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Discussions

Predicted and Observed Changes in Summertime Biogenic and Total Organic Aerosol in the Southeast United States from 2001 to 2010

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Abstract

Biogenic secondary organic aerosol (bSOA) is a major component of atmospheric particulate matter ($PM_{2.5}$) in the southeast United States especially during the summer, when emissions of biogenic volatile organic compound (VOCs) are high and emissions from anthropogenic sources enhance the formation of secondary particulate matter. We evaluate the performance of $PM_{2.5}$ organic aerosol predictions by a chemical transport model (PMCAMx) in response to significant changes in anthropogenic emissions during the summers of 2001 and 2010. Average predicted bSOA concentrations in the southeast US did not change appreciably from the summer of 2001 to the summer of 2010, while the anthropogenic SOA decreased by 45%. As a result, the biogenic fraction of total OA increased from 0.46 in 2001 to 0.63 in 2010. Partitioning effects due to reduced anthropogenic OA from 2001 resulted in 0.4 μg m^{-3} less biogenic OA on average in the southeast US in the summer of 2010. This was offset by biogenic SOA increases due to higher biogenic vapor emissions in the warmer 2010 summer. Little noticeable difference was observed in OA prediction performance in the southeast US between the two summer simulation periods. The fractional error of OA predictions remained practically the same (0.41 and 0.44 at CSN sites and 0.40 to 0.41 at IMPROVE sites in the summers of 2001 and 2010 respectively). The fractional bias of OA predictions increased from 0.10 to 0.22 at CSN sites and decreased from 0 to -0.09 at IMPROVE sites between the two periods. Removing the NO_x-dependence of SOA formation yields resulted in higher fractional error and fractional bias at both CSN and IMPROVE sites in both summer periods, demonstrating the efficacy of the current formulation of SOA yields. Our

analysis suggests that the changes in biogenic OA in this forested relatively polluted region appear to be dominated by the partitioning effects and the NO_x effects on SOA yields.

1 Introduction

Many anthropogenic pollutants contribute to the formation of organic aerosol (OA), a major component of atmospheric particulate matter ($PM_{2.5}$). This material can be directly emitted in the particle phase as primary OA (POA) or formed during the oxidation of volatile organic compounds (VOCs) and condensation or nucleation of their low volatility or semi-volatile oxidation products forming secondary OA (SOA). Emissions from natural sources of VOCs, including isoprene, monoterpenes, and sesquiterpenes have been found to be significant contributors to $PM_{2.5}$ mass in the form of biogenic SOA (bSOA) (Murphy and Pandis, 2010). Significant efforts have been made to study bSOA formation in the southeast United States during the summer due to a combination of high emissions of biogenic VOCs (Sindelarova et al., 2014) along with the potential for significant anthropogenic influence on the corresponding processes (Carlton et al., 2010).

Enforcement of federal air quality regulations such as the Clean Air Act and its 1990 amendments, has led to significant reductions in the emissions of anthropogenic pollutants known to impact bSOA formation. US emissions of SO_2 decreased by over 50% between 1970 and 2000 (Smith et al., 2011) and these reductions continued between 2000 and 2010 (Klimont et al., 2013). Emissions of SO_2 contribute inorganic $PM_{2.5}$ mass in the form of sulfates, often the main acidic component of atmospheric aerosols (Weber et al., 2016). Pye et al. (2013) simulated the effects of acidity on SOA production during the oxidation of isoprene in the Community Multiscale Air Quality model (CMAQv5.0.1). They estimated that with their acid-dependent isoprene-SOA scheme, a 25% reduction in sulfur oxide emissions resulted in a 35-40% reduction in isoprene-derived SOA. A 25% reduction in nitrogen oxides (NO_x) was also tested, producing varied results via different pathways due to differences in NO_x-dependent SOA parameterizations. The authors observed modest reductions in underpredictions of total organic carbon (OC) from both IMPROVE and Chemical Speciation Network (CSN) sites using the most aggressive uptake scenario. On the other hand, Takahama et al. (2006) found very small, if any statistical correlation between observed OC and particle acidity during the Pittsburgh Air Quality Study. Plenty of uncertainty still exists regarding the role of isoprene in SOA formation. Isoprene itself has been found to reduce SOA formation from monoterpenes (McFiggans et al., 2019), which have significantly higher SOA yields than that of isoprene.

Reductions in anthropogenic emissions of NO_x have been a consequence of regulatory efforts to reduce tropospheric ozone (Simon et al., 2015). The NO_x level affects SOA formation by determining chemical pathways through which SOA is formed from various VOCs, including those from natural sources (Ziemann and Atkinson, 2012). Typically, SOA formation via oxidation of a VOC is measured under both low-NO_x and high-NO_x conditions (Ng et al., 2007; Lee et al., 2011) and these yields are used to implement NO_x-dependent SOA formation schemes in models for individual precursors, ultimately determined by the ratio of the rates of organo-peroxy radical reactions with NO (Lane et al., 2008). Impacts of NO_x emissions on SOA formation are further complicated, as reductions in NO_x have been linked to increases in ozone and OH radical concentrations in urban areas in the southern United States (Tsimpidi et al., 2008). In NO_x-limited (rural) areas, however, lower NO_x emissions decrease the amount of available oxidants for SOA formation. These complex interactions between various pollutants encourage the implementation of NO_x-dependence in air quality models to capture SOA concentration responses to changes in NO_x emissions in varied locales.

Another important mechanism for anthropogenic influence on bSOA formation is through gas-to-particle partitioning effects. The existence of already formed particle-phase SOA encourages the particle-phase partitioning of additional SOA mass (Liang et al., 1997; Leach et al., 1999; Kroll et al., 2007). This means that the partitioning of bSOA components to the particle phase is facilitated by the presence of anthropogenic secondary aerosol. Implementation of semivolatile SOA partitioning schemes typically follows an approach where the products of SOA forming reactions are lumped to surrogate species according to their volatility such as the Odum 2-product model (Odum et al., 1996) or the volatility basis set approach (Donahue et al., 2006; Lane et al., 2008b) which allows for an arbitrary number of volatility bins. Carlton et al. (2018) found that up to 67% of bSOA mass in the southeast US could be attributed to semivolatile partitioning during July 2013. With anthropogenic emissions of VOCs decreasing from 22 Tg yr^{-1} to 14 Tg yr^{-1} between 2000 and 2010 in the United States (Xing et al., 2013), it is likely that there have been changes in bSOA concentrations due to partitioning effects especially in areas such as the southeast US. Relative humidity (RH) is believed to have varied effects on the SOA yields of biogenic precursors. Isoprene SOA yields have been found to be suppressed at higher RH under high-NO_x conditions (Nguyen et al., 2011; Zhang et al., 2011). However, RH has also been found to enhance SOA formation from aromatic compounds, such as toluene (Kamens et al., 2011; Jia and Xu, 2018). Under low-NO_x conditions, toluene SOA yields have followed the opposite trend with increasing RH (Cao and Jang, 2010; Hinks et al., 2018).

