Source apportionment of biogenic contributions to ozone formation over the United States

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1 **ABSTRACT**

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3 Vegetation is the leading emitter of volatile organic compounds (VOC), a key
4 ingredient for ozone formation. The contribution of biogenic VOC (BVOC) emissions to
5 regional ozone formation needs better quantification so that air quality regulators can
6 effectively design emission control strategies. One of the key uncertainties for modeling
7 BVOC emissions comes from the estimation of photosynthetically active radiation (PAR)
8 reaching canopy. Satellite insolation retrieval data provide an alternative to prognostic
9 meteorological models for representing the spatial and temporal variations of PAR. In
10 this study, biogenic emission estimates generated with the MEGAN and BEIS biogenic
11 emissions models using satellite or prognostic PAR are used to examine the contribution
12 of BVOC to ozone in the United States. The Comprehensive Air Quality Model with
13 Extensions (CAMx) is applied with Ozone Source Apportionment Technology (OSAT)
14 and brute force zero-out sensitivity runs to quantify the biogenic contributions to ozone
15 formation during May through September 2011. The satellite PAR retrievals are on
16 average lower than modeled PAR and exhibit better agreement with SCAN and
17 SURFRAD network measurements. Using satellite retrievals instead of modeled PAR
18 reduces BEIS and MEGAN estimates of isoprene by an average of 3%-4% and 9%-12%,
19 respectively. The simulations still overestimate observed ground-level isoprene
20 concentrations by a factor of 1.1 for BEIS and 2.6 for MEGAN. The spatial pattern of
21 biogenic ozone contribution diagnosed from OSAT differs from the brute force zero-out
22 sensitivity results, with the former more smoothly distributed and the latter exhibiting
23 peak impacts near metropolitan regions with intense anthropogenic NO_x emissions.
24 OSAT tends to apportion less ozone to biogenics as BVOC emissions increase, since that
25 shifts marginal ozone formation toward more NO_x-limited conditions. By contrast, zero-
26 out source apportionment of ozone to biogenics increases with BVOC emissions. OSAT
27 simulations with BEIS show that BVOCs typically contribute 10-19% to regional ozone
28 concentrations at nonattainment receptor sites during episode days.

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30 Keywords: biogenic emissions, photosynthetically active radiation (PAR), Ozone Source
31 Apportionment Technology (OSAT), CAMx, Ozone, Geostationary Operational
32 Environmental Satellite (GOES)

1. Introduction

The national average ambient ozone concentration in the United States has decreased by 22% since 1990 due to Clean Air Act (CAA) regulations of nitrogen oxides (NO_x) and volatile organic compounds (VOC) emissions (Simon et al. 2014). Air quality improvement has been verified by long-term space observations (Duncan et al., 2013; Lamsal et al., 2015). However, ozone continues to exceed regulatory limits in nonattainment areas near major cities (https://ozoneairqualitystandards.epa.gov/OAR_OAQPS/OzoneSliderApp/index.html#). States with nonattainment areas are required to prepare State Implementation Plans (SIPs) to demonstrate future ozone compliance (EPA, 2014a). Correctly quantifying the contribution of different source sectors to ozone formation is crucial for the development of effective emission control strategies (Lefohn et al, 1998; Reitze, 2004; Cooper et al., 2015). Non-anthropogenic sources such as wildfire (Jaffe and Wigder, 2012), stratospheric intrusion (Langford et al., 2009; Lin et al., 2012) and biogenic emissions (Roselle et al., 1991; Pierce et al., 1998; Mao et al., 2013) can influence the performance of anthropogenic control strategies.

BVOC emissions contribute 75%-80% of total U.S. VOC emissions in the Environmental Protection Agency (EPA) 2011 National Emissions Inventory (2011NEIv2) (EPA, 2015). The leading BVOC species, isoprene, reacts rapidly with hydroxyl radicals to form ozone (Pierce et al., 1998; Zhang et al., 2000). The high ratio of BVOC to total VOC emission makes BVOC emissions a significant contributor to regional ozone concentrations, especially over the heavily forested Southeast U.S. (Fiore et al., 2005; Mao et al., 2013; Park et al., 2013). Estimations of BVOC emissions are subject to large uncertainty and are not well constrained by proxy concentrations (i.e. formaldehyde) observed from space. Hence, estimates of isoprene emissions by different biogenic emission models can vary more than a factor of two (Shim et al., 2005; Warneke et al., 2010).

BVOC emission estimates depend on ambient temperature, land use categories, emission factors associated with different plant functional type (PFT), leaf area index (LAI), and the amount of radiation reaching the canopy known as photosynthetically active radiation (PAR) (Lamb et al., 1993; Guenther et al. 2012). The most widely used biogenic emissions models in U.S. regulatory modeling are the Biogenic Emission

Inventory System (BEIS; Pierce et al., 1998; Bash et al., 2015), and the Model of Emissions and Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006; Guenther et al., 2012). MEGAN tends to estimate more isoprene emissions than BEIS and with different spatial patterns, mainly due to the difference in emission factor settings and the algorithms to parameterize response to temperature and light (Pouliot and Pierce, 2009; Warneke et al., 2010; Kota et al., 2015; Wang et al., 2017). Several studies have used satellite observations of clouds to infer solar radiation fields and replace meteorological model generated estimates of PAR (Pour-Biazar et al. 2007; Carlton and Baker, 2011; Sakulvanotvittaya et al. 2012; Zhang et al. 2017).

