

Drought Impacts on Secondary Organic Aerosol: A Case Study in the Southeast United States

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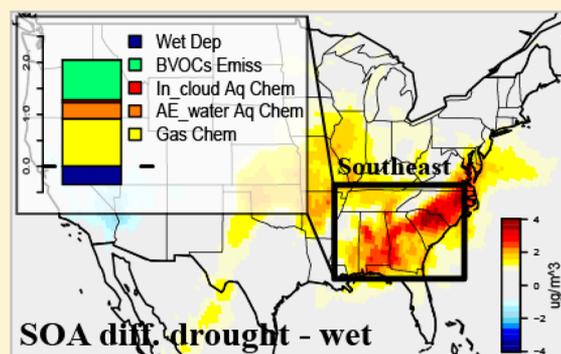
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Supporting Information

ABSTRACT: Secondary organic aerosol (SOA) is a significant component of fine particulate matter, and it has increased during past drought periods in the U.S. Here, we use the Community Multiscale Air Quality (CMAQ) model to characterize the complex effects of drought on SOA through a case study comparing a drought period (June 2011) and a wet period (June 2013) over the southeast U.S. The model simulates a 68% ($1.7 \mu\text{g}/\text{m}^3$) higher SOA concentration at the surface during drought and attributes 98% of this increase to biogenic SOA. Through model sensitivity simulations, the SOA increase associated with drought is attributed to 54% from accelerated gas-phase reactions oxidizing volatile organic compounds (VOCs) to SOA, 45% from higher emissions of biogenic VOCs, 18% from enhanced acid-catalyzed production of isoprene SOA in aerosol water due to changing sulfate, 3% from enhanced in-cloud aqueous phase chemistry. Because the higher SOA levels overwhelm the reduced precipitation, there is an increase in wet deposition flux in the drought month which offsets 20% of the total SOA increase. If anthropogenic emissions are held constant, anthropogenic SOA is 51% higher during drought, highlighting the importance of meteorological impacts on chemistry.



INTRODUCTION

Fine particulate matter ($\text{PM}_{2.5}$, particles with an aerodynamic diameter less than or equal to $2.5 \mu\text{m}$) is a criteria pollutant impacting air quality, human health, and climate. The dominant sink of major $\text{PM}_{2.5}$ constituents in the atmosphere is wet removal,¹ which means ambient $\text{PM}_{2.5}$ levels are sensitive to changing hydroclimate. For example, drought, a type of hydroclimate extreme characterized by prolonged periods of precipitation shortage, high temperatures, and soil moisture deficit,² has been shown to be associated with higher $\text{PM}_{2.5}$ pollutions in the US.^{3–5} Abnormal atmospheric conditions during drought are expected to affect chemical production/loss rates, hence changing the atmospheric lifetime of gases and aerosols. In addition, high temperature and low soil moisture during drought can affect the land-atmosphere exchange of dust and emissions of biogenic volatile organic compounds (BVOCs).^{6,7} Furthermore, drought leads to increasing fire activities and the associated emissions.^{8,9} As such, the effects of drought on $\text{PM}_{2.5}$ are complex, being impacted not only wet removal but also emissions and chemistry.

Organic aerosol (OA) has been identified as the key contributor to the overall $\text{PM}_{2.5}$ increase in the southeastern (SE) US during past drought periods.^{4,5} Elevated OA during droughts can be attributed to the combined effects of drought conditions on deposition, natural emissions (e.g., wildfires,

BVOCs emissions), and atmospheric processing (e.g., chemistry),⁵ but how those processes respond to drought individually has not been characterized. Hence, the relative importance of these processes remains unknown.

The dominant component of OA in summer in the SE US is secondary organic aerosol (SOA),^{10–12} with biogenic isoprene and monoterpenes being the dominant SOA precursors.^{13–18} Therefore, this study focuses on the response of biogenic SOA to summer drought in the SE US. We apply the Community Multiscale Air Quality (CMAQ) modeling system^{16,19–23} (version 5.0.2) to understand the complex effects of the 2011 severe summer drought on biogenic SOA in the SE US. This model version has been revised to incorporate key updates on isoprene SOA chemistry and emissions,²¹ monoterpene SOA, and multigenerational aging process.¹⁶ Through model sensitivity simulations, we will separate the overall response of SOA to drought into different process-level contributions, including wet deposition, BVOCs emissions, in-cloud aqueous chemistry, aerosol water aqueous chemistry, and gas-phase chemistry. Besides these processes, fire emissions are also important for organic aerosols in the SE

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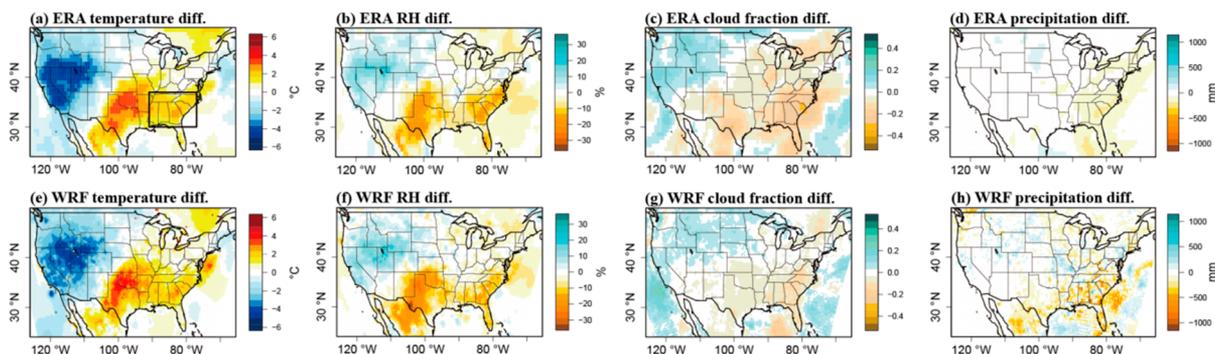


Figure 1. Differences of monthly mean (a, e) 2m temperature, (b, f) 2m RH, (c, g) total cloud cover fraction, and (d, h) total precipitation between June 2011 and June 2013 from ERA-Interim reanalysis data set (1st panel) and WRF simulation (2nd panel). The black rectangle in (a) denotes the SE US domain.

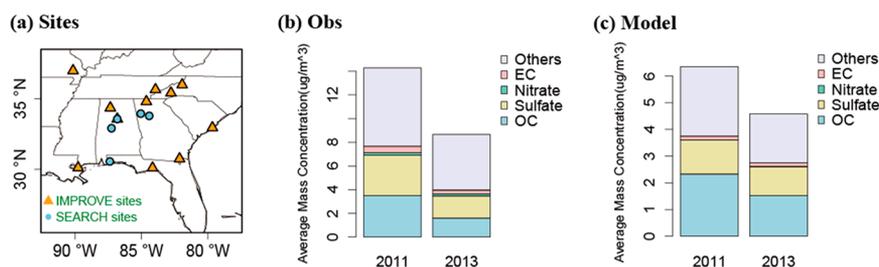


Figure 2. (a) Locations of surface monitoring sites in the Southeast U.S. (b) Observed and (c) modeled surface $PM_{2.5}$ concentrations at the monitoring locations averaged over the Southeast U.S. domain during June 2011 and June 2013. The ammonium, fine soil, and sea salt are included in others. Note the y-axis has different scales in (b) and (c).

US, although the associated contribution is more episodic than biogenic emissions. We acknowledge that enhanced wildfire activities during drought can cause an increase in OA due to fire emissions of both primary OA (POA) and precursor gases leading to SOA formation,^{4,24,25} but the detailed analysis of drought-induced fire emissions on SOA will be left for a future study.