The southeast US has been a focus for research on SOA formation in the past due to a high level of biogenic emissions and nearby anthropogenic pollution sources. Lu et al. (2014) leveraged data obtained from the Southern Oxidant and Aerosol Study (SOAS) in 2013 to provide evidence of anthropogenically enhanced biogenic SOA formation. They found that anthropogenic sulfate and NO_x in the area impacts 43-70% of measured organic aerosol during the summer. It remains to be seen which of these effects, if any, are the most significant regarding the ability of chemical transport models to reproduce the observed OA concentrations.

In this work, we investigate the ability of the Particulate Matter Comprehensive Air Quality Model with Extensions, PMCAMx, relying largely upon NO_x-dependent SOA yields and equilibrium semivolatile partitioning, to reproduce changes in predicted bSOA between the summers of 2001 and 2010. Skyllakou et al. (2021) evaluated the ability of PMCAMx to link changes in emissions to predicted $PM_{2.5}$ concentrations in 1990, 2001, and 2010 for the purpose of investigating health outcomes. The authors found that while anthropogenic emissions decreased over this period, biogenic OA was predicted to increase from 2001 to 2010 in the southeast US mainly due to higher temperatures in the latter period. Here, we investigate this further by implementing improved sesquiterpene SOA chemistry in PMCAMx, evaluating OA prediction performance, and determining the effect of NO_x-dependence and partitioning on predicted bSOA with the goal of identifying the need for additional SOA parameterizations in the model.

2 Model Description

PMCAMx (Karydis, et al., 2010; Murphy and Pandis, 2010; Tsimpidi et al., 2010) is a state-of-the-art chemical transport model, using the framework of CAMx, the Comprehensive Air Quality Model with Extensions (Environ, 2006) that is used to simulate the advection, diffusion, dry and wet deposition, gas and aqueous-phase chemistry, and atmospheric aerosol physical and chemical processes. A 10-size (30 nm to 40 μm) aerosol sectional approach (Gaydos et al., 2003) is used to track the dynamic evolution of aerosol mass and composition. This model simulates the concentrations of aerosol sulfate, nitrate, ammonium, sodium, chloride, water, dust, elemental carbon, and both primary and secondary organics (represented as a series of lumped species in the Volatility Basis Set). The ISORROPIA aerosol thermodynamics model (Nenes et al., 1998) is used in this application to calculate the gas/particle partitioning of semi-volatile inorganic species. The condensation and evaporation of inorganic species are simulated in this application assuming equilibrium between the bulk inorganic gas and aerosol phases. The distribution of mass partitioned in each phase to the various aerosol size sections is determined using weighting factors calculated based on the effective surface area in each section (Pandis et al., 1993).

Organic aerosol evolution is modeled using the Volatility Basis Set approach (Donahue et al., 2006; Lane et al., 2008b). SOA is split into anthropogenic (aSOA) and biogenic (bSOA) components formed from a variety of SOA-forming VOCs from both human and natural sources. Biogenic SOA formation from isoprene, monoterpenes, and sesquiterpenes is modeled. The latter two are modeled as lumped chemical species meant to represent the entire monoterpene and sesquiterpene families of compounds, respectively. Both aSOA and bSOA are simulated using 4 volatility bins ranging from saturation concentration of 10^0 to 10^3 μg m^{-3} at 298 K and use NO_x-dependent SOA formation yields (Lane et al., 2008a; Day, 2014). Improved SOA formation yields from sesquiterpenes have been included for the purposes of this study (Sippial et al., 2022). Primary organic aerosol (POA) is simulated using 8 volatility bins ranging from saturation concentration of 10^{-1} to 10^6 μg m^{-3} at 298 K. Gas-phase chemistry is described using the Carbon Bond 05 (CB5) mechanism (Yarwood et al., 2005). Water vapor influences indirectly the SOA formation in PMCAMx, through its involvement in the gas-phase chemistry, e.g., leading to the production of OH radicals. The mechanism used here includes 193 reactions of 79 gas-phase chemical species. Aqueous-phase chemistry is simulated using the Variable Size Resolution Model of Fahey and Pandis (2001). Notably, particle acidity effects are not included in the model. This is a candidate process for model improvement if inconsistencies arise between the changes in modeled and observed OA.

3 Model Application

PMCAMx was applied with a simulation domain covering the contiguous United States using a grid of 132 by 82 cells with horizontal dimension of 36 x 36 km (total area of 4752 x 2952 km^2), and 14 layers of varying height up to maximum altitude around 13 km. The domain is equivalent to that of Skyllakou et al. (2021). We apply this simulation approach for the summer

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months (June, July, and August) of 2001 and 2010. Predictions for the summer of 1990 are not used in our analysis due to the lack of available measurements of organic carbon in the southeast United States during that period. The first two days of simulation output from each period were removed from the analysis to account for model spin-up.

Meteorological fields were simulated using the Weather Research and Forecasting model (WRFv3.6.1) to provide PMCAMx with wind components, diffusivity, temperature, pressure, humidity, clouds, and precipitation inputs. The initial and boundary conditions for WRF simulations were generated using the ERA-Interim global climate re-analysis database, along with land-use information, soil categories, and terrain height retrieved from the United States Geological Survey. WRF was configured in the manner recommended for air quality simulations (Gilliam and Pleim, 2010; Rogers et al., 2013; Hogrefe et al., 2015).

Anthropogenic emissions for the simulations were obtained from the historical emissions inventories of Xing et al. (2013) and include both gaseous and primary particulate emissions. Emissions in this inventory are resolved by source category, however this level of detailed information was not pertinent to the analysis in this work. A detailed description of these emissions is provided by Skyllakou et al. (2021). The Model of Emissions of Gases and Aerosols from Nature version 3 (MEGAN3) (Guenther et al., 2018) was used to calculate biogenic emissions for all simulations.

The subdomain of focus for this study is the southeast United States, as defined by the boundary in Figure 1. Selected changes in emissions used for the two summer simulation periods in the southeast United States are summarized in Figure 2. Significant reductions in key anthropogenic emissions affecting SOA formation have taken place. SO_2 emissions in the US fell by 47% between the summers of 2001 and 2010 from an average of 348 g h^{-1} km^{-2} to 184 g h^{-1} km^{-2}. Over the same period, NO_x emissions were reduced by 42% from 245 g h^{-1} km^{-2} to 141 g h^{-1} km^{-2}. NO_x emissions changes can have competing effects in terms of SOA formation depending on the levels of other pollutants.