A variety of source apportionment techniques can quantify the contributions of different emission sources to pollutant concentrations (Mcnally et al., 2009; EPA 2010; EPA 2014b; Collet et al., 2014; Goldberg et al., 2016). Ozone Source Apportionment Technology (OSAT) in the Comprehensive Air-quality Model with Extensions (CAMx, Ramboll Environ 2015) tracks the contributions of different emission sectors, source regions, as well as initial and boundary conditions to simulated ozone concentrations (Ramboll Environ 2015). OSAT apportions ozone to NO_x or VOC depending on which precursor was the limiting factor of ozone production, as determined by the ratio of hydrogen peroxide and nitric acid production (Dunker et al, 2002). By contrast, brute force sensitivity analysis computes the change in ozone if a source is completely removed (zero-out) or reduced by a specified percent. Due to nonlinearities, zero-out source contributions do not necessarily sum to total ozone concentrations (Cohan and Napelenok, 2011).

This study applies OSAT and brute force sensitivity analysis in CAMx to examine the contributions of BVOC emissions from different source regions to ozone in the continental U.S. from May – September 2011. Source apportionment is conducted for three BVOC datasets, generated by BEIS and MEGAN with satellite radiation inputs, and by BEIS with radiation data from the prognostic meteorological model.

2. Methodology

2.1 BVOC emission estimates using satellite PAR

PAR satellite products are processed at the University of Alabama in Huntsville (UAH) based on the latest retrieval algorithm from Geostationary Operational Environmental Satellite (GOES) visible imagery (Pour-Biazar et al., 2007; Pour-Biazar et al., 2015; Zhang et al., 2017). UAH collaborates with the Infrared Measurements and Water Vapor Studies Group (IR group) at the National Aeronautics and Space Administration (NASA) Marshall Space Flight Center (MSFC) to generate and archive several GOES derived products including cloud albedo, surface albedo and surface insolation for use in meteorological and air quality models (Haines et al., 2003).

In this PAR parameterization scheme, a conversion factor CF is introduced to represent the portion of incoming solar radiation (insolation) that is in photosynthetically active wavelengths. The formulation for CF encapsulates the impact of cloud attenuation and zenith angle (Pour-Biazar et al., 2015; Zhang et al., 2017) and has been validated with the data provided by Pinker and Laszlo (1992) and Frouin and Pinker (1995).

Supplemental document File S1 provides more detail on the CF function formulation.

The raw PAR retrieval products are in the format of hourly gridded files with 4km horizontal resolution and available with 13 snapshots from 11:45 GMT to 23:45 GMT each day. The retrieval products cover most of the continental United States (CONUS) except the Northwest corner of Washington State due to the projection (Pour-Biazar et al., 2015). The raw satellite PAR products are mapped to U.S. EPA's national 12km modeling domain (12US2) and are interpreted to integer hours using the spatial allocator tool (<https://www.cmascenter.org/sa-tools/>). All other meteorological inputs used to drive BEIS or MEGAN, such as soil moisture and temperature in the surface layer, wind speed, and 24-hr accumulated rain, are derived from a U.S. EPA 2011 Weather Research Forecast (WRF) simulation (EPA, 2014c).

Seven sites of direct continuous measurements of PAR in the Surface Radiation Budget Network (SURFRAD) (<http://www.esrl.noaa.gov/gmd/grad/surfrad/>) as well as 40 selected sites for incoming solar radiation observation from paired pyranometers at the Soil Climate Analysis Network (SCAN) (<http://www.wcc.nrcs.usda.gov/scan/>) are used for comparison during the simulation time in order to evaluate the PAR and insolation retrieval products from the GOES satellite.

Due to the inherent difference between BEIS and MEGAN in considering the response of isoprene emission with sunlight in canopy (Pouliot and Pierce, 2009), different treatments are used to swap the GOES insolation/PAR retrieval products with default weather model radiation outputs. For MEGAN, since the parameterization has the option to either use the generic PAR scaled from the weather model simulation for incoming solar radiation (e.g. the output parameter ‘RGRND’ in WRF with the scaling factor 0.5) or use satellite retrieved PAR (Guenther et al., 2006), the UAH’s PAR products were directly used. For BEIS, the incoming solar radiation rather than PAR is used as an input and is separated into direct and diffuse components (Pierce et al., 1998). Therefore, the GOES insolation product is used in BEIS for consistency.

This study applies BEIS (v3.14; Pierce et al., 1998) with prescribed LAI information for 230 land use categories in Biogenic Emission Landuse Database version 3 with 1km resolution and the county-level vegetation speciation from the 1992 Forest Inventory and Analysis database (Bash et al., 2016). MEGAN (v2.1; Guenther et al., 2012) is run with LAI information from re-gridded 8-day averaged Moderate Resolution Imaging Spectroradiometer (MODIS) MCD15A2 products for years 2003 to 2011 (<http://lar.wsu.edu/megan/guides.html>). MEGAN PFT settings follow the 16 PFT classification scheme used in the community land model (CLM) version 4 with the horizontal resolution 30 arc-seconds for year 2008 (Lawrence et al., 2011).