MATERIALS AND METHODS

Drought Conditions. Meteorology. The SE US experienced a severe drought in summer 2011.^{26,27} It was chosen as a typical drought period for the southern US in our previous case study (W2015).⁴ As a contrast to the drought month, June 2013 was a wet month for the SE US, with above-normal precipitation and near-normal mean temperature compared with the long-term average.^{28,29} Figure 1a-d compares the monthly mean surface 2m temperature, relative humidity (RH), total cloud cover fraction, and total precipitation between June 2011 and 2013 for the continental US using the reanalysis data set of the European Centre for Medium-Range Weather Forecasts (ECMWF) Reanalysis Interim (ERA-Interim),³⁰ with a resolution of $0.75^\circ \times 0.75^\circ$. The study domain is SE US ($30^\circ N - 37^\circ N$, $77^\circ W - 91^\circ W$) (Figure 1a). Over this domain, mean surface 2m temperature, RH, cloud cover, and total precipitation was $27^\circ C$, 66%, 0.26, and 59 mm respectively in June 2011, compared to the corresponding value of $26^\circ C$, 74%, 0.44, and 168 mm for June 2013 (Figure S1). The higher temperatures, lower RH, less cloud fraction, and lower precipitation during the drought period (June 2011) were captured by the Weather Research and Forecasting (WRF) simulations (Figure 1e-h), which serve as inputs of the CMAQ model (described in the section Model Description). In the following analysis, we chose June 2011 as the drought

period and June 2013 as the wet period to conduct the case study.

Observations. Figure 2a shows the locations of surface sites from the Southeastern Aerosol Research and Characterization (SEARCH) and Interagency Monitoring of Protected Visual Environments (IMPROVE) networks in the study domain.³¹ Figure 2b shows the observed monthly mean $PM_{2.5}$ by species averaged over the site locations in the SE domain during the drought period (June 2011) and wet period (June 2013). The site-mean $PM_{2.5}$ concentrations over SE was $14 \mu g/m^3$ in June 2011, 65% higher than that in June 2013 ($8.7 \mu g/m^3$). Organic carbon (OC) and sulfate dominate the enhancement of $PM_{2.5}$ during the drought, contributing 33% and 28% to the increase, respectively. OC increased by 117%, from $1.6 \mu g/m^3$ (wet) to $3.5 \mu g/m^3$ (drought). Sulfate increased by 84%, from $1.9 \mu g/m^3$ (wet) to $3.4 \mu g/m^3$ (drought). The comparison between W2015 and Figure 2b is presented in Section 1 of the Supporting Information (SI). Both works identify that OC has the large enhancement during drought among all species examined. Considering SOA is the major contributor to total OC in the SE in summer,^{11-13,32} such enhancement is most likely caused by SOA. Indeed, primary aerosol such as elemental carbon (EC) has a smaller relative increase (81%) than that of OC. Therefore, we focus on the changes in individual SOA components due to drought in the following analysis.

Model Description. Chemical Transport Model Configuration. The CMAQ modeling system version 5.0.2, with additional updates including isoprene SOA chemistry,²¹ monoterpene SOA chemistry and multigenerational oxidation process,¹⁶ and adjustment of biogenic emissions, is used to simulate $PM_{2.5}$ components in June 2011 and June 2013 (May 28th through July first, with the first 4 days as spin up) over the

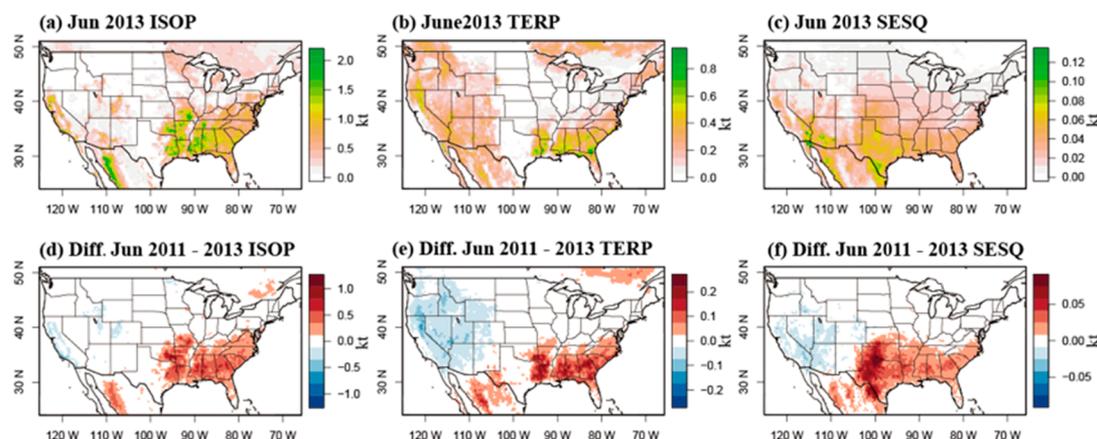


Figure 3. BEIS-simulated biogenic emissions of isoprene (left), monoterpenes (middle), and sesquiterpenes (right) in June 2013 (upper panel) and the changes of these emissions between June 2011 and June 2013 (lower panel).

contiguous U.S. The model resolution is 36×36 km horizontally with 35 vertical layers. The input meteorological fields are simulated by the WRF Model version 3.3.1 for summer 2011 and 2013, respectively.

SOA typically forms in the atmosphere when organic gases react with oxidants to produce semivolatile or nonvolatile products that can be absorbed into the organic fraction of PM. Also, the aqueous fraction of PM can absorb the organic species to form SOA. In the model, the SOA species are composed by anthropogenic SOA (SOA_{anthro}), biogenic SOA (BSOA), and in-cloud SOA (SOA_{cl}). BSOA is further decomposed by precursors, including isoprene SOA, monoterpenes SOA, and sesquiterpenes SOA. Besides, all semivolatile organic aerosols in the model undergo condensed-phase oligomerization reactions to produce nonvolatile products and the resultant SOA produced is referred to anthropogenic or biogenic originated oligomers. Therefore, BSOA species in the model consist of isoprene SOA, monoterpenes SOA, sesquiterpenes SOA, and biogenic originated oligomers. For isoprene SOA, the formation pathway includes not only the gas phase reaction with oxidants, but also the aqueous aerosol pathways of epoxide in aerosol water.²¹

Emission. Anthropogenic emissions are based on the 2011 National Emission Inventory (NEI), which are processed by the Sparse Matrix Operator Kernel Emissions (SMOKE) model version 3.5.1. As this study focuses on the perturbation of drought on biogenic SOA, we hold anthropogenic emissions constant between the two months of June 2011 and June 2013. Although the emissions amounts from large point sources are the same, different meteorology between the two months may change the plume elevation height as the plume rise is calculated in-line in the model. We also hold dust and sea salt and emissions from wildfires constant, and are based on the NEI 2011. The uncertainty due to fixed anthropogenic emissions and wildfire emissions will be discussed in the section of model evaluation and SI Section 2.

