 of the 2011 NEI as compiled by EPA for anthropogenic emissions [EPA, 2014c]. The Continuous Emission Monitoring System (CEMS) database temporalized by Eastern Regional Technical Advisory Committee software was used to create electric generation unit (EGU) emissions. This inventory allocates larger emissions of NO_x during hotter days due to increased electricity demand [He *et al.*, 2013] but does not include an estimate of additional NO_x emitted by small peaking units. Mobile emission estimates from cars, trucks, and motorcycles were computed with the Motor Vehicle Emission Simulator 2014 (MOVES2014) [EPA, 2014c]. Biogenic emissions in the baseline simulation were calculated using BEIS version 3.6 [Pouliot and Pierce, 2009]. The Mid-Atlantic Regional Air Management Association (MARAMA) prepared total emissions for our model domain. Boundary conditions were initialized using the GEOS-Chem version 8-03-02 global chemistry model [Bey *et al.*, 2001] at a horizontal resolution of 2.0° latitude \times 2.5° longitude, as described in Henderson *et al.* [2014].

3. Results

3.1. Baseline Model Simulation

During July 2011, NASA conducted a comprehensive aircraft and ground measurement campaign in Maryland called Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ). This campaign provided a temporally and spatially rich collection of trace gas and aerosol observations throughout the lower troposphere [Crawford *et al.*, 2014]. This data set offers an unprecedented opportunity to compare regional air quality models to comprehensive atmospheric observations.

Figure 1 (left column) compares ozone (O_3) and two important ozone precursors, NO_y and formaldehyde (HCHO), from the baseline model simulation to P3-B aircraft observations. All observations were taken between altitudes of 300–5000 m within the Maryland airshed. In Figure 1 (left column, top row)—the scatterplot of modeled ozone versus observed ozone—we show a slope near unity (1.06) and a normalized mean bias (NMB) of -6.90% indicating a small underestimate of ozone above the surface. Because the NMB is under 10%, the baseline simulation shows good agreement with the observations of ozone. The root-mean-square error (RMSE) of the baseline simulation of ozone is 9.88 ppbv. In supporting information Figure S3, we provide a comparison to surface observations, which shows even better agreement with the baseline simulation.

Comparing modeled NO_y and HCHO to observations of the same quantities shows large discrepancies. The model simulation overestimates NO_y by nearly a factor of 2: a slope of 1.91 and a NMB of $+86.2\%$. An overestimate of NO_y is also seen at the Edgewood, Maryland, ground site as shown in Figure S4; instrument description is provided in Martins *et al.* [2012]. Conversely, the model simulation underestimates HCHO by nearly a factor of 2: a slope of 0.61 and a NMB of -28.3% . Although ozone is being predicted with considerable skill, the ozone precursors (NO_y and HCHO) are not. In supporting information Figures S5–S8, we show comparisons of NO_2 , alkyl nitrates, nitric acid, and isoprene.

The overestimate of NO_y and underestimate of HCHO by the baseline model simulation are more pronounced at the lowest altitudes of the P3-B aircraft spirals. In Figure 2, we show vertical profiles of measured ozone, NO_y , and HCHO binned in 500 m intervals and the closest CAMx model grid point, matched spatially and temporally during all flights. The median value of observed NO_y at the lowest altitude is below the 25th percentile of simulated NO_y , while the median value of observed HCHO is above the 75th percentile of simulated HCHO. Ozone is underestimated for the lowest sampled altitudes but agrees well with observations above 2.5 km; the underestimate of ozone, however, is not seen directly at the surface (Figure S3).

3.2. Updated “Beta” Model Simulation

We update the CAMx model platform based on recommendations from recent scientific literature outlined in section 1. The four changes are as follows:

1. Update the gas-phase chemistry from CB05 [Yarwood *et al.*, 2005] to CB6r2 [Hildebrandt-Ruiz and Yarwood, 2013], which better represents alkyl nitrate photochemistry.
2. Update the biogenic emissions from BEIS version 3.6 to MEGAN version 2.1, which increases isoprene emissions [Guenther *et al.*, 2012].
3. Reduce NO_x emissions from mobile sources (on road, off road, and nonroad) by 50% within our model domain [Anderson *et al.*, 2014].
4. Increase the dry deposition velocities of isoprene nitrates (INTR) and multifunctional alkyl nitrates (NTR2) to be the same as nitric acid (HNO_3) [Horowitz *et al.*, 2007].