2.2 WRF-SMOKE-CAMx simulation platform

The ozone modeling platform for this study uses the CAMx model with meteorological inputs from the Weather Research and Forecasting (WRF, Skamarock et al., 2008) model, anthropogenic emissions from the Sparse Matrix Operator Kernel Emissions (SMOKE, <https://www.cmascenter.org/smoke/>) model, and biogenic emissions from BEIS or MEGAN to provide biogenic emissions. The domain setting follows the US Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) 2011 modeling platform (12US2; EPA, 2014a), covering CONUS as well as portions of Canada and Mexico with 12-km horizontal resolution (Figure 1). The modeling examines the 2011 ozone season with a 5-month simulation

from May 1 to September 30. Table 1 outlines model configurations for each component of the platform.

Meteorological modeling is performed with the Advanced Research WRF core (WRF-ARW) version 3.4. Important physical module option selections in this study include the Rapid Radiative Transfer Model for General Circulation Models (RRTMG) scheme for shortwave and longwave radiation calculation, Asymmetrical Convective Model version 2 (ACM2) scheme for planetary boundary layer (PBL), Pleim-Xiu scheme for land surface model, Morris double moment scheme for microphysics module, and Kain-Fritsch scheme with Ma and Tan (2009) trigger function for cumulus physics module. Analysis nudging was performed above the PBL by assimilating corresponding temperature, moisture and wind speeds from the 12km North American Mesoscale (NAM) analysis database. Sea surface temperatures are initialized with a 1 km data set from the Group for High Resolution Sea Surface Temperatures (GHR SST) (Stammer et al., 2003). More details concerning the modeling configuration and processing are provided in the Technical Support Document of EPA OAQPS (EPA, 2014c). The 2011 WRF meteorological data has been extensively evaluated on a national scale and was found to outperform previous meteorological modeling efforts (EPA, 2014c). In terms of the key meteorological inputs to impact the biogenic emission estimates and ozone simulation performance in this study, the surface temperatures are slightly underpredicted, except for a slight overprediction in the early morning hours. Water vapor mixing ratios are generally underpredicted in the central and western US and over-predicted in the eastern states. Wind speeds are slightly overpredicted in the early morning and slightly underpredicted in the evening and night, while precipitation is overestimated in elevated terrain such as Northern California and the Pacific Northwest.

The U.S. EPA developed a national 2011 emission inventory as part of their 2011 modeling platform in support of the 2015 National Ambient Air Quality Standards (NAAQS) for ozone (EPA, 2015). The 12US2 gridded emission inventory generated by SMOKE is based on the 2011 National Emissions Inventory, version 2 (2011NEIv2). The inventory uses hourly 2011 continuous emissions monitoring system (CEMS) data for electrical generation units (EGUs) emissions, hourly onroad mobile emissions, and 2011 day-specific wild and prescribed fire data.

The host photochemical transport model used in this study is CAMx version 6.20 (Ramboll Environ 2015). CAMx is a 3D air quality model commonly used for attainment demonstrations (EPA, 2014b) and has been shown to perform well in previous applications (Baker and Scheff, 2007; Simon et al., 2012). The configuration of CAMx applied in this study is shown in Table 1. Clear sky photolysis rates and ozone columns for CAMx are obtained by processing NASA OMI ozone column satellite observations (<ftp://toms.gsfc.nasa.gov/pub/omi/data/ozone/Y2011/>). Initial and boundary conditions for CAMx are derived from a 2011 GEOS-Chem simulation with 2 by 2.5 degree resolution and up to 38 vertical layers (Henderson et al., 2014). Global emissions are based on Emission Database for Global Atmospheric Research (EDGAR) with EPA regional improvements for U.S., Canada, Europe, Mexico, and Asia. A complete description of the methodology and evaluation of the GEOS-Chem modeling can be found in Henderson et al. (2014).

Modeling results of the 2011 ozone season including maximum daily 8-hour ozone (MDA8), hourly nitrogen dioxide (NO₂) and hourly isoprene concentrations are evaluated with monitoring data from the Air Quality System (AQS), a national database of ambient air pollution including criteria pollutants and speciated particulates maintained by EPA (<https://www3.epa.gov/airquality/airdata/>). A variety of statistical metrics including mean observed, mean modeled, correlation coefficient (R), normalized mean bias (NMB), normalized mean error (NME) and fractional bias (FB) are calculated at each available monitor (see supplemental document File S2 for the definitions of those metrics).