The southeast U.S. has high biogenic emissions of isoprene, monoterpenes, and sesquiterpenes (Figure 3a–c), the three major biogenic SOA precursors included in the model. These emissions are calculated every hour using WRF simulated temperature and solar radiation as inputs to the Biogenic Emission Inventory System (BEIS) version 3.14. Based on the model calculation, higher temperature and radiation during drought lead to higher BVOCs emissions;^{2,7} simulated emissions of biogenic isoprene, monoterpenes, and sesquiter-

penes over the study domain increase by 33%, 23%, and 44%, respectively, in the drought month compared to the wet month (Figure 3d–f). But the true effects of drought on biogenic emissions should involve other stress factors such as soil moisture stress and air pollution stress, which can ultimately suppress BVOCs emissions^{33–35} depending on the severity and duration of drought.^{4,33} However, these factors are not incorporated in BEIS3.14, partly because the current understanding of drought effects on BVOCs emissions is still highly uncertain. Because there was no direct measurements of BVOCs emission fluxes over the study region and period to verify the model calculation, we turned to surface isoprene measurements from the Photochemical Assessment Monitoring Stations (PAMS) network in the southeast U.S. for an indirect evaluation of the model. The PAMS data showed an average 95% increase in isoprene concentrations during the drought month (11 ppb carbon) compared to the wet month (5.5 ppb carbon) (SI Table S1). Similar increases of isoprene concentrations from the PAMS network were also found in our previous analyses of other drought regions/periods.^{4,5} Although PAMS measurements are isoprene concentrations rather than emissions, these data suggest an increase of isoprene emissions during the drought periods examined, likely driven by higher temperature and radiation, especially during the beginning of drought when root-zone soil moisture was not yet depleted. By comparison, CMAQ-simulated changes of isoprene concentrations at the PAMS locations also show an average increase of 70% during the drought month (13 ppb carbon) compared to the wet month (7.8 ppb carbon). Despite the high bias of simulated isoprene concentrations for both periods, the model correctly captures the ~ 5 ppb carbon enhancement of isoprene concentrations during the drought month, lending support to the simulated increase in BVOCs emissions between the drought and wet period. An in-depth analysis of drought stress on BVOCs emissions would require ecosystem-scale flux measurements which were not available. In the following analysis, we simply use BEIS-simulated BVOCs emissions for the drought and wet month, respectively, although we acknowledge a large uncertainty may exist in the amount of emission changes between the two months.

Model Evaluation. Figure 2c shows CMAQ-simulated $PM_{2.5}$ concentrations and speciation at the site locations averaged over the southeast for June 2011 and June 2013. Compared to observations, model $PM_{2.5}$ is about a factor of 2 too low for both months, with a mean mass concentration of

Table 1. Description of the Different Simulations

simulation case name	year of meteorology	emission year for BVOCs	description
2013_Base	2013	2013	base simulation for the wet month.
2011_Base	2011	2011	base simulation for the drought month.
2011_BVOC13	2011	2013	drought month simulation with wet-month BVOCs emissions.
2013_BVOC11	2013	2011	wet month simulation with drought-month BVOCs emissions.
2013_Base_NoWdAq	2013	2013	same as 2013_base, but without wet deposition and in-cloud aqueous chemistry.
2011_BVOC13_NoWdAq	2011	2013	same as 2011_BVOC13, but without wet deposition and in-cloud aqueous chemistry.
2013_Base_NoAq	2013	2013	same as 2013_base, but without in-cloud aqueous chemistry.
2011_BVOC13_NoAq	2011	2013	same as 2011_BVOC13, but without in-cloud aqueous chemistry.

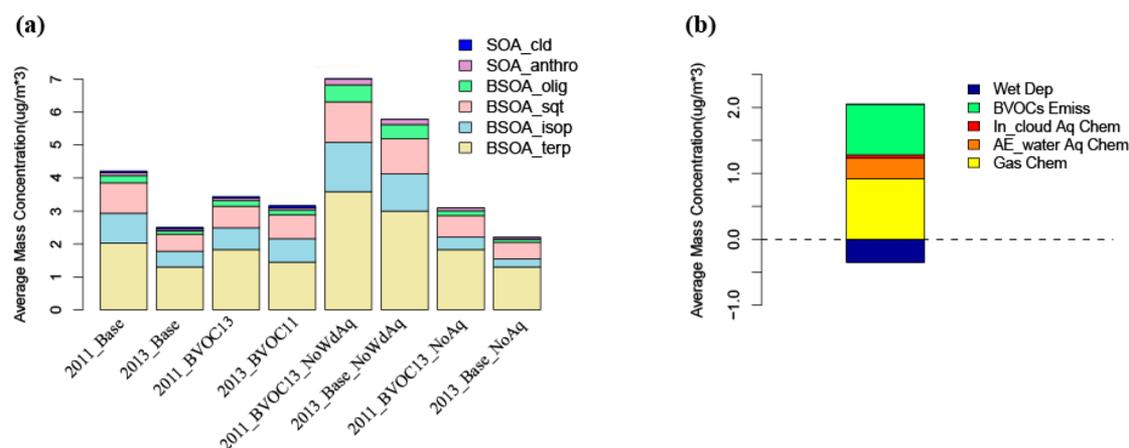


Figure 4. (a) CMAQ simulated monthly mean SOA concentrations by species averaged over the SE US domain from different sensitivity simulations. (b) Breakdown of regional mean SOA difference between the drought and wet month into contributions of different processes, including wet deposition, BVOCs emissions, in-cloud aqueous chemistry, aerosol water aqueous chemistry, and gas-phase chemistry. The names of the processes in (b) correspond to the names of the symbols in Table 2.

$4.6 \mu\text{g}/\text{m}^3$ in June 2013 and $6.3 \mu\text{g}/\text{m}^3$ in June 2011. In spite of the overall low bias, the model simulates a 39% increase in $\text{PM}_{2.5}$ concentrations for the drought month, which is consistent with observed relative change of 65% for $\text{PM}_{2.5}$. The model attributes nearly 46% and 10% of the $\text{PM}_{2.5}$ increase to the increase of OC and sulfate, respectively. OC is 54% higher in the drought month than the wet month, and for sulfate the relative increase is 17%. The simulated OC enhancement (54%) is about a factor of 2 low compared to the observed enhancement of 117%. However, the model correctly simulates that the large enhancement in OC is the key driver of increasing $\text{PM}_{2.5}$ over the SE during the drought.

Scatterplots (SI Figure S2) show that the model and observations of $\text{PM}_{2.5}$, sulfate, and OC are significantly correlated spatially ($p < 0.05$), with correlation coefficients larger than 0.5 for all the comparisons. The model can correctly capture the spatial distribution of individual aerosol components and the sign of OC changes during the drought month. For the wet month, model $\text{PM}_{2.5}$, sulfate, and OC has a mean bias of $-4.1 \mu\text{g}/\text{m}^3$, $-0.77 \mu\text{g}/\text{m}^3$, and $-0.12 \mu\text{g}/\text{m}^3$, respectively. The corresponding model bias for the dry month is $-7.9 \mu\text{g}/\text{m}^3$, $-2.2 \mu\text{g}/\text{m}^3$, and $-1.2 \mu\text{g}/\text{m}^3$, all being factors larger than the bias in the wet month. This implies the model under-predicts the drought effect on $\text{PM}_{2.5}$, a problem identified also for coupled chemistry-climate models.⁵

This under-prediction of $\text{PM}_{2.5}$ increase between the two months can be partly attributed to the same fire and anthropogenic emissions for the wet and drought period used in the simulations, and a detailed discussion of this is

provided in SI Section 2. We purposely used the same fire and anthropogenic emissions for the wet and drought period so as to focus on the effects of biogenic emissions and meteorology on SOA. More in-depth analysis on the influence of drought-induced fire emissions and anthropogenic VOCs emissions on SOA will be a future research direction.