Anthropogenic VOC emissions decreased by 31% between the summer of 2001 and the summer of 2010 from 898 to 623 g h^{-1} km^{-2}. This reduction is expected to have led to a reduction of anthropogenic OA between the two periods, which should cause a decrease in biogenic OA due to partitioning effects. The magnitude of this effect is quantified in a subsequent section. Increases in the emissions of all biogenic VOCs were estimated between the summer of 2001 and the summer of 2010 due to higher temperatures in the second period. Isoprene, monoterpene, and sesquiterpene emissions increased by 27%, 18%, and 21%, respectively as predicted by MEGAN3. This of course would tend to increase bSOA concentrations between the two periods all other factors (NO_x, partitioning) being equal. The temperature increase is depicted in Figure S1.

A sensitivity test removing the NO_x-level dependency of SOA formation yields is considered in this work to determine the efficacy of these parameterizations in capturing the various types of SOA concentration changes that would result from reductions in NO_x emissions.

4 Results

4.1 Organic aerosol predictions

Average predicted bSOA for the summers of 2001 and 2010 is shown in Figure 3. A small increase of around 5% (2.19 µg m^{-3} to 2.35 µg m^{-3}) in the average bSOA concentration in the southeast United States is predicted from 2001 to 2010. This change is much less than the increase (18-27%) in biogenic VOC emissions in the same area.

The biogenic fraction of predicted total OA is shown for both simulation periods in Figure 4. A notable increase was observed between the summers of 2001 and 2010 in the southeast from 46 to 63%. This result points to competing effects producing the changes observed in predicted OA. The small increase in bSOA concentration, especially when compared to the larger increases in biogenic VOC emissions, points to other processes partially offsetting the increases in bSOA. Anthropogenic SOA decreased significantly between the two summers from 2.5 µg m^{-3} in 2001 to 1.3 µg m^{-3} in 2010. This accounts for most of the increase in the biogenic fraction. Primary organic aerosol (POA) also decreased between the two periods, but only by a small amount (0.1 µg m^{-3}). A breakdown of individual bSOA precursor contributions to total predicted average bSOA concentrations in the southeast United States is provided in Figure S2. Relative contributions from the individual VOC precursors did not change appreciably between the two simulation periods. Between the summer of 2001 and the summer of 2010, contributions to bSOA increased slightly for isoprene (21% to 23%) and sesquiterpenes (35% to 37%) while the contribution from monoterpenes decreased slightly (44% to 40%).

Predictions of OA concentrations were compared to available measurements of OA in the southeast United States during the two simulation periods. Measurements from both the primarily urban CSN network (US EPA, 2002) as well as the primarily rural IMPROVE network

(IMPROVE, 1995) were used to consider various site locations which could impact the level of anthropogenic influence on SOA formation. Metrics for model prediction evaluation here include the fractional error and fractional bias given by:

$$\text{Fractional Error} = \frac{2}{N}\sum_{i=1}^{N}\frac{|P_i - O_i|}{P_i + O_i} \quad (1)$$

$$\text{Fractional Bias} = \frac{2}{N}\sum_{i=1}^{N}\frac{P_i - O_i}{P_i + O_i} \quad (2)$$

where *N* is the number of valid measurements, O_i is a single daily measurement, and P_i is a single daily average predicted concentration in the simulation cell where measurement *i* was taken. Daily average OA concentration measurements from CSN (2001: 7 sites; 2010: 36 sites) and IMPROVE (2001: 13 sites; 2010: 15 sites) sites in the southeastern US (Figure 1) are included in the evaluation dataset.

Scatter plots illustrating model OA prediction performance in the southeast United States for summer 2001 and summer 2010 are shown in Figure 5. The corresponding performance metrics for the two simulation periods and measurement networks are provided in Figure 6. In terms of fractional error, OA prediction performance is consistent across the two time periods and site types with the fractional error varying between 0.4 and 0.44. Fractional bias shows greater variability between time periods and networks, with a minimum of -0.09 for rural sites in 2010 and a maximum of +0.22 for urban sites in 2010. While the variability in bias is higher, it never exceeds the bias goals of chemical transport model predictions of ±0.30 (Boylan and Russell, 2006). The consistent performance suggests that the model adequately reproduces OA concentrations in the two time periods. Also, the significant change in anthropogenic emissions does not appear to affect the model error, while the small tendency for overprediction becomes a small tendency towards underprediction.

The predicted changes at individual sites that were online in both years are directly compared to corresponding observed changes between the two time periods in Figure 7. The changes in OA concentrations are aggregated monthly for each monitor, to reduce the amount of noise in analyzing the changes. The ability of PMCAMx to reproduce the observed changes in each monitoring site is encouraging; large changes in observed concentrations generally correspond to large changes in predicted concentrations. Most inconsistencies in the direction of the change between predictions and measurements occur when the changes are small in magnitude with two noteworthy exceptions. One of these exceptions is for the month of June at the Okefenokee National Wildlife Refuge (Georgia, IMPROVE) site. Here, measurements of 10, 11, and 23 µg m^{-3} were recorded on June 3, 9, and 12, respectively. This is due to two reported fires in the refuge that are not in the emissions inventory used with PMCAMx. The abnormally high measured $PM_{2.5}$ concentrations on these three days result in a much higher predicted decrease in measured $PM_{2.5}$ at this location between 2001 and 2010 (-4.7 µg m^{-3}) than the model is able to reproduce (+1.4 µg m^{-3}). Removing these three days from the analysis reduces the change in measured $PM_{2.5}$ to -1.7 µg m^{-3}. The changes in measured and predicted $PM_{2.5}$ concentrations at the Okefenokee NWR site are in better agreement for the other two months. Measured $PM_{2.5}$ decreased by 1.6 µg m^{-3} while predicted $PM_{2.5}$ decreased by 0.3 µg m^{-3} in the month of July. In August, measured $PM_{2.5}$ decreased by 2.3 µg m^{-3} and predicted $PM_{2.5}$ decreased by 1.7 µg m^{-3} between 2001 and 2010. The other outlier is for the month of July at the Shining Rock Wilderness (North Carolina, IMPROVE). At this location, only one daily measurement was available during July 2001. This means that the entire monthly average of July 2001 (10 measurements) was only compared to one measurement, resulting in a problematic comparison. This datapoint has been excluded from Figure 7 as well as the formal analysis.

4.2 Effect of semi-volatile partitioning

Changes in biogenic emissions between 2001 and 2010 are larger than the change in bSOA concentration predicted by the model pointing to offsetting factors that we explore here. Differences in semivolatile partitioning between the two periods are a potential competing effect that could explain the small change in bSOA concentrations. The large decreases in anthropogenic emissions result in less SOA formed via the oxidation of anthropogenic SOA precursors. Less existing particle phase OA will then result in smaller fractions of biogenic SOA compounds partitioning into the particle phase. This is consistent with the significant predicted increase in the biogenic fraction of total OA with only a small increase in bSOA concentration.