2.3 Ozone source apportionment setup

OSAT is used to apportion ozone to its precursor source emissions. The 12US2 domain is segmented into 6 different source regions grouped by the geographic area comprising the multi-jurisdictional organization regions; Western Regional Air Partnership (WRAP), Central Regional Air Planning Association (CenRAP), Lake Michigan Air Directors Consortium (LADCO), Visibility Improvement State and Tribal Association of the Southeast (VISTAS), and Mid-Atlantic/Northeast Visibility Union (MANE-VU). All other locations are classified as ‘other’ including portions of Mexico and Canada. See Figure 1 for a map of the 12US2 source regions.

Emissions are broken into 6 source sector categories for source apportionment; electrical generation units (EGUs), non-EGUs (NEGU), area sources (AREA), on-road mobile (ONROAD), off-road mobile (OFFROAD), and biogenic (BIOS). Area sources include prescribed and wild fires. Marine and rail traffic emissions are grouped with off-road mobile emissions.

In addition to tagging different emission regions and sectors, the impacts from boundary conditions (lateral boundary and top boundary) as well as initial conditions are also tracked with OSAT.

OSAT results are processed following the procedure recommended by EPA (2010). In summary, daily 8-hour average contributions corresponding with MDA8 ozone concentrations above the 2008 national ambient air quality standard (NAAQS) are averaged together for an overall contribution count. We focus our ozone apportionment analysis on the monitor with the highest 2010-2012 ozone design value within each of 22 ozone nonattainment areas(see Figure 1 and Appendix Table S1 for the detail locations).

In total 3 OSAT analysis runs are conducted each using different BVOC emission estimates, namely the default EPA biogenic emission estimates from BEIS, biogenic emission estimates from BEIS using satellite insolation retrievals, and biogenic emission estimates from MEGAN using satellite PAR retrievals. Due to the limitation of available computational resources, OSAT was not applied with the combination of MEGAN biogenic emissions and WRF-based PAR. The impact of MEGAN relative to BEIS and of WRF PAR relative to satellite-based PAR can be assessed from the three simulations that were conducted.

2.4 Brute force emission perturbation simulation

A set of brute force emission perturbation runs is conducted to calculate the direct impacts of emission reductions for comparison with the OSAT results. In summary, three groups of brute force runs are conducted. The first group of simulation removes all biogenic VOC emissions. The second group of simulations scales down the U.S. BVOC emissions estimates by 50% either from default BEIS, BEIS with satellite insolation, or MEGAN with satellite PAR. The last group of simulations removes the BVOC emissions only from the LADCO region.

3 Results and Discussion

3.1 Insolation and PAR estimates from WRF and GOES

Insolation and PAR estimates from the WRF model and GOES satellite are evaluated with corresponding hourly ground pyranometer measurements at SCAN and SURFRAD monitors. Table 2 summarizes performance across evaluation sites with the statistics calculated only during daytime when satellite retrievals have nonzero insolation values. The satellite-based estimates of insolation and PAR outperform WRF in terms of R values and index of agreement (IOA). The satellite data substantially reduce the overestimation bias of WRF for insolation, reducing NMB from 19% to 7%. For PAR, using the satellite retrieval instead of WRF reduces NMB from 24% to 9% and NME from 35% to 22%. Spatially, the satellite retrievals achieve better agreement with evaluation sites in the West and Midwest than in the Eastern U.S. (Figure 2). The NMB values in California sites for insolation comparison are less than 10% while there exist a few sites located in New England with NMB>40%. The spatial pattern of UAH's insolation/PAR retrieval products' error is consistent with the previous evaluations of different time periods (Zhang et al. 2017) and may result from the limited capacity of the current algorithm to correctly account for a highly heterogeneous distribution of precipitable water on insolation (Pour-Biazar et al., 2015).

3.2 Isoprene emission estimates from BEIS and MEGAN

MEGAN estimates higher isoprene emission rates than BEIS over most regions. Spatially, the two models show similar hotspots for isoprene emissions over the broadleaf forests of the Southern U.S. and lower emission rates over the Midwest and Pacific Northwest (Figure S1). BEIS shows a strong peak in emissions over Southern Missouri and Northern Arkansas, while MEGAN shows a more widespread high emission "plateau" over Southern states. The contrasting spatial patterns may be due to the different PFT database usage (BELD4 versus CLM) and different parameterizations of the response of isoprene to sunlight in the two biogenic models (Pouliot and Pierce, 2009).

Figure 3 provides histograms comparing estimates of isoprene emissions as well as available PAR from the five OSAT source regions using different BVOC emission models with WRF-based or GOES-based PAR inputs. Isoprene emissions estimated with MEGAN are roughly a factor of 2 higher than estimates from BEIS, especially over the heavily forested regions in VISTAS and CenRAP. Using satellite data leads to less isoprene emissions on average than its counterpart cases using WRF incoming solar radiation simulation. However, the BEIS isoprene estimates are less sensitive to the change of radiation input than MEGAN (2%-3% change for BEIS isoprene and 9%-12% change for MEGAN with the smallest change region in LADCO and the largest change region in VISTAS). This greater sensitivity of isoprene emissions to sunlight in MEGAN than in BEIS arises from differences in the algorithms used to parametrize PAR. MEGAN uses PAR as a direct input to its multilayer canopy model while BEIS computes direct and diffuse PAR based on input data for total incoming solar radiation at the top of the canopy (Pouliot and Pierce, 2009). The algorithms lead MEGAN to assume lower PAR than BEIS in the simulations conducted here.