We label the CAMx simulation with these four changes as the Beta simulation and compare the same trace gases (O_3 , NO_y , and HCHO) from this updated run to P3-B aircraft observations in Figure 1 (right column). The Beta simulation exhibits substantial improvement in the estimate of ozone precursors. The NMB of NO_y has improved from $+86.2\%$ to $+22.4\%$, and the NMB of HCHO has improved from -28.3% to -0.47% . The RMSE of NO_y and HCHO both improve: NO_y from 3.09 ppbv to 1.71 ppbv and HCHO from 1.34 ppbv to 0.93 ppbv. The NMB of NO_y at the Edgewood, MD, ground monitor also improves from $+46.9\%$ to -7.8% using this new model platform (Figure S4). The Beta simulation yields similar predictions of ozone compared to the original calculation: the baseline has a NMB of -6.90% , whereas the Beta simulation

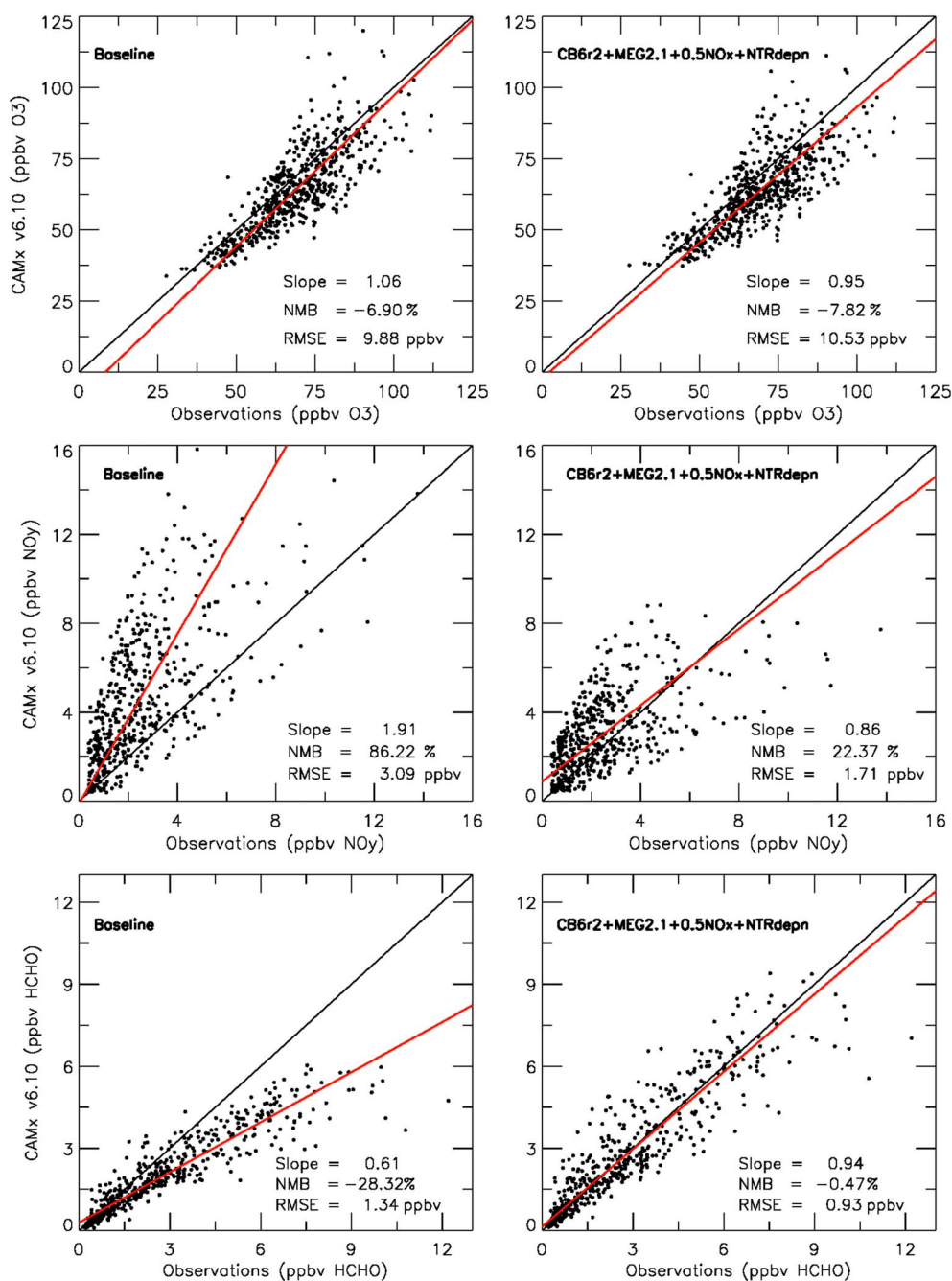


Figure 1. Observations acquired by the P3-B aircraft during DISCOVER-AQ Maryland in July 2011 compared to model output from CAMx version 6.10 at the nearest model grid point and closest hourly interval. The closest hourly model output is matched to each 1 min averaged P3-B observation; both quantities are then averaged over the same 10 min interval. (left column) Baseline simulation; (right column) updated Beta simulation. (top row) O₃, (middle row) NO_y, and (bottom row) HCHO. Black lines represent the 1:1 line, while red lines represent the linear best fit.

has a NMB of -7.82% . The RMSE of the ozone degrades slightly from 9.88 ppbv to 10.53 ppbv. Deteriorating performance of ozone in the Beta simulation may be due to not enough recycling of multifunctional alkyl nitrates to NO₂ in the CB6r2 gas-phase mechanism.

The Beta simulation also shows better agreement with the vertical profiles of NO_y and HCHO (Figure 2). The median value of observed NO_y is much closer to the median value of modeled NO_y. At altitudes above 2.5 km, there is