To examine the impact of changes in semivolatile partitioning on predicted bSOA concentrations, we estimated the fraction of the total (gas and particulate) biogenic SOA components present in 2010 that would partition to the particle phase if the particle phase anthropogenic SOA remained constant from 2001 to 2010 (2.51 µg m^{-3}), rather than decreasing to 1.37 µg m^{-3}. We assume that the total bSOA material concentration (sum of gas and particle phase) in 2010 does not change with this hypothetical increase in anthropogenic SOA. The difference between this estimated bSOA concentration (2.7 μg m^{-3}) in this scenario and the predicted biogenic SOA concentration during the summer of 2010 (2.3 μg m^{-3}) is a good estimate of the effect of semivolatile partitioning on predicted biogenic SOA (-0.4 μg m^{-3}). These results are illustrated in Figure 8. If anthropogenic OA remained the same from 2001 to 2010, the biogenic SOA concentration in 2010 would be about 15% higher. In that case the bSOA would increase by 24% from 2001 to 2010, a change that is consistent with the increases in biogenic VOC emissions between the two periods (27%, 18%, 21% for isoprene, monoterpenes, and sesquiterpenes, respectively). Therefore, differences in semivolatile partitioning are predicted to have offset to large extent the increased bSOA due to the higher biogenic emissions in this warmer period.

4.3 Effect of NO_x-dependence

We investigated also the effects of the NO_x-dependencies of the biogenic SOA yields on both simulation periods and site location types. As a sensitivity test, the same simulations (summer 2001 and summer 2010) were performed with NO_x-independent SOA formation yields for biogenic SOA. This was done by setting the NO_x-level branching ratio to zero, effectively setting the biogenic SOA formation yields equal to their low-NO_x level in all conditions. In most cases for bSOA, this represents a higher-yield scenario when compared to the NO_x-dependent base case (Lane et al., 2008a).

The average bSOA concentrations for these two additional simulations are shown in Figure 9. For both simulation periods, the average bSOA concentration in the southeast United States increased when compared to the simulations with NO_x-dependent yields. The average predicted bSOA concentration in the southeast United States for the summer of 2001 in the sensitivity test became 2.97 μg m^{-3} (previously 2.19 μg m^{-3}) and 2.84 μg m^{-3} (previously 2.35 μg m^{-3}) for 2010. This increase is consistent with expectations based on the assumed NO_x dependence of the biogenic SOA yields.

The increase in bSOA due to the use of the low-NO_x yields was 35% in the summer of 2001 and 22% in the summer of 2010, therefore the reduction in NO_x emissions resulted in a change of the NO_x effect on SOA by approximately 13% of the total biogenic SOA. The biogenic fractions of total OA also increased due to the use of low-NO_x yields compared to the NO_x-dependent simulations (Figure 10). For summer 2001 the biogenic fraction was 0.50 (previously

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0.46) and for summer 2010 the biogenic fraction was 0.65 (previously 0.63). These results suggest that the reductions of NO_x emissions during the decade caused an increase of the bSOA by roughly 10% based on the PMCAMx predictions.

OA prediction performance scatter plots for the NO_x-independent bSOA yield simulations are shown in Figure 11 and performance metrics are shown in Figure 12. This sensitivity test produced weaker performance for OA. The fractional error increased in both simulation periods and for both networks when compared to the results of the base case simulation with the NO_x-dependent yields. The minimum fractional error for the low-NO_x scenario was 0.43 (IMPROVE, summer 2010) and the maximum was 0.53 (CSN, summer 2010). All fractional biases increased by around 0.2, ranging from +0.10 (IMPROVE, summer 2010) to +0.42 (CSN, summer 2010). Performance in this sensitivity test is notably worse in the summer of 2010, indicating that the NO_x-dependent bSOA yields implemented in PMCAMx are important at capturing the dynamics of SOA formation with significant concurrent changes in anthropogenic and biogenic emissions.

5 Conclusions

Emissions of most anthropogenic pollutants influencing SOA formation decreased significantly from 2001 to 2010 in the southeast United States. NO_x emissions were reduced by 42%, impacting NO_x-dependent SOA formation yields as well as oxidant levels and the corresponding oxidation pathways. Anthropogenic VOC emissions were reduced by 31%, in turn reducing anthropogenic OA and impacting the gas-to-particle partitioning of semi-volatile biogenic SOA components. SO_2 emissions fell by 47% over the same period which could impact any particle acidity effects on SOA formation although this potential effect was not considered here. PMCAMx simulations were performed covering two summer simulation periods of June, July, and August of 2001 and 2010 in order to evaluate the effectiveness of the model at reproducing changes in biogenic SOA between the two summers. This version of PMCAMx simulates SOA formation through semi-volatile partitioning of SOA species and NO_x-dependent SOA formation yields neglecting acidity effects and aqueous-phase processes.

The average predicted bSOA concentration in the southeast US increased from 1.86 μg m^{-3} to 1.89 μg m^{-3} from summer 2001 to summer 2010. The biogenic fraction of total OA based on PMCAMx increased from 46% to 63% over the same period, suggesting significant reductions in anthropogenic contributions. Anthropogenic OA levels were reduced significantly (45%), and

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this resulted in around 0.4 µg m^{-3} less predicted biogenic SOA through gas-to-particle partitioning effects.

With this reduced bSOA in 2010 due to partitioning effects and the NO_x-dependent SOA formation chemistry in this formulation of PMCAMx OA observations from IMPROVE and CSN monitoring sites are reproduced reasonably well and consistently in both summers (fractional error of 0.40 and 0.44; fractional bias of -0.09 and 0.22). Removing the NO_x-dependence of the SOA formation yields had negative impacts on model performance, increasing fractional error and bias and at both time periods and at both types of monitoring sites. The results of this study suggest that a chemical transport model with NO_x-dependent yields for SOA precursors, including the explicit treatment of sesquiterpene SOA formation, and semivolatile partitioning of SOA mass using a method such as the volatility basis set has a reasonable performance in reproducing summertime atmospheric OA levels and their changes in response to significant changes in both anthropogenic and biogenic emissions.

Code and Data Availability. The model code and data used in this study are available from the authors upon request (spyros@chemeng.upatras.gr).

Author contributions. BTD performed the MEGAN and PMCAMx simulations, analyzed the results, and wrote the manuscript. PGR prepared the anthropogenic emissions and other inputs for the PMCAMx simulations. KS performed preliminary PMCAMx simulations and prepared model inputs. SNP and PJA designed and coordinated the study and helped in the writing of the paper. All authors reviewed and commented on the manuscript.

Competing Interests. The authors declare that they have no conflict of interest.