3.3 Ozone simulation performance using different BVOC emission estimates

Table 3 provides a summary of statistics for CAMx performance of hourly isoprene, NO₂ and MDA8 ozone at available AQS network sites (see Figure 1 for locations) during summer 2011 for the three OSAT simulation cases using different biogenic emission configurations. The 'MEGAN_GOES' case on average over-estimates isoprene concentrations by a factor of 2.3. The over-estimation of ground isoprene concentration by the other two BEIS cases is much smaller with the NMB values 28% for case 'BEIS_EPA' and 29% for case 'BEIS_GOES'. The CenRAP region (NMB=404%) and WRAP region (NMB=401%) have the most severe over-estimation for isoprene concentrations. This is probably due to MEGAN estimates of much higher isoprene emission rates than BEIS at the AQS evaluation sites over those two regions (see Figure S1). MEGAN over-estimates of ground isoprene concentrations have been found in other modeling studies (Ying and Krishnan, 2010; Carlton and Baker, 2011; Zhang et al., 2017; Wang et al. 2017). Use of GOES insolation data slightly improved model performance

for ground-level isoprene on high ozone days (using 50 ppbV for observed hourly ozone as the threshold to calculate statistics).

CAMx model performance for hourly NO₂ concentrations differs little among the three simulation cases since the insolation inputs barely impact biogenic NO_x emission estimates. On average, the CAMx model overestimates the NO₂ concentrations by 9%-13% with NME around 75%. This suggests that despite site-specific errors, any systemic overestimation of NO_x emissions by the emissions inventory is slight.

All three CAMx runs simulated ozone reasonably well with a high correlation (R=0.74-0.75) and low bias (NMB=11%-14%) and error (NME=17%-19%). The change in ozone is slight despite the large change in BVOC because ozone is NO_x-limited over most of the domain. In terms of national average performance, the CAMx cases with biogenic emission using satellite data have slightly better ozone results than the WRF case, decreasing the simulation bias from 14% to 11-12% and error from 19% to 18-19%. Case 'BEIS_GOES' has the best overall ozone performance of the three BVOC dataset runs while the case 'MEGAN_GOES' has better model performance during episode days. Spatially, the cases with BEIS emissions have better ozone performance for peak ozone simulation in the Midwest while the MEGAN case has better ozone performance in the Northeast and California (Figure 3).

3.4 OSAT source apportionment

Spatial distributions of the OSAT-derived contributions of biogenic VOC sources from the six source regions to average MDA8 ozone are shown in Figure 4 for each of the three biogenic simulations. The average magnitude of biogenic contribution to 2011 summer ozone varies from 2 ppbV to 17 ppbV with peak values in California and some central states. Even though the VISTAS region has the largest BVOC emission rate in the U.S. (Figure 2), its OSAT contribution to regional ozone formation is relatively modest with the typical value 5-11ppbV. The CAMx OSAT algorithm attributes ozone production to VOCs only when ozone forms under VOC-limited conditions (Dunker et al., 2002). Ozone formation in the VISTAS region is typically NO_x-limited due to intense BVOC emissions in the Southeast. Hence, CAMx OSAT attributes most of the ozone in this region to NO_x rather than VOCs. The modeling of NO_x-limited ozone

conditions in the Southeast is consistent with OMI satellite observations of formaldehyde and NO₂ (Duncan et al., 2010).

OSAT results show that the majority of ozone impacts occur within the source region, and that BVOC emissions from each region have modest impacts on downwind regions. BVOC emissions from WRAP and CenRAP contribute up to 1-3 ppbV of ozone to some locations in New England states. By contrast, prevailing wind conditions preclude MANE-VU emissions from substantially influencing ozone in other regions during the period simulated.

Figure 6 shows pie charts of ozone source apportionment results at the nonattainment receptor sites tracked by the 6 major source sectors (BIOS, EGU, NEGU, ROAD, NONROAD, AREA) as well as boundary conditions (see Figure 1 and Table S1). Results are presented for each of the three biogenic emission configurations. For all three OSAT simulations, the impact from boundary conditions is diagnosed as the top contributor to regional MDA8 ozone formation averaged for all the nonattainment sites over the episode days (nearly 50% in WRAP region and 22-30% for the rest of US). Ozone source contributions in most locations range from 17-30% from onroad sources, 7-20% from offroad sources, 5-8% from area sources, 4-7% from non-EGU point sources, and 1-11% from EGUs. Biogenic VOC sources on average contribute 10-19% of regional ozone formation with higher contributions in the VISTAS region and the lower contributions in the WRAP region. The biogenic contributions presented here are in line with similar studies that examine different regions in the United States (EPA 2010; Alpine Geophysics, 2012; Collet et al., 2014; Goldberg et al., 2016).

For individual sites located in the Denver-Boulder-Greeley-Fort Collins-Loveland nonattainment area, the BCON contribution reaches as high as 80% (see Table S2). This reflects the importance of stratospheric ozone intrusions at some high altitude locations, which was also reported in similar OSAT studies (McNally et al., 2009; EPA 2014b).