The large low bias of $\text{PM}_{2.5}$ and constituent species in CMAQ has been reported by previous studies for the southeast U.S. during the summer.¹⁶ Since nitrate concentrations are low in the summer, sulfate and OC contribute most to the bias in $\text{PM}_{2.5}$. Such a bias can be attributed to inaccurate meteorological predictions, uncertainties in biogenic emissions, under-representation of SOA pathways, and uncertainties in model assumptions and treatments in aerosol chemistry and microphysics.^{16,19,21,22,36,37} For SOA, the model used in this simulation has improved isoprene and monoterpenes chemistry and corrected the negative bias by some extent. The improvements include (1) SOA production from monoterpenes + NO_3 (OH, O_3 , O_3P) were treated individually;¹⁶ (2) SOA yields for monoterpene + NO_3 were updated;¹⁶ (3) the influence of multigenerational oxidation was added;¹⁶ (4) the production from isoprene by aqueous uptake of isoprene epoxydiols (IEPOX) was added;²¹ (5) the nucleophiles of IEPOX derived isoprene SOA was added.²¹ The remaining model bias could be attributed to outdated SOA yields for O_3/OH oxidation of monoterpenes.

Sensitivity Simulations. To separately estimate the contribution of specific processes, different sensitivity simulations were performed, as summarized in Table 1. The base

Table 2. Processes and Symbols Used to Analyze the Sensitivity Simulations

process	modeling	symbols ^a	meaning
wet deposition	wet condition: 2013_Base_NoWdAq - 2013_Base_NoAq	Wd_2013	changes in SOA due to wet scavenging, subject to meteorological conditions of the wet period
	drought condition: 2011_BVOC13_NoWdAq - 2011_BVOC13_NoAq	Wd_2011	same as Wd_2013, but under meteorological conditions of the drought period ^b
	difference: Wd_2011 - Wd_2013	Wet_Dep	response of SOA due to changes in wet scavenge under drought ^b
in-cloud aqueous chemistry	drought condition: 2013_Base -2013_Base_NoAq	Aq_2013	changes in SOA due to in-cloud aqueous chemistry process, subject to meteorological conditions of the wet period
	wet condition: 2011_BVOC13-2011_BVOC13_NoAq	Aq_2011	same as Aq_2013, but under meteorological conditions of the drought period ^b
	difference: Aq_2011 - Aq_2013	In_cloud_Aq_Chem	response of SOA due to changes in in-cloud aqueous chemistry under drought ^b
BVOCs emissions	2011_Base -2011_BVOC13	BVOCs_Emiss	changes in SOA due to increasing BVOCs emissions under drought, subject to meteorological conditions of the drought month
SOA chemistry	2011_BVOC13_NoWdAq - 2013_Base_NoWdAq	Gas_Chem	response of SOA due to changes in gas phase chemistry process under drought ^b
		AE_water_Aq_Chem	response of SOA due to changes in aerosol water aqueous chemistry process during drought ^b

^aThe names of the symbols in this table correspond to the names of the processes in Figure 4b. ^bSubject to BVOCs emissions of the wet period.

simulations of June 2011 (2011_base) and June 2013 (2013_base) are the simulations described above in the model description and evaluation section.

To evaluate the effects of increased BVOCs emissions under drought conditions on SOA, we conducted the 2011_BVOC13 simulation in which all the settings are the same as 2011_base except that BVOCs emissions are taken from 2013_base, and the 2013_BVOC11 simulation in which all the settings are the same as 2013_base except that BVOCs emissions are taken from 2011_base. The differences between the simulation results of 2011_BVOC13 (2013_BVOC11) and 2011_base (2013_base) represent the effects of drought-induced increases of BVOCs emissions on SOA under transport and oxidizing conditions of the drought (wet) period. Although the difference of BVOCs emissions between 2011_base and 2011_BVOC13 is the same as that between 2013_base and 2013_BVOC11, the response of SOA is expected to be different because of different meteorological conditions (drought vs wet) under which BVOCs is oxidized to form SOA.

The drought period is characterized by low precipitation and lower cloud fraction which should influence wet removal and in-cloud aqueous phase chemistry of SOA in the model.^{38,39} To investigate these processes, for each period we conducted one simulation turning off both wet deposition and in-cloud aqueous chemistry in the cloud process (2011_BVOC13_NoWdAq and 2013_base_NoWdAq) and another one turning off in-cloud aqueous chemistry only (2011_BVOC13_NoAq and 2013_base_NoAq). Note that for the drought period, the sensitivity simulations of 2011_BVOC13_NoWdAq and 2011_BVOC13_NoAq are based on 2011_BVOC13, rather than 2011_base, so as to exclude the effects of changing BVOCs emissions, therefore allowing for a direct comparison with the corresponding sensitivity simulations for the wet period.

RESULTS

Simulation results of regional mean SOA concentrations from the base and sensitivity simulations (c.f. Table 1) are presented

in Figure 4a and SI Table S2. Comparing the two base simulations, SOA concentrations increased by 68% or 1.7 $\mu\text{g}/\text{m}^3$ during the drought period, from 2.5 $\mu\text{g}/\text{m}^3$ (2013_Base) to 4.2 $\mu\text{g}/\text{m}^3$ (2011_Base), and 98% of this increase is attributed to increased BSOA (Figure 4a, SI Table S2). Within the BSOA category, isoprene SOA, monoterpenes SOA, sesquiterpenes SOA, and biogenic originated oligomers increased by 89%, 55%, 80%, and 109% respectively in the drought month relative to the wet month. Other SOA components including SOA_{anthro} and SOA_{clld} also increased, by 51% and 20% respectively (Figure 4a), although they contributed only 1.6% and 0.65% to the overall SOA increase in the drought month.

With these sensitivity simulations described in Table 1, we can decompose the increase in surface SOA during the drought period into contributions of individual processes, including wet deposition, BVOCs emissions, in-cloud aqueous chemistry, aerosol water aqueous chemistry, and gas-phase chemistry. Wet deposition and in-cloud aqueous chemistry are linked to the rainfall deficit and reduced cloud fractions during the drought. Increased BVOCs emissions provide more precursors to produce SOA. The multitude change in meteorological conditions during drought, including higher temperatures, lower RH, and lower cloudiness, is expected to affect the chemical processing of SOA and precursors in the atmosphere. Table 2 lists how the sensitivity simulations were used to derive the contributions from the above-mentioned processes and the different symbols used to analyze the model results, and Figure 4b summarizes the contribution of each process to the overall SOA change simulated by the model. Below we discuss the perturbation of drought on individual SOA process as revealed by different model sensitivity simulations (Figure 4b). As sulfate also shows a large change due to drought, sulfate concentration from each simulation scenario and the breakdown of individual process are also shown in SI Table S2 and SI Figure S6 as a comparison to the SOA changes.

Wet Deposition. The regional-mean Wd_2011 and Wd_2013 are 3.9 $\mu\text{g}/\text{m}^3$ and 3.6 $\mu\text{g}/\text{m}^3$, respectively, representing the portion of SOA concentration at the surface

removed by wet scavenging. The Wet_Dep ($0.35 \mu\text{g}/\text{m}^3$) indicates that the amount of SOA removed by wet scavenging is 10% higher during the drought relative to that of the wet period (Figure 4b). This change is about 20% of the magnitude of the overall SOA increase between 2011_Base and 2013_Base but in opposite sign, meaning that changes of SOA wet scavenging between the drought and wet month would lead to a reduction of SOA. This appears to be counterintuitive, as lower precipitation in June 2011 (SI Figure S7a) means reduced wet deposition. Indeed, the domain-mean wet deposition velocity of SOA decreased by 27%, from 0.03 m/s in the wet period (2013_Base) to 0.02 m/s in the drought period (2011_Base) (SI Figure S7b). The spatial distribution of the changes in SOA wet deposition velocity (SI Figure S7b) largely follows that of precipitation changes in the model (SI Figure S7a), confirming precipitation reduction as the driver of decreased wet deposition velocity during drought. However, the drought month has 68% higher SOA burden than the wet month over the study domain. The amount of SOA removed by wet deposition calculated by the model increased by 33% over the study domain, from 0.0024 kg/ha/hour in the wet month to 0.0032 kg/ha/hour in the drought month because the higher SOA levels overwhelm the reduced precipitation.