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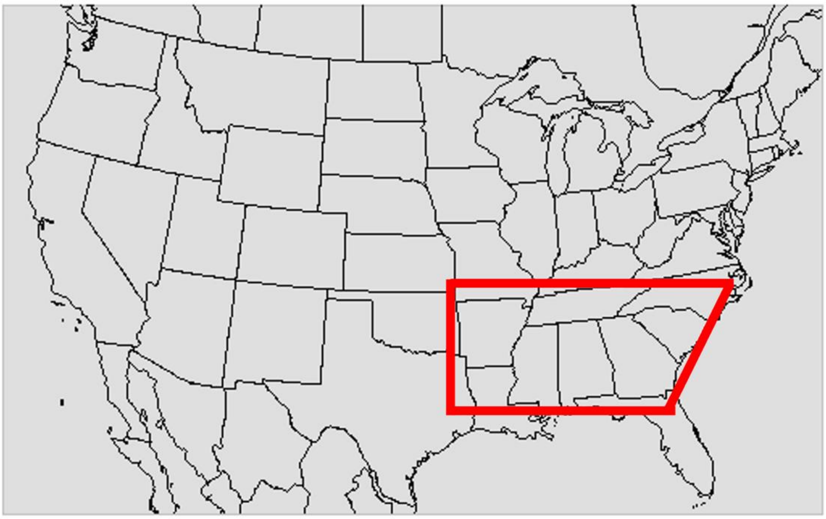

Figure 1: Contiguous United States simulation domain. The boundary of the southeast United States, for the purposes of the analysis in this work is highlighted in red.

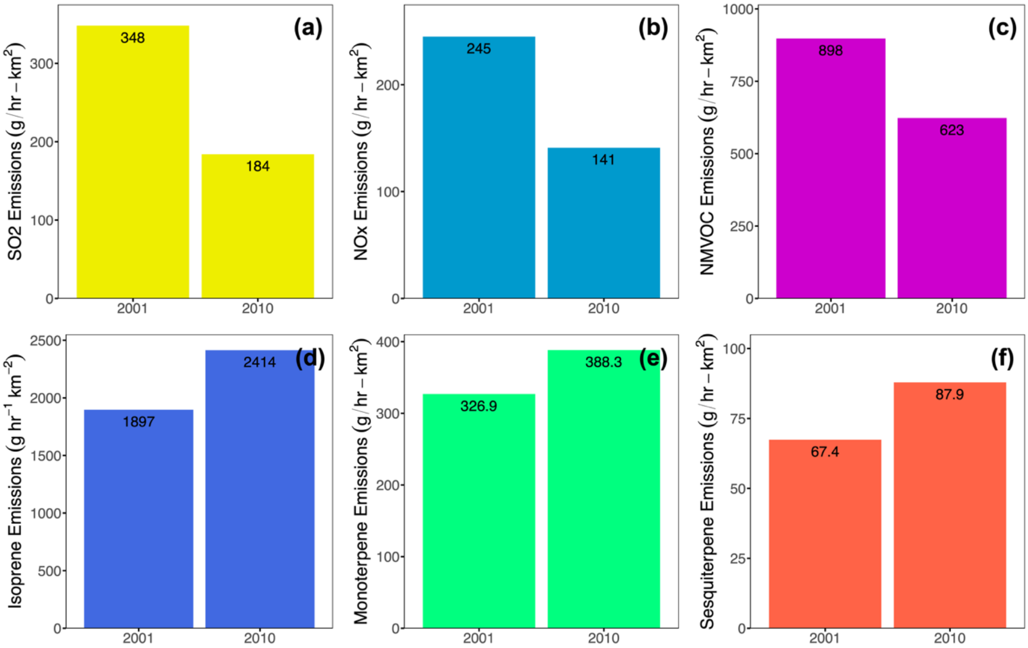

Figure 2: Average summer emissions of (a) sulfur dioxide (SO_2), (b) nitrogen oxides (NO_x), (c) non-methane volatile organic compounds (NMVOCs), (d) isoprene, (e) monoterpenes, (f) sesquiterpenes in the southeast United States.

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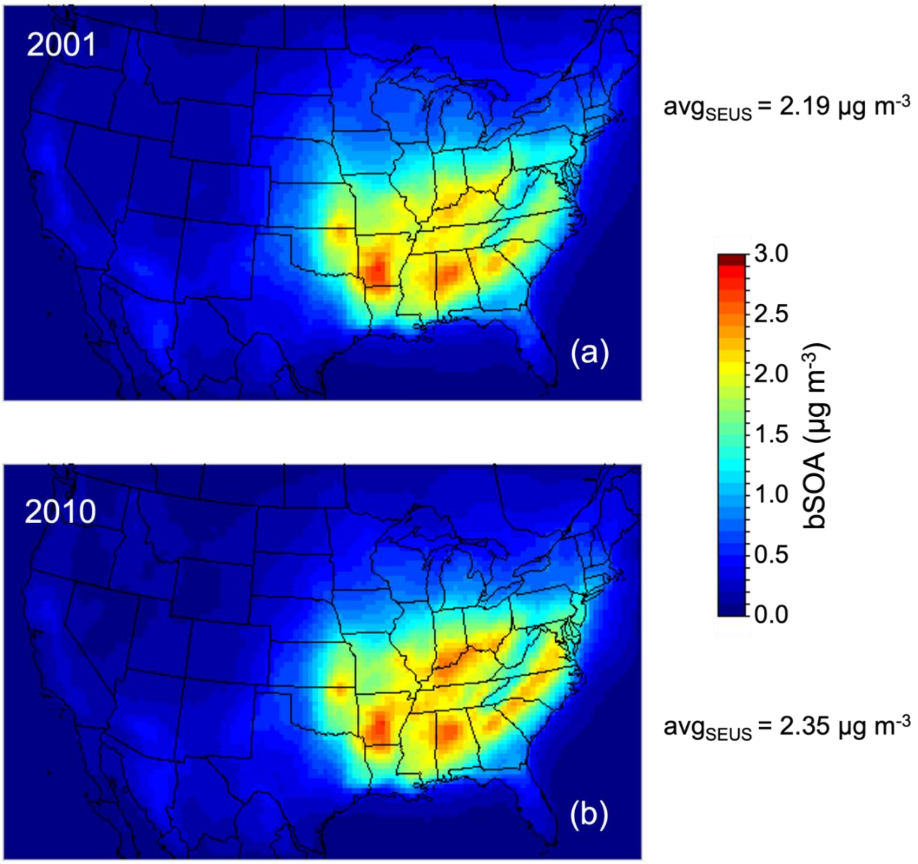
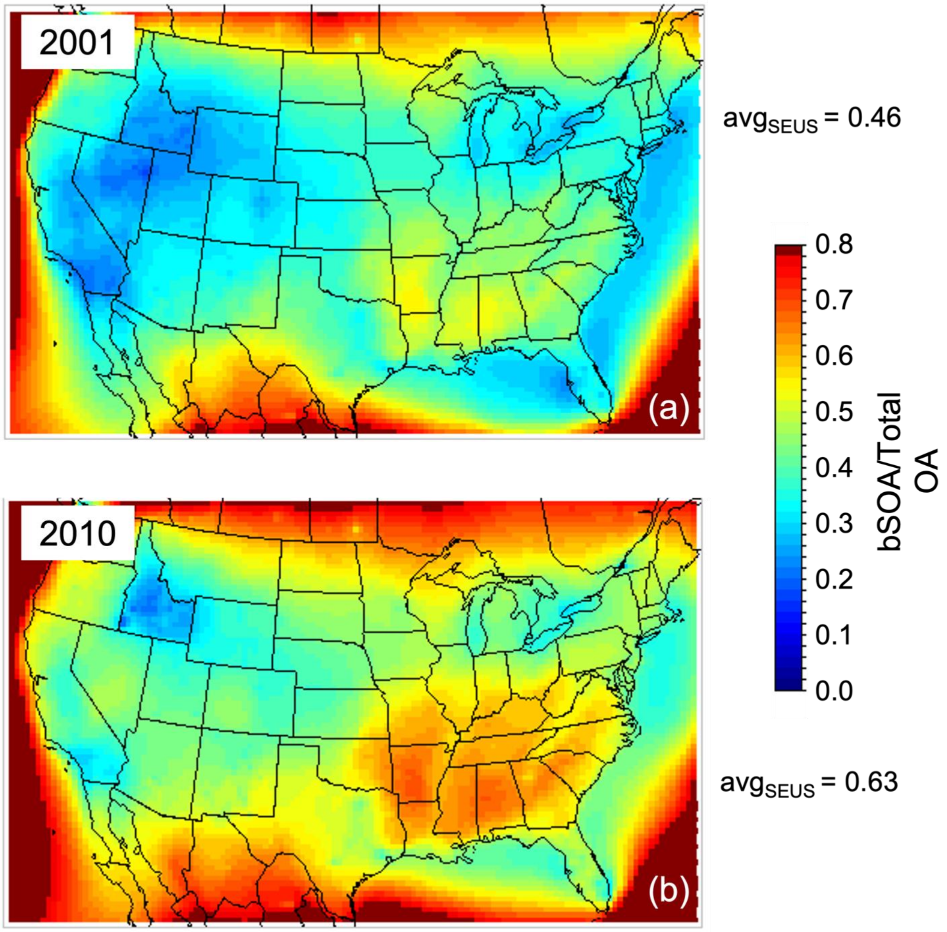