3.5 Comparing OSAT and brute force source apportionments

Figure 7 shows a map comparing average biogenic contribution to ozone formation during summer of 2011 estimated with CAMx OSAT and brute force zero-out analysis for the three BVOC emission cases. Spatially, OSAT produces a more smoothly

distributed field of contributions with a peak value in the Midwest (~14ppbV). Brute force indicates sharper peaks in BVOC contribution to ozone around metropolitan regions with intense anthropogenic NO_x emissions. This study used the OSAT2 scheme for ozone apportionment in CAMx, which allocate the net change in ozone to tracers under NO_x or VOC-limited conditions. The next version OSAT3 scheme adds the capability to account for NO_x recycling by tracking source attribution of nitrogen through all forms of NO_y (Yarwood and Koo, 2015). The NO titration effect may change Figure 7 in which differences in the contributions become more apparent over high-NO_x areas.

OSAT attributes less ozone to BVOC under the MEGAN case than the BEIS cases. This counter-intuitive result occurs because the larger BVOC emissions from MEGAN push ozone formation toward more NO_x-limited conditions, leading OSAT to attribute more ozone to NO_x rather than VOCs. OSAT considers marginal sensitivity of ozone, which is NO_x-limited over most of the CONUS domain during summer afternoons.

By contrast, the zero-out analysis shows a much bigger contribution of BVOC in the MEGAN case, since that case has more BVOC to zero out than BEIS. In each case, zeroing out BVOC emissions pushes ozone toward VOC-limited conditions, contrasting the mostly NO_x-limited marginal conditions considered by OSAT. In the LADCO region, the contribution of BVOC to ozone is similar in the OSAT and zero-out analyses, as shown in Figure S3. This is because isoprene is a smaller share of VOC in the LADCO region than in most other regions.

The nonlinearity of brute force ozone response to BVOC is illustrated in Figure S2, which compares ozone impacts from the zero-out and 50% BVOC reduction cases. The ozone impacts of zero out are far larger than double the impacts of the 50%-case, since ozone becomes increasingly VOC-limited as BVOC is reduced. More generally, the nonlinear response of ozone to emissions means that ozone cannot be strictly apportioned as a sum of zero-out contributions (Cohan and Napelenok, 2011). That hinders comparisons with OSAT, which apportions all ozone one-to-one to a precursor emission source or initial and boundary conditions.

Source contribution results can differ significantly between average conditions and ozone exceedance days. This is an important point that needs to be considered when formulating an ozone attainment strategy, since the standard is based on days with peak

ozone. Each of the source apportionment methods with different BVOC emission estimates shows an increasing role for BVOC on days with high ozone concentrations (Figure 8). This is more pronounced for the zero-out impact, since high ozone days tend to have warm and sunny conditions that enhance BVOC emissions. That leads ozone formation on these days to be more NO_x-limited, which dampens the OSAT source apportionment to BVOC. Zeroing-out BVOC more radically shifts the ozone formation regime to conditions that are unrealistic for this domain.

4 Conclusions

In this study, the WRF-SMOKE-CAMx modeling platform is utilized with OSAT and zero-out source apportionment to explore the contributions of biogenic emissions to ambient ozone concentrations in nonattainment areas in the United States during summer 2011. Since BVOC emission estimates are sensitive to solar radiation and vary between models, we apply two widely used BVOC emission models (BEIS and MEGAN) with both modeled and satellite-observed radiation data.

Application of satellite insolation/PAR data reduces the under-prediction of clouds in the prognostic weather model (i.e. WRF) and improves agreement with surface radiation monitors. BEIS with the GOES insolation retrieval achieved the best performance for simulating ground-level isoprene and ozone concentrations. MEGAN produced higher estimates of BVOC emissions that tended to over-predict isoprene and ozone concentrations.

OSAT and zero-out source sensitivity runs yielded different results for apportionment of ozone to biogenic emissions. Spatially, the BVOC emission contribution to regional ozone formation is relatively smoothly distributed in OSAT, whereas in the zero-out analysis it exhibits peak impacts near NO_x-rich metropolitan regions. During episode days with higher BVOC emissions, OSAT tends to apportion less ozone to biogenics due to the shift of marginal ozone formation more toward NO_x-limited conditions. By contrast, zero-out attributes more regional ozone formation to biogenic sources due to the greater amount of BVOC to zero-out on those days. OSAT simulation results for the BEIS_GOES case found that domain-wide biogenic emissions contribute an average of 10%-19% of ozone formation at nonattainment receptor sites during ozone NAAQS

434 exceedance episode days. The difference of ozone source apportionment resulting from
435 the choice of biogenic emission models (BEIS vs MEGAN) is far greater than the
436 difference resulting from the choice of PAR inputs (WRF vs GOES satellite-based PAR).