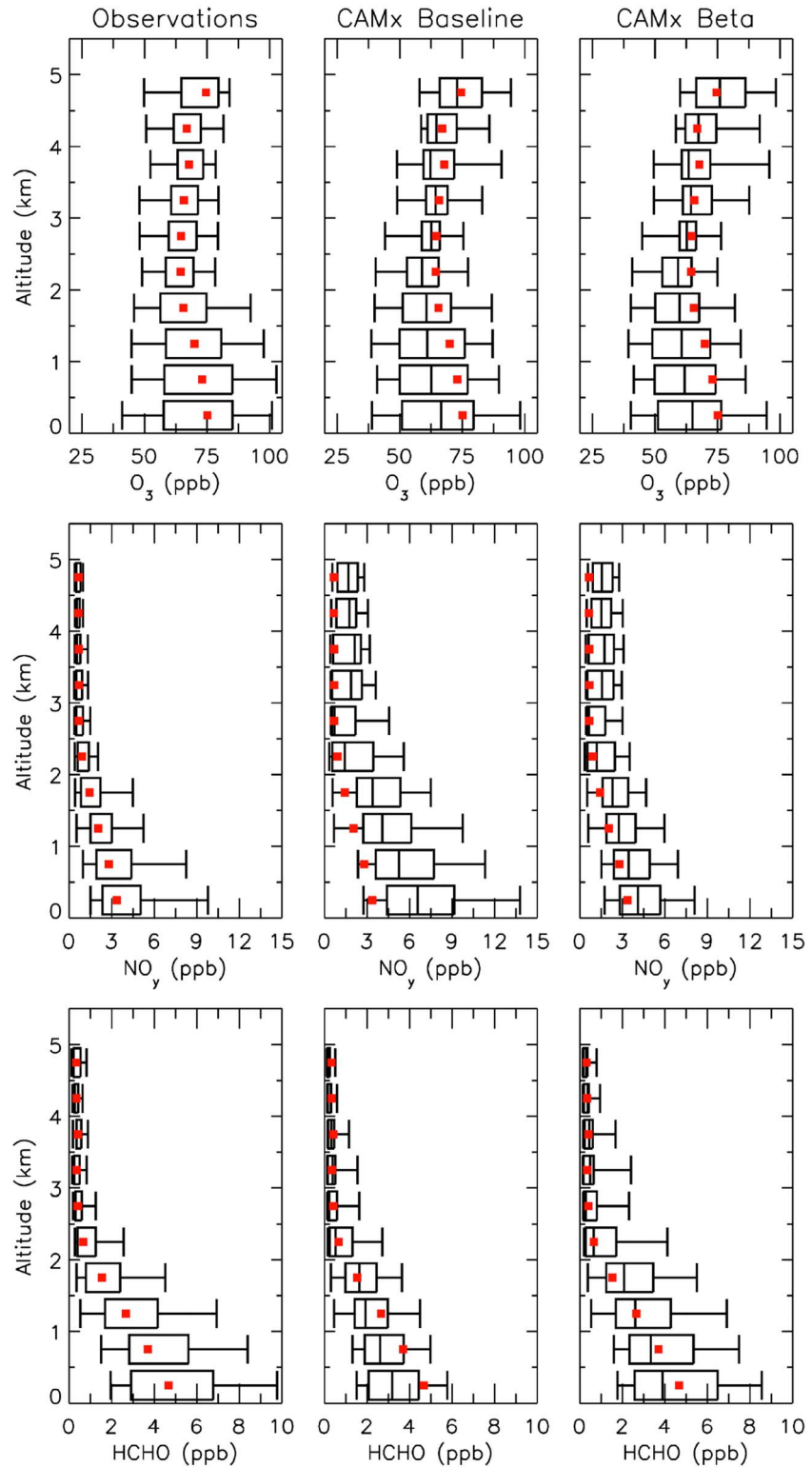


Figure 2. Vertical profiles of O₃, NO_y, and HCHO binned in 500 m intervals, showing the 5th, 25th, 50th, 75th, and 95th percentiles. (left column) One minute averaged data from the P3-B aircraft; (middle column) baseline simulation; (right column) updated Beta simulation. Model output from CAMx version 6.10 is matched spatially and temporally to the P3-B measurements at 1 min intervals. (top row) O₃, (middle row) NO_y, and (bottom row) HCHO. Red squares