Figure 3: Predicted average summer bSOA concentration for (a) 2001 and (b) 2010. The average value for the southeast US region is provided.



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555 **Figure 4:** Average fraction of predicted organic aerosol that is from biogenic sources for (a) 2001
556 and (b) 2010.

557

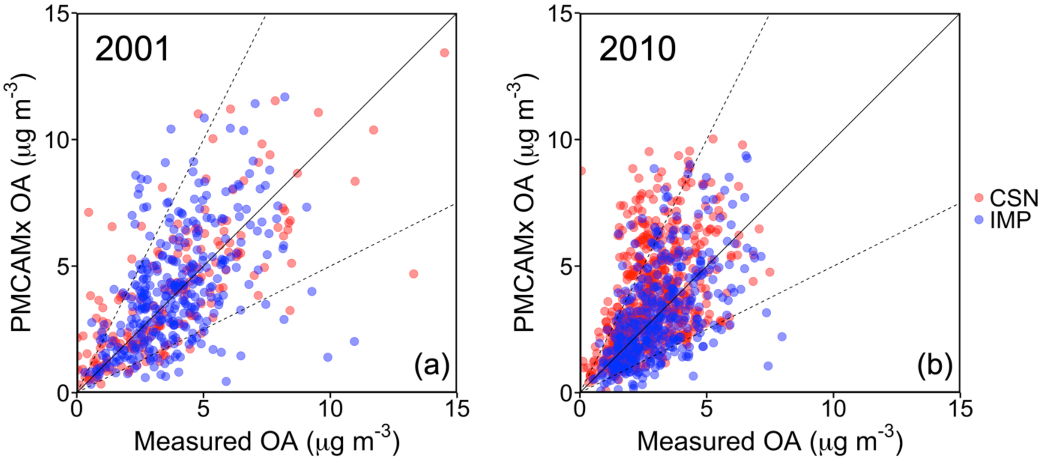

Figure 5: Comparison of predicted daily average OA concentrations with available daily OA measurements in the southeast US from CSN (red) and IMPROVE (blue) sites for the summers of (a) 2001 and (b) 2010.

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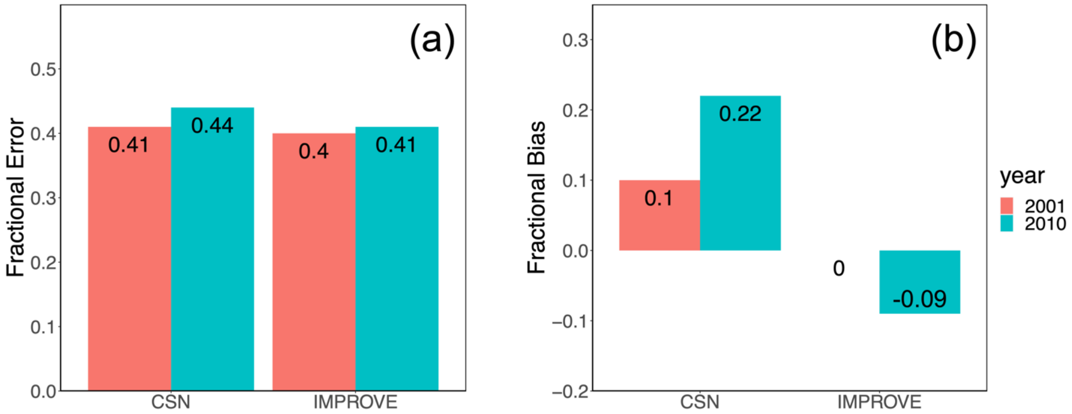

Figure 6: Summary of OA prediction performance in the southeast US based on the fractional error and fractional bias of daily average OA predictions when compared to daily measurements from CSN and IMPROVE sites for the summers of 2001 and 2010.