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444 conditions used in the 12km 12US2 domain to run CAMx simulations.
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Table 1. Configurations of WRF-BEIS/MEGAN-CAMx modeling platform used in this study

WRF			
Version:	WRF-ARW v3.4	Shortwave/longwave radiation:	RRTMG ^a
Domain setting:	12km CONUS (396×246)	PBL scheme:	ACM2 ^b
Vertical resolution:	35 layer w/ P_{top} = 50 hPa	Surface layer scheme:	Monin-Obukhov
Land surface model:	Pleim-Xiu	Sea surface temperature (SST):	1km SST data from GHRSSST ^c
Microphysics:	Morris double moment	Cumulus physics:	Kain-Fritsch w/ trigger function
Analysis nudging:	U, V, T, Q above PBL	Initial field:	12km NAM ^d analysis (12NAM)
BEIS			
Version:	BEIS v3.14	Land cover and vegetation speciation:	1km BELD3 ^e for 230 land use type
Leaf-area index:	2 sets of vegetation species specified values (summer .vs. winter)	Emission factor:	Leaf scale, land use type specified
Adjustment factor for isoprene emission:	Temperature, light	PAR input:	Split between direct diffused PAR based on insolation input (WRF or GOES ^f)
MEGAN			
Version:	MEGAN v2.1	Land cover and vegetation speciation:	30 sec 16 PFT types in CLM ^g
Leaf-area index:	MODIS ^h 8-day average	Emission factor:	Canopy-scale, 1km pre-gridded
Adjustment factor for isoprene emission:	Temperature, light, LAI, humidity, wind	PAR input:	Direct input either from WRF (half of insolation) or GOES retrieval
CAMx			
Version:	CAMx v6.20	Anthropogenic emission:	2011NEIv2 ⁱ
Boundary conditions:	GEOS-Chem	Gas-phase chemistry:	CB6r2 ^j
Photolysis:	2011 clear sky photolysis w/ OMI ^k	Chemistry solver:	Euler-Backward Iterative (EBI)
Dry deposition:	Zhang et al. (2003)	Vertical diffusion:	K-theory
Vertical advection solver:	Implicit backward-Euler hybrid	Horizontal advection solver:	Pricewise Parabolic Method (PPM)

Note: a-The Rapid Radiative Transfer Model for GCMs; b-Asymmetrical Convective Model version 2; c-Group for High Resolution Sea Surface Temperatures; d-North American Model; e-Version 3 of the Biogenic Emissions Land use Database; f- Geostationary Operational Environmental Satellite; g-Community Land Model; h- Moderate Resolution Imaging Spectroradiometer; i-2011National Emission Inventory version 6.2; j-Carbon Bond gaseous mechanism version 6.3 with extension; k-Ozone Measurement Instrument

Table 2. Evaluation of GOES insolation/PAR retrieval products during May-September 2011 with available ground observations at SCAN and SURFRAD network

	N ^a	OBS ^b (W/m2)	SIM ^c (W/m2)	R ^d	RMSE ^e (W/m2)	MB ^f (W/m2)	NMB ^g	NME ^h
GOES_insolation	67823	243	265	0.96	108	13	7%	26%
WRF_insolation	67823	243	289	0.91	144	47	19%	31%
GOES_PAR	12758	104	113	0.94	40	9	9%	22%
WRF_PAR	12758	104	130	0.92	62	25	24%	35%

Note: a-total observation records; b-mean observation; c-mean simulation; d-correlation coefficient; e-root mean square error; f-mean bias; g-normalized mean bias; h-normalized mean error

Table 3 Statistics for CAMx performance relative to ground-level observations of hourly isoprene, nitrogen dioxide (NO₂), and maximum daily 8 hour ozone (MDA8) at AQS network sites during summer of 2011 for the three biogenic emissions cases.