indicate the median values of the observations, which are shown on all panels to facilitate visual comparison.

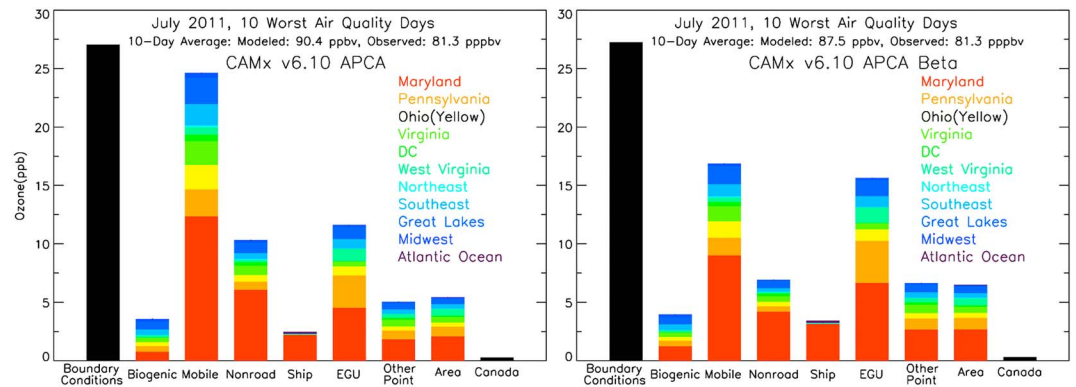


Figure 3. Ozone attributed to source sectors separated by U.S. states and the region of Canada that is in the modeling domain (Figure S1) during the 10 worst air quality days in July 2011 at 2 P.M. local time at the Edgewood, MD, monitoring site, located 30 km east-northeast of Baltimore: (left) baseline simulation and (right) updated Beta simulation.

