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

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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 μg/m³) 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 (PM_{2.5}, particles with an aerodynamic diameter less than or equal to 2.5 μm) is a criteria pollutant impacting air quality, human health, and climate. The dominant sink of major PM_{2.5} constituents in the atmosphere is wet removal,† which means ambient 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,† has been shown to be associated with higher PM_{2.5} pollutants 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.5,9 As such, the effects of drought on 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 PM_{2.5} increase in the southeastern (SE) US during past drought periods.6,5 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 system16,19−23 (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 monoterpenic 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
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, 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. 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. 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 from ERA-Interim reanalysis data set (1st panel) and WRF simulation (2nd panel). The black rectangle in (a) denotes the SE US domain.

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. Figure 2b shows the observed monthly mean PM2.5 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 PM2.5 concentrations over SE was 14 μg/m3 in June 2011, 65% higher than that in June 2013 (8.7 μg/m3). Organic carbon (OC) and sulfate dominate the enhancement of PM2.5 during the drought, contributing 33% and 28% to the increase, respectively. OC increased by 117%, from 1.6 μg/m3 (wet) to 3.5 μg/m3 (drought). Sulfate increased by 84%, from 1.9 μg/m3 (wet) to 3.4 μg/m3 (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, 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, monoterpenes SOA chemistry and multigenerational oxidation process, and adjustment of biogenic emissions, is used to simulate PM2.5 components in June 2011 and June 2013 (May 28th through July first, with the first 4 days as spin up) over the drought period and June 2013 as the wet period to conduct the case study.
emissions of biogenic 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. 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 constant 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). 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 sesqui-

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).
The model attributes nearly 46% and 10% of the PM2.5 to anthropogenic emissions for the wet and drought period respectively. The corresponding model bias for the dry month is larger than the bias in the wet month. This implies the model under-predicts the drought effect on PM2.5, a problem identified also for coupled chemistry-climate models.5

This under-prediction of PM2.5 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 PM2.5 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 PM2.5. 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.5,6,10,21,22,36,37

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 + NO3 (OH, O3, O3P) were treated individually;16 (2) SOA yields for monoterpenes + NO3 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 O3/ OH oxidation of monoterpenes.

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

<table>
<thead>
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<th>process</th>
<th>modeling</th>
<th>symbols*</th>
<th>meaning</th>
</tr>
</thead>
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<td>WD_2013</td>
<td>changes in SOA due to wet scavenging, subject to meteorological conditions of the wet period</td>
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<tr>
<td></td>
<td>drought condition: 2011_BVOC13-NoWdAq - 2011_BVOC13-NoAq</td>
<td>WD_2011</td>
<td>same as WD_2013, but under meteorological conditions of the drought period</td>
</tr>
<tr>
<td></td>
<td>difference: WD_2011 - WD_2013</td>
<td>Wet_Dep</td>
<td>response of SOA due to changes in wet scavenging under drought b</td>
</tr>
<tr>
<td>in-cloud aqueous chemistry</td>
<td>drought condition: 2013_Base-2013_Base_NoAq</td>
<td>Aq_2013</td>
<td>changes in SOA due to in-cloud aqueous chemistry process, subject to meteorological conditions of the wet period</td>
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<tr>
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<td>wet condition: 2011_BVOC13-2011_BVOC13_NoAq</td>
<td>Aq_2011</td>
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</tr>
<tr>
<td>BVOCs emissions</td>
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<td>BVOCs_Emiss</td>
<td>changes in SOA due to increasing BVOCs emissions under drought, subject to meteorological conditions of the drought month</td>
</tr>
<tr>
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<td>Gas_Chem</td>
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<td></td>
<td>2011_BVOC13_NoWdAq</td>
<td>AE_water_Aq_Chem</td>
<td>response of SOA due to changes in aerosol water aqueous chemistry process during drought</td>
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“The names of the symbols in this table correspond to the names of the processes in Figure 4b. b Subject 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. 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 μg/m³ during the drought period, from 2.5 μg/m³ (2011_Base) to 4.2 μg/m³ (2013_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_ana and SOA_dsd 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 μg/m³ and 3.6 μg/m³, respectively, representing the portion of SOA concentration at the surface
removed by wet scavenging. The Wet_Dep (0.35 μg/m³) 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 SO₂ emissions,5,6 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 g/m³) than that in the wet month (0.49 g/m³) (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 μg/m³, 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 SO₂ 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 °C) than in the wet period (11 °C). The In_cloud_Aq_Chem can be broken down into a 5% contribution by SOA₂ld 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 μg/m³) than in the wet period (0.60 μg/m³), 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 μg/m³ (Figure 4b), about 45% of the overall SOA increase (1.7 μg/m³) 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 μg/m³ (33%) of isoprene SOA, 0.19 μg/m³ (25%) of monoterpenes SOA, 0.26 μg/m³ (34%) of sequiterpenes SOA, and 0.05 μg/m³ (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 μg/m³, consisting of 0.23 μg/m³ for isoprene SOA, 0.15 μg/m³ for monoterpenes SOA, and 0.22 μg/m³ for sequiterpenes SOA, and 0.04 μg/m³ 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 BVOC 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 μg/m³, 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 μg/m³ increase from the semivolatile partitioning pathways (refer as gas phase pathway in the following) (Gas Chem) and a 0.31 μg/m³ 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.17,43–44 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,35 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 BVOC emissions). SOAanthro and BSOA contribute 2% and 98% of this total SOA increase through the gas-phase pathway, respectively. The overall increase of SOAanthro concentrations is 51% (0.03 μg/m³) during drought, which is totally due to the enhancement of SOAanthro formed by gas-phase chemistry pathway because of no increase of anthropogenic VOCs emissions and no aqueous phase pathway for SOAanthro in the model. Within the BSOA category, isoprene SOA, monoterpenes SOA, sequeiterpenes 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 NH₃/NH₄⁺, 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 SO₂ 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 μg/m³ to 1.2 μg/m³, 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 VOC 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_{aero} 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.

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**Notes**

The authors declare no competing financial interest.

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