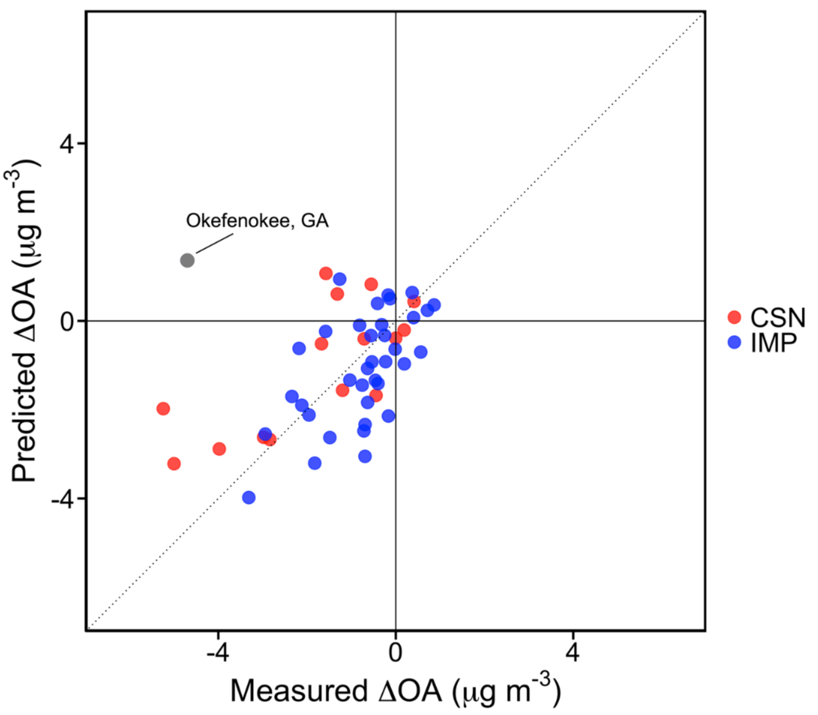

Figure 7: Change in predicted and measured OA concentrations from summer 2001 to summer 2010 using monthly average predicted OA concentrations and monthly averaged measurements from CSN and IMPROVE sites.

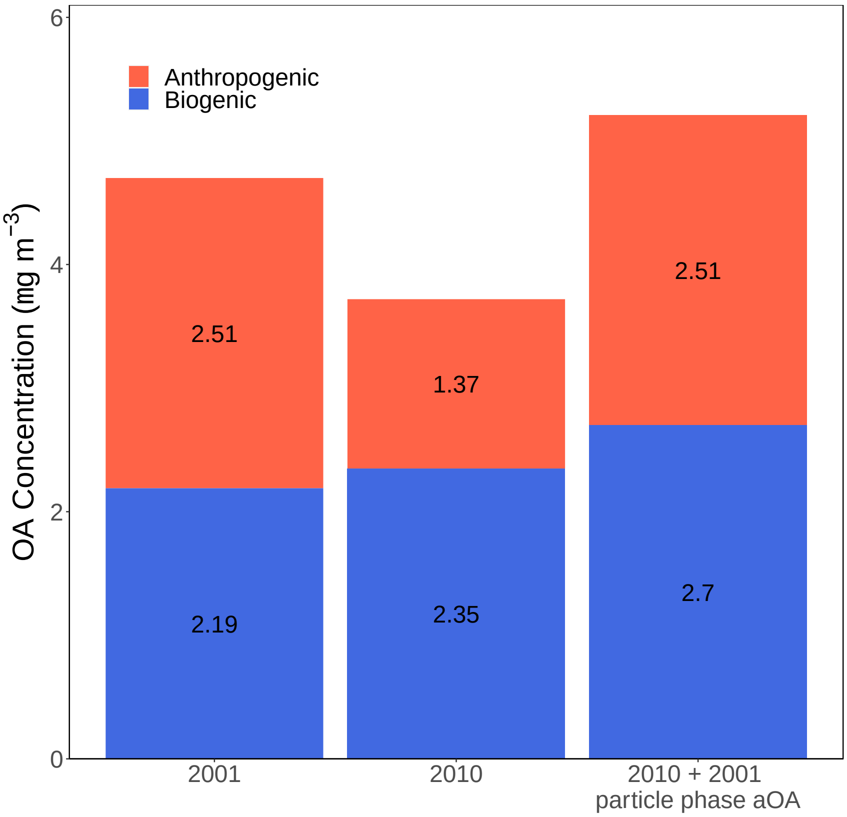

Figure 8: Predicted average summer OA concentration in the southeast US, resolved by anthropogenic or biogenic source for the 2001 and 2010 summer periods, as well as the 2010 summer period with 2001 particle phase anthropogenic OA to test the partitioning effect on biogenic OA in 2010.

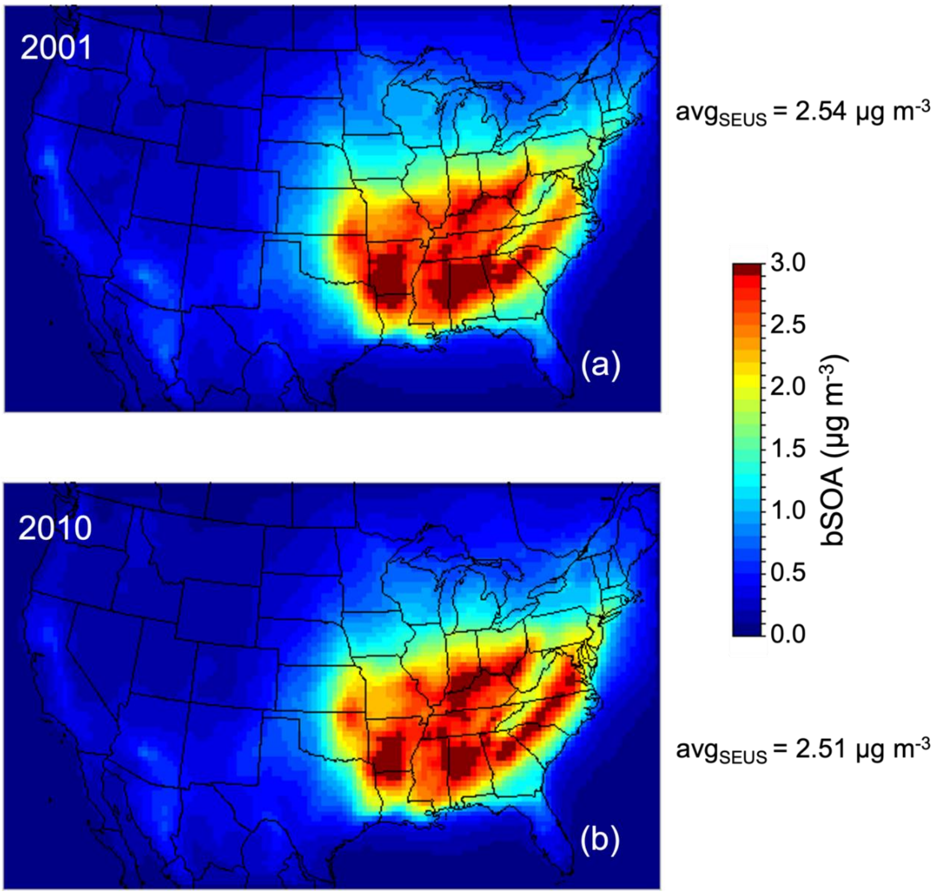

Figure 9: Predicted average summer bSOA concentration for (a) 2001 and (b) 2010 with NO_x-independent (low-NO_x) yields. The average value for the southeast US region is provided.