no improvement in the simulation of NO_y , likely due to an overestimate of HNO_3 within the GEOS-Chem global model used to initialize the CAMx boundaries (Figure S9). At these altitudes, HNO_3 is photochemically inactive and the overestimate will have minimal impact on ozone formation. The median value of observed HCHO is also much closer to the median value of HCHO from the Beta simulation. However, there is now a large overestimate in the simulation of isoprene (Figure S6), which suggests errors in the isoprene to formaldehyde conversion processes in CB6r2; Mao *et al.* [2013] show that improvements to isoprene oxidation processes in air quality models are still needed. We also compare the isoprene observations to a CAMx simulation with a recently released version of BEIS version 3.61 [Bash *et al.*, 2015], which shows the best agreement with observations (Figure S10); BEIS version 3.61 has improved land use and canopy representation. Similar to our study, Kota *et al.* [2015] also showed an overestimate of isoprene using MEGAN version 2.1 in southeast Texas. The comparison of observed ozone to values from the Beta simulation exhibits similar features as the comparison for the baseline simulation. The NMB of seven trace gases for the baseline, each modification isolated separately, and Beta simulations are given in Table S3.

3.3. Changes to Ozone Attributed to Mobile Versus Large Point Sources

The NEI shows on-road and off-road mobile source emissions account for the largest portion of the total NO_x emissions, 61% of the total (Figure S11). In Maryland the percentage is even larger; NO_x emissions from on-road and off-road sources account for 72% of total NO_x emissions. Figure 3 depicts ozone attributed to emissions from individual states (denoted by color) as well as from various source sectors (each histogram). Results are shown for both the (Figure 3, left) baseline and (Figure 3, right) Beta simulations, for the 10 worst modeled air quality days in July 2011 at Edgewood, Maryland; observed surface ozone during these 10 days is 81.3 ppbv (only 6 of the top 10 worst modeled days match the top 10 worst observed days). We have chosen to focus on Edgewood (the location shown as the filled circle in Figure 4) because this site causes the Baltimore region to be in moderate nonattainment of the 2008 national ambient air quality standard for ozone [EPA, 2014d]. In the baseline simulation (Figure 3, left)—generated from the NEI—on-road sources are responsible for the largest portion (24.6 ppbv) of total surface ozone. Ozone attributed to electric generating units (EGUs) accounts for the second largest single sector (11.6 ppbv) during the 10 worst air quality days at Edgewood. The NEI indicates that EGUs are responsible for 14% of total NO_x emissions, and 11% within the state of Maryland.

In the Beta simulation, we keep emissions from EGUs identical to the baseline simulation because the NEI is developed from observed Continuous Emissions Monitoring System (CEMS) data. There is strong scientific basis [Anderson *et al.*, 2014] to link the overestimate in NO_y to mobile source emissions since they represent more than 50% of the NO_x emissions inventory. The Beta simulation (Figure 3, right) attributes more ozone to EGUs and less ozone to mobile sources. While on-road mobile sources are still the primary individual source sector contributing to surface ozone, they are responsible for 7.7 ppbv less ozone compared to the baseline simulation: 24.6 ppbv to 16.9 ppbv, a drop of 31.4%. Ozone attributed to nonroad sources also shows a similar percentage drop. Despite identical emissions of NO_x from EGUs in the two simulations, electricity generation is responsible for 4.0 ppbv more ozone in the Beta run, increasing from 11.6 to 15.6 ppbv, a 34.6% increase.