There is no observation of organic aerosol wet deposition between the two periods to verify the above model result. However, supporting evidence can be found from long-term measurements of wet deposition fluxes of inorganic ions at a few sites in the southeast U.S. from the National Trends Network (NTN) of National Atmospheric Deposition Program (NADP, <http://nadp.isws.illinois.edu/NADP/>). The NADP data shows an increase of both sulfate and nitrate deposition fluxes during the drought month compared to the wet month (SI Figure S7c–f). Similar increases were also found in our previous analysis of the same drought period but with a different model (GEOS-Chem).⁴ The NADP data provides more than 30 years of wet deposition measurements (inorganic ions only) which covers multiple drought periods, thus it allows us to investigate if an increase of aerosol wet deposition is a general feature for other drought periods. As sulfate concentrations in the U.S. have declined over the past decades due to reduced SO_2 emissions,^{40,41} we linearly detrended domain-mean monthly sulfate wet deposition flux between January 1986 and December 2015. The detrended deposition time series was then correlated with the domain-mean drought index of standardized precipitation evapotranspiration index (SPEI, <http://spei.csic.es/>). The Pearson correlation coefficient between the two (SI Figure S8) is small yet significant negative ($r = -0.21$, $p < 0.001$). As negative SPEI means drought, this implies drought months (SPEI < 0) would have a higher wet deposition of sulfate, consistent with the model sensitivity analysis of SOA deposition presented above, although we acknowledge the weak correlation from the NADP data indicates a large uncertainty surrounding that statement.

In-Cloud Aqueous Chemistry. The model predicts lower cloud fraction and reduced liquid water content of clouds in the drought period. Simulated average liquid water content of clouds over the SE domain is 21% lower in the drought month ($0.39 \text{ g}/\text{m}^3$) than that in the wet month ($0.49 \text{ g}/\text{m}^3$) (SI Figure S9a). The average cloud top layer heights are lower in June 2011 (1578 m) than in June 2013 (2654 m). Despite these changes, the predicted In_cloud_Aq_Chem is positive, at $0.05 \mu\text{g}/\text{m}^3$, contributing to about 3% of the overall surface

SOA concentrations increase between the drought and wet base simulations (Figure 4b). This can be attributed to higher temperatures not only at the surface but also above the PBL during the drought period which accelerated the rate of SO_2 and BVOCs oxidation in clouds. SI Figure S9b show the difference of simulated air temperature at the height of 2.4 km above the ground between the drought and the wet periods. At this altitude, air temperature was still 9% higher in the drought period ($12 \text{ }^\circ\text{C}$) than in the wet period ($11 \text{ }^\circ\text{C}$). The In_cloud_Aq_Chem can be broken down into a 5% contribution by SOA_{old} and 95% by BSOA. The majority (91%) of the BSOA difference results from changes in isoprene SOA formed via the acid-catalyzed epoxide pathway in aerosol water which is sensitive to sulfate. This reaction pathway via the acid-catalyzed epoxide and its sensitivity to sulfate will be discussed in detail in the SOA chemistry section. The simulated sulfate concentrations are listed in SI Table S2 and Figure S6. The in-cloud aqueous-phase chemistry is found to contribute 49% (58%) of surface sulfate concentrations in the drought (wet) month compared to the respective base simulation (SI Table S2). The drought period has a higher sulfate production in the cloud ($0.64 \mu\text{g}/\text{m}^3$) than in the wet period ($0.60 \mu\text{g}/\text{m}^3$), which is consistent with the observed higher sulfate concentrations in drought (SI Figure S2), and 16% of this increase is found to result from enhanced in-cloud aqueous phase chemistry process (SI Figure S6). As acknowledged above, inaccurate prediction of meteorological conditions such as cloud cover and cloud properties can cause uncertainty and bias in the simulation of In_cloud_Aq_Chem . This uncertainty, however, is not expected to affect our conclusion as the in-cloud aqueous chemistry process accounts for only 3% of the total SOA increase.

BVOCs Emissions. The BVOCs_Emiss is $0.77 \mu\text{g}/\text{m}^3$ (Figure 4b), about 45% of the overall SOA increase ($1.7 \mu\text{g}/\text{m}^3$) between the drought and wet base simulations and almost entirely (98%) attributed by the change in BSOA. The BSOA change can be further broken down to $0.25 \mu\text{g}/\text{m}^3$ (33%) of isoprene SOA, $0.19 \mu\text{g}/\text{m}^3$ (25%) of monoterpenes SOA, $0.26 \mu\text{g}/\text{m}^3$ (34%) of sesquiterpenes SOA, and $0.05 \mu\text{g}/\text{m}^3$ (7%) of biogenic originated oligomers. When the same amount of BVOCs emission changes is applied to the meteorological conditions of the wet month, that is, by comparing 2013_Base and 2013_BVOC11, BSOA differs by $0.66 \mu\text{g}/\text{m}^3$, consisting of $0.23 \mu\text{g}/\text{m}^3$ for isoprene SOA, $0.15 \mu\text{g}/\text{m}^3$ for monoterpenes SOA, and $0.22 \mu\text{g}/\text{m}^3$ for sesquiterpenes SOA, and $0.04 \mu\text{g}/\text{m}^3$ of biogenic originated oligomers. These values are all smaller by 10–20% than the corresponding ones for the drought month, in spite of the same magnitude of perturbation in BVOCs emissions. This indicates that SOA production per unit increase of BVOCs emissions is 10–20% larger under drought conditions than wet conditions in the SE, possibly due to enhanced chemical oxidation in the former. Discussion about enhanced chemical formation of SOA during the drought is presented in the following section.

SOA Chemistry. Besides BVOCs emissions, wet removal, and in-cloud aqueous phase chemistry as discussed above, the changes of meteorological conditions during drought will affect net chemical production rate of SOA, which can explain the rest of the simulated changes in SOA between 2011_Base and 2013_Base. For example, the production of SOA depends on gas phase reactions and aqueous phase reactions in aerosol water, both expected to be perturbed by drought conditions of higher temperature, lower humidity, and increased solar

radiation at the ground due to reduced cloud cover. While different wind fields and boundary layer dynamics between the drought and wet period can influence the inflow and outflow of SOA and precursor gases over the study region, we assume such transport effects to be small, considering fast reaction rates of BVOCs (seconds to hours) forming the majority of SOA in the region and the dominant effect of wet scavenging on SOA lifetime which has been examined above. In order to isolate the chemistry process, we examine the difference between 2011_BVOC13_NoWdAq and 2013_Base_NoWdAq, as both simulations use the same BVOCs emissions while excluding the effects of wet deposition and in-cloud chemistry. The difference of SOA concentrations between 2011_BVOC13_NoWdAq and 2013_Base_NoWdAq is $1.2 \mu\text{g}/\text{m}^3$, about 72% of the overall SOA increase between the wet and drought base simulation. As shown in Figure 4b, this change can be further divided into a $0.92 \mu\text{g}/\text{m}^3$ increase from the semivolatile partitioning pathways (refer as gas phase pathway in the following) (Gas_Chem) and a $0.31 \mu\text{g}/\text{m}^3$ increase from the aqueous phase pathway in aerosol water (AE_water_Aq_Chem). These changes contribute about 54% and 18% of the overall SOA increase between the wet and drought base simulations, respectively.