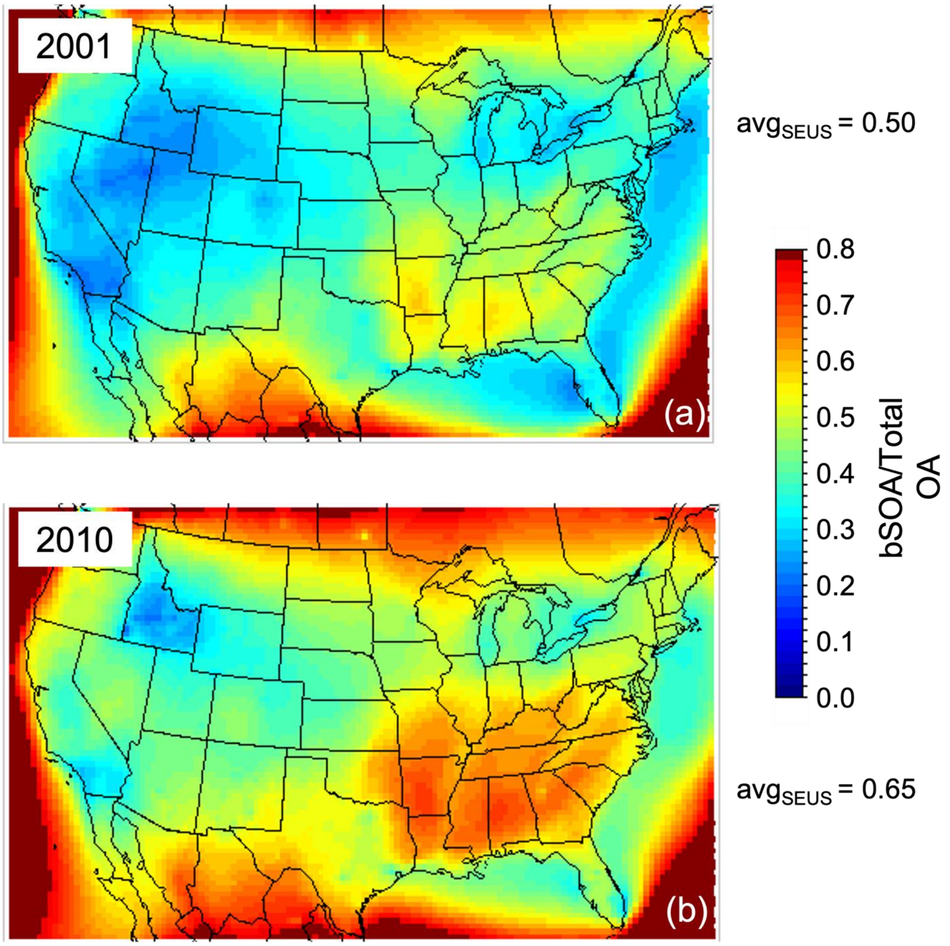

Figure 10: Average fraction of predicted organic aerosol that is from biogenic sources for (a) 2001 and (b) 2010 with NO_x-independent (low-NO_x) yields. The average value for the southeast US region is provided

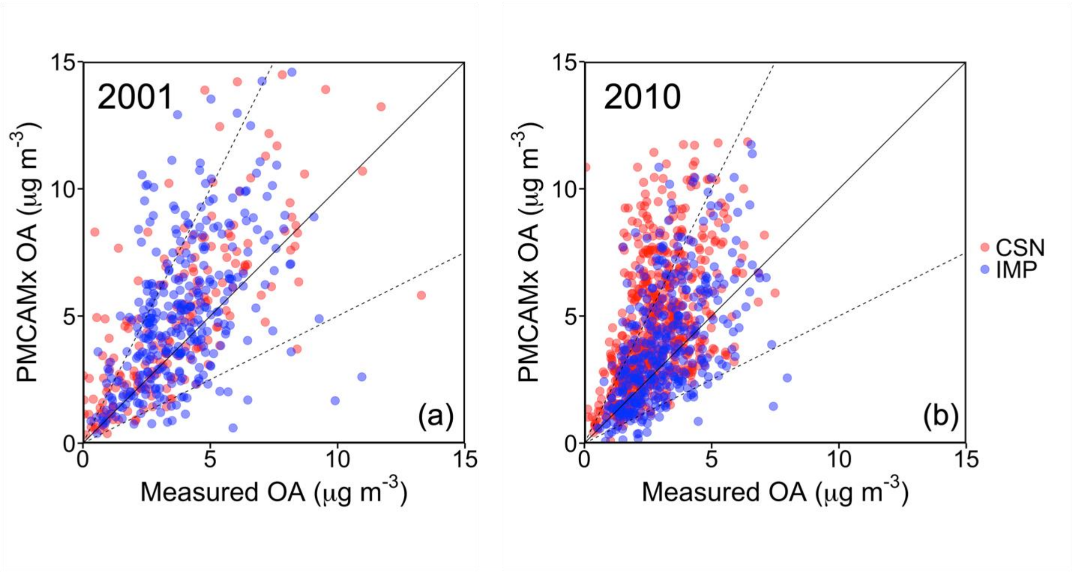

Figure 11: Comparison of predicted daily average OA concentrations using NO_x-independent (low-NO_x) yields with available daily OA measurements in the southeast US from CSN (red) and IMPROVE (blue) sites for the summers of (a) 2001 and (b) 2010.

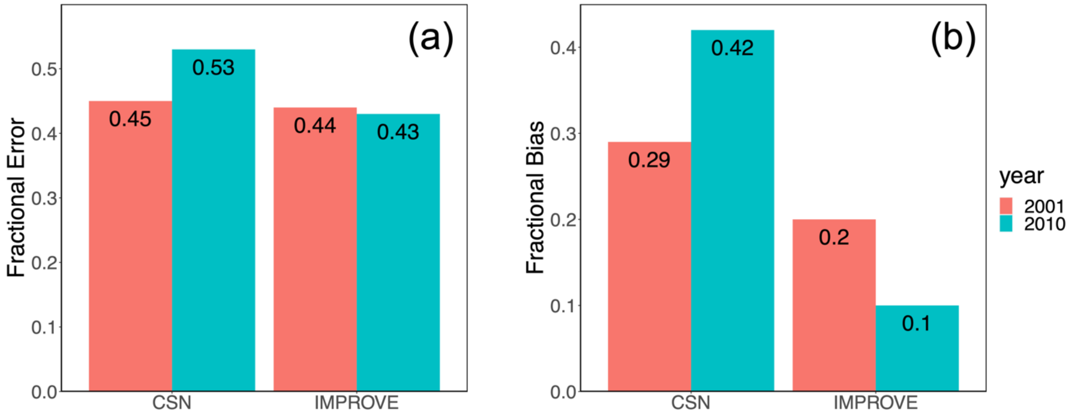

Figure 12: Summary of OA prediction performance in the southeast US based on the fractional error and fractional bias of daily average OA predictions using NO_x-independent (low-NO_x) yields when compared to daily measurements from CSN and IMPROVE sites for the summers of 2001 and 2010.