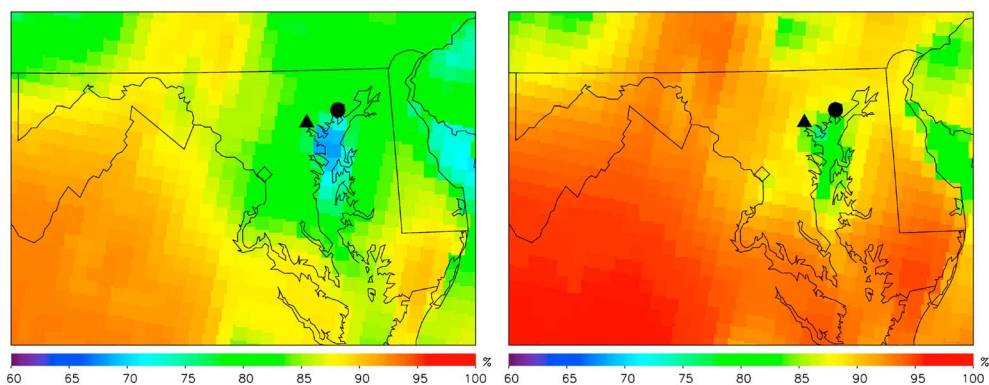


Figure 4. Percentage of ozone formed in the NO_x limited production regime during July 2011 averaged over daytime (8 A.M.–8 P.M. local time) for the entire month in the (left) baseline simulation and (right) updated Beta simulation. The filled triangle denotes Baltimore, Maryland, and the filled circle denotes Edgewood, Maryland.

The ozone attributed to EGU emissions shows a large increase because CB6r2 gas-phase chemistry has faster photolysis of NO_2 than CB05 and increased modeled HO_2 and RO_2 concentrations driven by greater biogenic emissions from MEGAN version 2.1. This implies greater ozone production efficiency, a topic to be treated in a separate paper. For the Beta simulation, EGUs and on-road mobile sources are now responsible for roughly the same fraction of surface ozone in Maryland. The change in surface ozone attribution to on-road mobile and EGU sources for the baseline compared to the Beta simulation is similar throughout the eastern United States for July 2011 (Figure S12).

3.4. Changes to Ozone Attributed to NO_x and VOC Limitations

The overestimate of NO_y and underestimate of HCHO in the baseline simulation suggests that ozone in the original model framework may be produced in a more VOC limited ozone production regime than occurs in the actual atmosphere, even though NO_x remains the key pollutant. To better grasp the relationship between modeled and observed ozone precursors, we plot ozone as a function of NO_y for the observations and two model simulations (Figure S13). The observed slope of the linear best fit indicates 20.9 ppbv of ozone per ppbv of NO_y in the Maryland airshed, whereas the baseline simulation indicates a slope of 8.6. Ozone becomes more sensitive to NO_y in the updated Beta model platform, which yields a slope of 13.3. We also compare HCHO as a function of NO_y (Figure S14). The linear best fit of the observations show 1.39 ppbv of HCHO per ppbv of NO_y ; the baseline model has a linear fit of 0.45, but the Beta simulation show a slope of 1.28, which is closer to the observations. The sensitivity of ozone to the abundance of its precursors is captured better in the updated Beta model platform.

We also use an OSAT simulation to calculate the amount of ozone formed in NO_x limited and VOC limited environmental conditions. Figure 4 shows the percentage of ozone production attributed to a NO_x limited ozone regime. In the baseline simulation, 65–85% of ozone in the Baltimore vicinity is attributed to a NO_x limited environment. The updated Beta simulation uniformly shows more ozone production in a NO_x limited regime. The biggest differences occur over the Chesapeake Bay. The Beta simulation shows 80–95% of ozone is produced in a NO_x limited environment in the Baltimore vicinity. Instead of being in the “transition region”—the region on the EKMA diagram in which ozone production occurs due to both VOC and NO_x limitation—the area is now squarely in a region of NO_x limited ozone production. This is consistent with observed changes in ozone resulting from NO_x emission reductions [Gilliland *et al.*, 2008].