Gas Phase Pathway. The net production of SOA from gas phase reactions depends on oxidant concentrations, rate of gas-phase oxidation of organic compounds, partitioning between the particle and the gas phase, and particle-phase oligomerization, which are all parametrized with a strong temperature dependence in the model.^{17,42–44} Warm-season droughts are often associated with higher temperatures and reduced cloudiness. These conditions accelerate gas-phase photochemical reactions, resulting in higher oxidant levels in the lower atmosphere that increase the rate of oxidation of BVOCs. Observed formaldehyde (HCHO) concentrations from PAMS network showed an average 78% increase in the drought month compared to the wet month (SI Table S3). SI Figure S10 shows the difference in simulated surface-level HCHO concentrations between 2011_BVOC13_NoWdAq and 2013_Base_NoWdAq. While both simulations have the same BVOCs emissions, the domain-mean HCHO differs by 15%, increasing from 1.7 ppbv in the wet period (2013_Base_NoWdAq) to 2.0 ppbv in the drought period (2011_BVOC13_NoWdAq). As HCHO is a high-yield product from gas phase oxidation of volatile organic compounds,⁴⁵ the increase of HCHO is a certain indication of increasing VOC oxidation reactions in the gas phase under drought conditions. On the other hand, temperature controls the partitioning of semivolatile species between gas and aerosol phases through the enthalpies of vaporization and the saturation concentration, with the equilibrium shifting more toward gas phase as temperature increases. In the model, this effect does not seem to play a dominating role and the net change is a 54% increase in gas-phase pathway during the drought month compared to the wet month (under the same BVOCs emissions). $\text{SOA}_{\text{anthro}}$ and BSOA contribute 2% and 98% of this total SOA increase through the gas-phase pathway, respectively. The overall increase of $\text{SOA}_{\text{anthro}}$ concentrations is 51% ($0.03 \mu\text{g}/\text{m}^3$) during drought, which is totally due to the enhancement of $\text{SOA}_{\text{anthro}}$ formed by gas-phase chemistry pathway because of no increase of anthropogenic VOCs emissions and no aqueous phase pathway for $\text{SOA}_{\text{anthro}}$ in the model. Within the BSOA category, isoprene SOA, monoterpenes SOA, sequiterpenes SOA, and biogenic originated

oligomers produced through the gas-phase pathway increased by 22%, 20%, 14%, and 20% respectively in the drought month compared to the wet month.

Aqueous Phase Pathway in Aerosol Water. Besides the gas-phase pathway discussed above, isoprene SOA can form in aerosol water via the acid-catalyzed epoxide pathway.²¹ The model indicates that this pathway contributes to about 76% of isoprene SOA and 16% of total SOA in the southeast U.S. (SI Figure S11 and SI Table S4). The aerosol acidity in the model is computed through the thermodynamic equilibrium model of ISORROPIA II⁴⁶ and hence the hydronium ion concentration (H^+) is sensitive to the sulfate concentrations. Compared with $\text{NH}_3/\text{NH}_4^+$, the H^+ is more sensitive to the sulfate concentrations. SI Table S5 lists relevant parameters for the isoprene SOA epoxide aqueous chemistry in aerosol water in different sensitivity simulations. Resulting from gas-phase chemistry alone, surface concentrations of accumulation mode sulfate increases by 22% in the drought period (2011_BVOC13_NoWdAq) relative to the wet period (2013_Base_NoWdAq) (SI Table S2), due to higher temperatures and higher OH promoting oxidation rate of SO_2 in the gas phase (see above). Along with a charge balance to the increased sulfate concentrations, the H^+ concentration in aerosols increased by 22%. The aerosol water concentrations decreased by 10% in the drought in spite of higher sulfate concentrations, most likely due to the lack of sufficient moisture supply. The aerosol acidity increased in the drought period due to an increase in H^+ and decrease in liquid water content. As acidity increases, the isoprene epoxides derived aerosols are increased as a result of more efficient uptake by aqueous aerosols and quicker rates of particle-phase reactions.²¹ Furthermore, the aerosol surface area increased by 7% in the drought month between the two sensitivity simulations (2011_BVOC13_NoWdAq and 2013_Base_NoWdAq) largely due to enhanced SOA formation from gas-phase reactions. Conversion of epoxides to the aerosol phase is increased as particle surface area increases.²¹ As a result, the isoprene SOA concentrations from epoxide aqueous phase pathways increases by 37%, from $0.85 \mu\text{g}/\text{m}^3$ to $1.2 \mu\text{g}/\text{m}^3$, about 18% of total SOA enhancement in the drought.

DISCUSSION

As a type of hydroclimate extremes, drought intensity and frequency are projected to increase over many parts of the U.S. Our analysis provides information on how SOA would respond to the complex changes of the atmosphere and the land biosphere during drought conditions by conducting detailed sensitivity analysis examining chemical, physical and emissions processes. The two leading factors driving the SOA increase during drought are gas-phase reactions and BVOCs emissions. These two factors in combination explain almost all of the simulated SOA changes in the southeast U.S. during the 2011 summer drought. Our analysis points to the importance of understanding stress-induced BVOCs emissions during drought, which is arguably the most uncertain aspect in the CMAQ model used here.

One uncertainty or limitation of this study lies in the approach to delinearize the effects of individual processes by using sensitivity simulations that remove specific processes. Future work will be needed to consider how drought conditions change the interplay or coupling between different processes, for example the feedback of stress-induced BVOCs emissions on atmospheric oxidants (i.e., ozone). Another

uncertainty or limitation is that we did not consider the changes of anthropogenic emissions or emissions from wildland fires (including primary OC emissions) during drought. These topics are left for future work. Nevertheless, we showed an ~50% increase in anthropogenic SOA in the model without any increase of anthropogenic VOCs emissions. In reality, anthropogenic VOCs emissions should increase as temperature increases,^{47,48} which would lead to an even larger increase of anthropogenic SOA during drought. SOA_{anthro} should play a more significant role in populated urban/suburban areas, such as the Atlanta metropolitan area in the southeast U.S. where the ratio of anthropogenic VOCs and biogenic VOCs are estimated to be 1:2.⁴⁹ The implication of this finding is that anthropogenic emissions should be regulated more stringently during drought in order to mitigate the adverse air quality, but more analysis is needed to focus on finer spatial scales in order to investigate the drought impacts on air quality due to anthropogenic SOA changes over urban/suburban areas. In summary, this study provides a quantified estimate of drought effects on surface air pollution due to SOA and calls for air quality management and research related to hydroclimate extremes such as drought.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b04842.

(PDF)

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■ REFERENCES

- (1) Textor, C.; Schulz, M.; Guibert, S.; Kinne, S.; Balkanski, Y.; Bauer, S.; Bernsten, T.; Berglen, T.; Boucher, O.; Chin, M. Analysis and quantification of the diversities of aerosol life cycles within AeroCom. *Atmos. Chem. Phys. Discuss.* **2006**, *5* (5), 8331–8420.
- (2) Trenberth, K. E.; Dai, A.; Schrier, G. V. D.; Jones, P. D.; Barichivich, J.; Briffa, K. R.; Sheffield, J. Global warming and changes in drought. *Nat. Clim. Change* **2014**, *4* (1), 17–22.
- (3) Hallar, A. G.; Molotch, N. P.; Hand, J. L.; Livneh, B.; McCubbin, I. B.; Petersen, R.; Michalsky, J.; Lowenthal, D.; Kunkel, K. E. Impacts

of increasing aridity and wildfires on aerosol loading in the intermountain Western US. *Environ. Res. Lett.* **2017**, *12*, 014006.