sites			BEIS_WRF				BEIS_GOES				MEGAN_GOES			
		OBS ^a (ppbV)	SIM ^b (ppbV)	R ^c	NMB ^d (%)	NME ^e (%)	SIM (ppbV)	R	NMB (%)	NME (%)	SIM (ppbV)	R	NMB (%)	NME (%)
Isoprene	CENRAP(68) ^f	0.24	0.43	0.38	76%	144%	0.44	0.38	79%	141%	1.23	0.51	404%	416%
	LADCO(4)	0.36	0.33	0.54	-8%	76%	0.35	0.58	-3%	76%	0.54	0.54	50%	104%
	MANE-VU(26)	0.52	0.55	0.42	7%	90%	0.54	0.4	5%	87%	1.5	0.46	189%	223%
	VISTAS(12)	2.14	1.59	0.39	-26%	65%	1.66	0.45	-22%	62%	4.59	0.48	114%	138%
	WRAP(32)	0.1	0.19	0.3	90%	170%	0.18	0.37	87%	156%	0.49	0.44	401%	431%
	US_average	0.67	0.62	0.41	28%	109%	0.63	0.44	29%	104%	1.67	0.49	232%	262%
Isoprene (w/ threshold O ₃ > 50 ppb)	CENRAP(58)	0.38	0.76	0.3	113%	173%	0.63	0.33	79%	140%	1.89	0.48	404%	413%
	LADCO(3)	1.04	0.98	0.33	-8%	63%	0.82	0.38	-21%	65%	1.26	0.38	22%	76%
	MANE-VU(25)	0.9	1.1	0.35	20%	92%	0.95	0.33	1%	84%	2.51	0.41	179%	211%
	VISTAS(11)	2.92	2.51	0.27	-15%	60%	2.26	0.41	-24%	56%	5.87	0.45	101%	117%
	WRAP(29)	0.26	0.48	0.1	78%	155%	0.44	0.22	60%	130%	1.1	0.32	317%	338%
	US_average	0.81	1.03	0.46	28%	99%	0.89	0.51	10%	86%	2.45	0.56	202%	222%
NO ₂	CENRAP(71)	7.5	9.4	0.49	26%	79%	9.1	0.49	22%	77%	9.4	0.49	26%	79%
	LADCO(22)	12.2	14.4	0.59	18%	68%	14	0.59	15%	67%	14.4	0.59	18%	69%
	MANE-VU(55)	11.2	10.2	0.44	-9%	66%	9.9	0.44	-12%	65%	10.2	0.44	-9%	66%
	VISTAS(31)	7.3	10.3	0.39	41%	94%	10.1	0.39	38%	93%	10.3	0.39	41%	94%
	WRAP(171)	8.4	7.3	0.48	-14%	70%	7	0.48	-17%	70%	7.3	0.48	-13%	70%
	US_average	9.3	10.3	0.48	12%	75%	10.0	0.48	9%	74%	10.3	0.48	13%	76%
MDA8 O ₃ (all)	CENRAP(191)	48.4	53.8	0.67	11%	20%	53.2	0.68	10%	19%	53.7	0.63	11%	21%
	LADCO(209)	45.5	49.4	0.79	9%	16%	49.7	0.79	7%	16%	49.7	0.8	9%	17%
	MANE-VU(201)	44.5	49.7	0.82	12%	18%	50.4	0.82	10%	17%	50.4	0.82	13%	19%
	VISTAS(276)	47	56.7	0.75	21%	23%	56.5	0.75	19%	22%	56.5	0.74	20%	23%
	WRAP(438)	51.2	52.9	0.70	17%	16%	51.7	0.70	15%	15%	51.7	0.70	1%	3%
	US_average	47.3	52.5	0.75	14%	19%	52.4	0.75	12%	18%	52.4	0.74	11%	17%
MDA8 O ₃ (>75 ppb)	CENRAP(153)	81.4	72.2	0.27	-11%	14%	72	0.26	-11%	14%	73.7	0.3	-9%	14%
	LADCO(164)	80.7	75.5	0.35	-6%	11%	74.6	0.35	-8%	11%	80.7	0.38	0%	11%
	MANE-VU(143)	82.2	83	0.33	1%	10%	80.8	0.32	-2%	10%	88.6	0.36	8%	14%
	VISTAS(160)	80	79.5	0.27	-1%	10%	78.4	0.26	-2%	10%	82.4	0.32	3%	12%
	WRAP(217)	82.8	69.7	0.35	-16%	17%	69.3	0.32	-16%	17%	69.7	0.42	-16%	18%
	US_average	81.9	73.6	0.32	-10%	14%	72.9	0.31	-11%	14%	75.5	0.37	-8%	15%

Note: a-mean observation; b-mean simulation; c-correlation coefficient; d-normalized mean bias; e-normalized mean error; f-the numbers in the parentheses denote total observation sites used in that region to do the model performance evaluation

Figure 1. Source regions for ozone source apportionment analysis and the AQS site locations for NO₂ (blue square), ozone (black cross 'x') and isoprene (green plus '+') for model performance evaluation as well as the site locations with the highest ozone design value for nonattainment areas in 2011 (solid black diamond; see Table S1).

Figure 2. Performance of GOES insolation retrievals (left) and GOES PAR retrievals (right) evaluated with corresponding ground pyranometer measurements in terms of average normalized mean bias (NMB) during May-September 2011.

Figure 3. Estimated isoprene emissions (top) and available PAR (bottom) at different regions in the 12US2 domain using BEIS or MEGAN biogenic emission models with GOES or WRF insolation/PAR data during May-September 2011.

Figure 4. Fractional bias (FB) of simulated maximum daily 8-hr ozone (MDA8) relative to observations when observed MDA8 ozone exceeds 75 ppbV at AQS monitors.

Figure 5. OSAT modeled contributions of biogenic sources from each source region to MDA8 ozone, averaged over May-September 2011 under the BEIS and MEGAN BVOC emission cases.

Figure 6. Average OSAT source contributions of 6 emission sectors and boundary conditions (BCON) to MDA8 ozone at nonattainment receptor sites in 5 U.S. regions under the three biogenic VOC emissions cases.

Figure 7. OSAT (left) and brute force zero-out (right) source apportionment of MDA8 ozone during summer 2011 to biogenic VOC sources from BEIS (top) and MEGAN (bottom), each with GOES satellite insolation.

Figure 8. Comparison of biogenic VOC contribution to ozone at nonattainment sites as attributed by OSAT (green triangles) and zero-out (blue diamonds) methods, for the case with BEIS (left) and MEGAN (right) emissions and satellite-retrieved insolation.