3.5. Changes to Ozone Source Region Attribution

Modifications to the model framework do not have a big effect on source attribution, but subtle differences are worth discussing. Figure S15 shows state-by-state attribution at the Edgewood, Maryland monitor for the 10 worst modeled air quality days during July 2011 for the baseline and Beta simulations. Maryland is the largest contributor to total ozone mixing ratios at Edgewood. States upwind of Maryland during hot summertime days, i.e., Pennsylvania, Virginia, and Ohio, contribute more than 4 ppbv each. Further discussion on the interstate transport of ozone is included in Goldberg *et al.* [2015]. When changing model platforms, Maryland

shows a slight rise in attribution (27.9 ppbv to 29.1 ppbv), while other states show small declines in ozone attribution (i.e., Virginia). The changes do not shift any state from being above or below 1 ppbv—a critical value legislated by the Cross-State Air Pollution Rule.

Each individual incremental change to the modeling platform alters the source region attribution. Figure S16 shows source region attribution of surface ozone at Edgewood during the 10 worst air quality days in July for five simulations: baseline, baseline with CB6r2 and increased alkyl nitrate deposition, baseline with MEGAN version 2.1 biogenics, baseline with 50% mobile NO_x emissions, and Beta. For the baseline simulation (left bar of Figure S16), Maryland is responsible for 30.9% of the total; interstate transport accounts for the other 69.1%. Improvement of the alkyl nitrate photochemistry and the mobile emissions inventory make ozone photochemistry more of a regional problem, as shown by the slightly reduced contributions from Maryland in the CB6r2 + NTRdepn and 50% mobile NO_x simulations, 29.3% and 30.0%, respectively. Changes to the biogenic emissions inventory, resulting in increased isoprene, make ozone photochemistry more of a local issue, with Maryland's contribution in the MEGAN version 2.1 simulation increasing to 36.0%.

4. Conclusion

CAMx, when modified with guidance provided by a field experiment, more realistically simulates the observed abundance of ozone precursors. We compare ozone precursors (NO_y and HCHO) and ozone measured during the July 2011 DISCOVER-AQ Maryland campaign to CAMx simulations. In the baseline simulation, there is good agreement between modeled and observed ozone, but poor agreement for NO_y and HCHO. We implemented four changes to the model: CB6r2 gas-phase chemistry, faster deposition of alkyl nitrates, reduced NO_x emissions from mobile sources, and increased isoprene emissions by switching to MEGAN version 2.1 biogenic emissions. Our results indicate that BEIS version 3.61 shows good agreement with isoprene observations, and we recommend this over BEIS version 3.6. The Beta runs dramatically improve the simulation of total reactive nitrogen, alkyl nitrates, and formaldehyde. Adding more recycling of alkyl nitrates to NO₂ in CB6r2 and refining isoprene photochemistry may further improve CAMx performance.

These modifications change the attribution of ozone to different source sectors and have important policy implications. Compared to the baseline simulations, mobile sources contribute 31.4% less to total ozone while EGUs contribute 34.6% more at Edgewood, Maryland. Ozone attributed to EGUs increase from 11.6 to 15.6 ppbv, while ozone attributed to mobile sources decreases from 24.6 to 16.9 ppbv. Ozone in the two model simulations is comparable and agrees reasonably well with observations, but the source attribution and targets for control strategies change substantially.

Prior research demonstrated that regional air quality models underestimate the benefit of NO_x control measures for surface ozone. If air quality models are used to forecast how future air quality regulations will affect surface ozone, they must simulate ozone within the correct production regime (i.e., NO_x limited versus VOC limited). For the Baltimore area, this updated model platform increases the percentage of the ozone formed in a NO_x limited regime from ~75 to ~85% of the total. Since the updated model platform places ozone in a more NO_x limited regime, it is possible a simulation of surface ozone long-term trends using these changes will resolve the long-standing difficulty in simulating the response of surface ozone to past reductions in ozone precursors.

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