- (4) Wang, Y.; Xie, Y.; Cai, L.; Dong, W.; Zhang, Q.; Zhang, L. Impact of the 2011 Southern U.S. Drought on Ground-Level Fine Aerosol Concentration in Summertime. *J. Atmos. Sci.* **2015**, *72* (3), 1075–1093.

- (5) Wang, Y.; Xie, Y.; Dong, W.; Ming, Y.; Wang, J.; Shen, L. Adverse effects of increasing drought on air quality via natural processes. *Atmos. Chem. Phys.* **2017**, *17* (20), 12827–12843.

- (6) Fuentes, J. D.; Lerdau, M.; Atkinson, R.; Baldocchi, D.; Bottenheim, J. W.; Ciccioli, P.; Lamb, B.; Geron, C.; Gu, L.; Guenther, A. Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review. *Bull. Am. Meteorol. Soc.* **2000**, *81* (7), 1537–1576.

- (7) Guenther, A. B.; Jiang, X.; Heald, C. L.; Sakulyanontvittaya, T.; Duhl, T.; Emmons, L. K.; Wang, X. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev.* **2012**, *5* (6), 1–58.

- (8) Veraverbeke, S.; Hook, S. J. Evaluating spectral indices and spectral mixture analysis for assessing fire severity, combustion completeness and carbon emissions. *Int. J. Wildland Fire* **2013**, *22* (5), 707–720.

- (9) Weinhold, B. Fields and Forests in Flames: Vegetation Smoke and Human Health. *Environ. Health Perspect.* **2011**, *119* (9), a386.

- (10) Attwood, A. R.; Washenfelder, R. A.; Brock, C. A.; Hu, W.; Baumann, K.; Campuzano-Jost, P.; Day, D. A.; Edgerton, E. S.; Murphy, D. M.; Palm, B. B. Trends in sulfate and organic aerosol mass in the Southeast U.S.: Impact on aerosol optical depth and radiative forcing. *Geophys. Res. Lett.* **2015**, *41* (21), 7701–7709.

- (11) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, *9* (1), 5155–5236.

- (12) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S.; Zhang, Q.; Kroll, J. H.; Decarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L. Evolution of organic aerosols in the atmosphere. *Science* **2009**, *326* (5959), 1525–1529.

- (13) Carlton, A. G.; de Gouw, J.; Jimenez, J. L.; Ambrose, J. L.; Attwood, A. R.; Brown, S.; Baker, K. R.; Brock, C.; Cohen, R. C.; Edgerton, S.; Farkas, C. M.; Farmer, D.; Goldstein, A. H.; Gratz, L.; Guenther, A.; Hunt, S.; Jaeglé, L.; Jaffe, D. A.; Mak, J.; McClure, C.; Nenes, A.; Nguyen, T. K.; Pierce, J. R.; de Sa, S.; Selin, N. E.; Shah, V.; Shaw, S.; Shepson, P. B.; Song, S.; Stutz, J.; Surratt, J. D.; Turpin, B. J.; Warneke, C.; Washenfelder, R. A.; Wennberg, P. O.; Zhou, X. Synthesis of the Southeast Atmosphere Studies: Investigating Fundamental Atmospheric Chemistry Questions. *Bull. Am. Meteorol. Soc.* **2018**, *99* (3), 547–567.

- (14) Krechmer, J. E.; Coggon, M. M.; Massoli, P.; Nguyen, T. B.; Crounse, J. D.; Hu, W.; Day, D. A.; Tyndall, G. S.; Henze, D. K.; Rivera-Rios, J. C.; Nowak, J. B.; Kimmel, J. R.; Mauldin, R. L., 3rd; Stark, H.; Jayne, J. T.; Sipila, M.; Junninen, H.; Clair, J. M.; Zhang, X.; Feiner, P. A.; Zhang, L.; Miller, D. O.; Brune, W. H.; Keutsch, F. N.; Wennberg, P. O.; Seinfeld, J. H.; Worsnop, D. R.; Jimenez, J. L.; Canagaratna, M. R. Formation of Low Volatility Organic Compounds and Secondary Organic Aerosol from Isoprene Hydroxyhydroperoxide Low-NO Oxidation. *Environ. Sci. Technol.* **2015**, *49* (17), 10330–10339.

- (15) Lopez-Hilfiker, F. D.; Mohr, C.; D'Ambro, E. L.; Lutz, A.; Riedel, T. P.; Gaston, C. J.; Iyer, S.; Zhang, Z.; Gold, A.; Surratt, J. D.; Lee, B. H.; Kurten, T.; Hu, W. W.; Jimenez, J.; Hallquist, M.; Thornton, J. A. Molecular Composition and Volatility of Organic Aerosol in the Southeastern U.S.: Implications for IEPOX Derived SOA. *Environ. Sci. Technol.* **2016**, *50* (5), 2200–2209.

- (16) Qin, M.; Hu, Y.; Wang, X.; Vasilakos, P.; Boyd, C. M.; Xu, L.; Song, Y.; Ng, N. L.; Nenes, A.; Russell, A. G. Modeling biogenic secondary organic aerosol (BSOA) formation from monoterpene reactions with NO₃: A case study of the SOAS campaign using CMAQ. *Atmos. Environ.* **2018**, *184*, 146–155.

- (17) Xu, L.; Guo, H.; Boyd, C. M.; Klein, M.; Bougiatioti, A.; Cerully, K. M.; Hite, J. R.; Isaacman-Vanwertz, G.; Kreisberg, N. M.; Knote, C. Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (1), 37–42.
- (18) Xu, L.; Suresh, S.; Guo, H.; Weber, R. J.; Ng, N. L. Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates. *Atmos. Chem. Phys.* **2015**, *15* (13), 7307–7336.
- (19) Carlton, A. G.; Bhawe, P. V.; Napelenok, S. L.; Edney, E. O.; Sarwar, G.; Pinder, R. W.; Pouliot, G. A.; Houyoux, M. Model Representation of Secondary Organic Aerosol in CMAQv4.7. *Environ. Sci. Technol.* **2010**, *44* (22), 8553–8560.
- (20) Appel, K. W.; Pouliot, G. A.; Simon, H.; Sarwar, G. Evaluation of dust and trace metal estimates from the Community Multiscale Air Quality (CMAQ) model version 5.0. *Geosci. Geosci. Model Dev.* **2013**, *6* (4), 883–899.
- (21) Pye, H. O.; Pinder, R. W.; Piletic, I. R.; Xie, Y.; Capps, S. L.; Lin, Y. H.; Surratt, J. D.; Zhang, Z.; Gold, A.; Luecken, D. J.; Hutzell, W. T.; Jaoui, M.; Offenberg, J. H.; Kleindienst, T. E.; Lewandowski, M.; Edney, E. O. Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation. *Environ. Sci. Technol.* **2013**, *47* (19), 11056–11064.
- (22) Pye, H. O. T.; Murphy, B. N.; Xu, L.; Ng, N. L.; Carlton, A. G.; Guo, H.; Weber, R.; Vasilakos, P.; Wyatt Appel, K.; Hapsari Budisulistiorini, S. On the implications of aerosol liquid water and phase separation for organic aerosol mass. *Atmos. Chem. Phys.* **2017**, *17* (1), 343–369.
- (23) Xie, Y.; Paulot, F.; Carter, W. P. L.; Nolte, C. G. Understanding the impact of recent advances in isoprene photooxidation on simulations of regional air quality. *Atmos. Chem. Phys.* **2013**, *13* (16), 8439–8455.
- (24) Westerling, A. L.; Swetnam, T. W. Interannual to decadal drought and wildfire in the western United States. *Eos. Trans. Am. Geophys. Union.* **2013**, *84* (49), 545–555.
- (25) Westerling, A. L.; Gershunov, A.; Brown, T. J.; Cayan, D. R.; Dettinger, M. D. Climate and Wildfire in the Western United States. *Bull. Am. Meteorol. Soc.* **2003**, *84* (5), 595–604.
- (26) NOAA's National Climatic Data Center; [https://www.ncdc.noaa.gov/temp-and-precip/us-maps/1/201106?products\[\]=tave-anom&products\[\]=prcp-diff#us-maps-select](https://www.ncdc.noaa.gov/temp-and-precip/us-maps/1/201106?products[]=tave-anom&products[]=prcp-diff#us-maps-select).
- (27) NOAA's National Climatic Data Center; <https://www.ncdc.noaa.gov/monitoring-content/temp-and-precip/drought/nadm/nadm-narr-201106.pdf>.
- (28) NOAA's National Climatic Data Center; [https://www.ncdc.noaa.gov/temp-and-precip/us-maps/1/201306?products\[\]=tave-anom&products\[\]=prcp-diff#us-maps-select](https://www.ncdc.noaa.gov/temp-and-precip/us-maps/1/201306?products[]=tave-anom&products[]=prcp-diff#us-maps-select).
- (29) NOAA's National Climatic Data Center; <https://www.ncdc.noaa.gov/monitoring-content/temp-and-precip/drought/nadm/nadm-narr-201306.pdf>.
- (30) Simmons, A. J.; Uppala, S. M.; Dee, D. P.; Kobayashi, S. ERA-Interim: New ECMWF reanalysis products from 1989 onwards. **2007**.
- (31) Canagaratna, M. R.; Jimenez, J. L.; Kroll, J. H.; Chen, Q.; Kessler, S. H.; Massoli, P.; Hildebrandt Ruiz, L.; Fortner, E.; Williams, L. R.; Wilson, K. R. Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications. *Atmos. Chem. Phys.* **2015**, *15* (1), 253–272.
- (32) Weber, R. J.; Sullivan, A. P.; Peltier, R. E.; Russell, A.; Yan, B.; Zheng, M.; De Gouw, J.; Warneke, C.; Brock, C.; Holloway, J. S. A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. *J. Geophys. Res. Atmos.* **2007**, *112*, D13302.
- (33) Zheng, Y. Q.; Unger, N.; Tadic, J. M.; Seco, R.; Guenther, A. B.; Barkley, M. P.; Potosnak, M. J.; Murray, L. T.; Michalak, A. M.; Qiu, X. M.; Kim, S.; Karl, T.; Gu, L. H.; Pallardy, S. G. Drought impacts on photosynthesis, isoprene emission and atmospheric formaldehyde in a mid-latitude forest. *Atmos. Environ.* **2017**, *167*, 190–201.
- (34) Lerda, M.; Loreto, F.; Centritto, M. Response of Isoprene Emission and Carbon Metabolism to Drought in White Poplar (*Populus alba*) Saplings. *New Phytol.* **2007**, *175* (2), 244–254.
- (35) Seco, R.; Karl, T.; Guenther, A.; Hosman, K. P.; Pallardy, S. G.; Gu, L.; Geron, C.; Harley, P.; Kim, S. Ecosystem-scale VOC fluxes during an extreme drought in a broad-leaf temperate forest of the Missouri Ozarks (central USA). *Global Change Biol.* **2015**, *21* (10), 3657–3674.
- (36) Zhang, H.; Chen, G.; Hu, J.; Chen, S. H.; Wiedinmyer, C.; Kleeman, M.; Ying, Q. Evaluation of a seven-year air quality simulation using the Weather Research and Forecasting (WRF)/Community Multiscale Air Quality (CMAQ) models in the eastern United States. *Sci. Total Environ.* **2014**, *473–474* (3), 275–285.
- (37) Simon, H.; Baker, K. R.; Phillips, S. Compilation and interpretation of photochemical model performance statistics published between 2006 and 2012. *Atmos. Environ.* **2012**, *61*, 124–139.
- (38) Carlton, A. G.; Turpin, B. I.; Altieri, K. E.; Seitzinger, S. P.; Mathur, R.; Roselle, S. J.; Weber, R. J. CMAQ model performance enhanced when in-cloud secondary organic aerosol is included: comparisons of organic carbon predictions with measurements. *Environ. Sci. Technol.* **2008**, *42* (23), 8798–8802.
- (39) Ervens, B. Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs. *Chem. Rev.* **2015**, *115* (10), 4157–4198.
- (40) Hand, J. L.; Schichtel, B. A.; Malm, W. C.; Pitchford, M. L. Particulate sulfate ion concentration and SO₂ emission trends in the United States from the early 1990s through 2010. *Atmos. Chem. Phys.* **2012**, *12* (21), 10353–10365.
- (41) Xing, J.; Pleim, J.; Mathur, R.; Pouliot, G.; Hogrefe, C.; Gan, C. M.; Wei, C. Historical gaseous and primary aerosol emissions in the United States from 1990 to 2010. *Atmos. Chem. Phys.* **2013**, *13* (15), 7531–7549.
- (42) Byun, D.; Schere, K. L. Review of the governing equations, computational algorithms, and other components of the models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Appl. Mech. Rev.* **2006**, *59* (1–6), 51–77.
- (43) Yu, S.; Bhawe, P. V.; Dennis, R. L.; Mathur, R. Seasonal and regional variations of primary and secondary organic aerosols over the continental United States: semi-empirical estimates and model evaluation. *Environ. Sci. Technol.* **2007**, *41* (13), 4690.
- (44) Zhang, Y.; Huang, J. P.; Henze, D. K.; Seinfeld, J. H. Role of isoprene in secondary organic aerosol formation on a regional scale. *J. Geophys. Res.* **2007**, *112*, D18310.
- (45) Bauwens, M.; Stavrou, T.; Muller, J. F.; De Smedt, I.; Van Roozendaal, M.; van der Werf, G. R.; Wiedinmyer, C.; Kaiser, J. W.; Sindelarova, K.; Guenther, A. Nine years of global hydrocarbon emissions based on source inversion of OMI formaldehyde observations. *Atmos. Chem. Phys.* **2016**, *16* (15), 10133–10158.
- (46) Fountoukis, C.; Nenes, A. ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K⁺-Ca²⁺-Mg²⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O aerosols. *Atmos. Chem. Phys.* **2007**, *7* (17), 4639–4659.
- (47) Rubin, J. I.; Kean, A. J.; Harley, R. A.; Millet, D. B.; Goldstein, A. H. Temperature dependence of volatile organic compound evaporative emissions from motor vehicles. *J. Geophys. Res.* **2006**, *111*, D03305.
- (48) Strong, J.; Whyatt, J. D.; Metcalfe, S. E.; Derwent, R. G.; Hewitt, C. N. Investigating the impacts of anthropogenic and biogenic VOC emissions and elevated temperatures during the 2003 ozone episode in the UK. *Atmos. Environ.* **2013**, *74*, 393–401.
- (49) Unal, A.; Hu, Y.; Chang, M. E.; Talat Odman, M.; Russell, A. G. Airport related emissions and impacts on air quality: Application to the Atlanta International Airport. *Atmos. Environ.* **2005**, *39* (32), 5787–5798.