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Secondary Organic Aerosol from Sesquiterpene and Monoterpene Emissions in the United States

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Emissions of volatile organic compounds (VOC) from vegetation are believed to be a major source of secondary organic aerosol (SOA), which in turn comprises a large fraction of fine particulate matter in many areas. Sesquiterpenes are a class of biogenic VOC with high chemical reactivity and SOA yields. Sesquiterpenes have only recently been quantified in emissions from a wide variety of plants. In this study, a new sesquiterpene emission inventory is used to provide input to the Models-3 Community Multiscale Air Quality (CMAQ) model. CMAQ is used to estimate the contribution of sesquiterpenes and monoterpenes to SOA concentrations over the contiguous United States. The gas-particle partitioning model of CMAQ was modified to include condensable products of sesquiterpene oxidation and to update values of the enthalpy of vaporization. The resulting model predicts July monthly average surface concentrations of total SOA in the eastern U.S. ranging from about 0.2–0.8 µg m⁻³. This is roughly double the amount of SOA produced in this region when sesquiterpenes are not included. Even with sesquiterpenes included, however, the model significantly underpredicts surface concentrations of particle-phase organic matter compared to observed values. Treating all SOA as capable of undergoing polymerization increases predicted monthly average surface concentrations in July to 0.4–1.2 µg m⁻³, in closer agreement with observations. Using the original enthalpy of vaporization value in CMAQ in place of the values estimated from the recent literature results in predicted SOA concentrations of about 0.3–1.3 µg m⁻³.

1. Introduction

A large portion of ambient fine particulate matter is organic aerosol from secondary processes (1). The largest source of secondary organic aerosol (SOA) is believed to be from oxidation of volatile organic compounds (VOC) released from vegetation because, on global and continental scales, SOA-forming emissions from vegetation are more than an order of magnitude larger than those from anthropogenic sources (2–4).

The three primary classes of SOA-forming biogenic VOC are isoprene (C₅H₈), monoterpenes (C₁₀H₁₆), and sesquiterpenes (C₁₅H₂₄). Isoprene has the largest emissions (5) but has a relatively small aerosol yield (e.g., 6). Monoterpenes have been relatively widely studied and are known to be a significant source of SOA (e.g., 2). Sesquiterpenes have received relatively little attention in part because of a lack of emissions data, which has only recently begun to be addressed. Sesquiterpenes are emitted from both agricultural and natural plants (7). On the basis of recent emission data and using the Model of Emissions of Gases and Aerosols from Nature (MEGAN; (5)) version 2.02, Sakulyanontvittaya et al. (8) estimated sesquiterpene emissions for the contiguous U.S., northern Mexico, and southern Canada to be 202 × 10^6 metric tons (14 µg m⁻² h⁻¹) or about 16% of monoterpene emissions in July 2001 and 8 × 10^6 metric tons (0.57 µg m⁻² h⁻¹) or about 10% of monoterpene emissions in January 2002. These estimates are highly uncertain because emission rates determined from recent plant enclosure measurements exhibit large unexplained variations, and the representation of measurements from some plant functional types (PFTs) is very limited (8, 9).

Sesquiterpenes could be a major source of atmospheric SOA because of their reactivity and high aerosol yields relative to most other SOA precursors (10–12). However, only a few studies to date have attempted to estimate concentrations of SOA produced from sesquiterpene emissions (13–16). All but one of these studies (15) used preliminary estimates of sesquiterpene emissions that were simply derived as constant fractions of monoterpene or other biogenic volatile organic compound (BVOC) emissions, without consideration of the distinct environmental controls on sesquiterpene emissions or differences in relative emissions by PFT between sesquiterpenes and other BVOC. Vizuete et al. (15) developed a sesquiterpene emissions model based on limited emissions measurements supplemented by estimates for other plants inferred from taxonomic relationships but did not perform detailed chemistry and transport modeling.

This study uses the new sesquiterpene and monoterpene emissions estimates developed by Sakulyanontvittaya et al. (8) with a modified version of the CMAQ (Models-3 Community Multiscale Air Quality) version 4.5 atmospheric chemistry and transport model to estimate the contributions of sesquiterpenes and monoterpenes to SOA formation over the contiguous U.S. The study compares the contribution and spatial distribution of SOA formation from sesquiterpenes and monoterpenes, examines the sensitivity of SOA concentrations to polymerization of SOA, and examines the sensitivity of the enthalpy of vaporization value used to adjust partitioning parameters to environmental temperatures.

2. Methodology

CMAQ Model and Inputs. This study uses CMAQ, version 4.5, modified to include sesquiterpene species in the SAPRC99 chemical mechanism (17) and the third generation aerosol module (AERO3), with an option to test the effect of polymerization of SOA. AERO3 includes a two-product gas-particle partitioning model (18, 19) for absorption and evaporation of secondary organic matter from the aerosol phase. The CMAQ configuration and options used in this study are provided in Table S1 of the Supporting Information.

In the original version of CMAQ version 4.5 with the SAPRC99 chemical mechanism, the only biogenic com-
pound class that contributes to SOA formation is the monoterpane class, TRP1, which is a lumped species based on α-pinene, β-pinene, Δ3-carene, sabine, and limonene (17). Five primarily anthropogenic classes (cresols, higher alkanes, higher olefins, toluene, and xylene) also contribute to SOA formation. In this study, gas-phase reactions, gas-particle partitioning, and transport and removal processes were added for three classes of sesquiterpenes and their associated oxidation products: β-caryophyllene, which is treated explicitly; a lumped class of relatively fast reacting sesquiterpene compounds represented by α-humulene; and a lumped class of more slowly reacting sesquiterpene compounds, for which the assigned rate constants represent the average of reported values for α-cedrene and α-copaene. These two sesquiterpene classes are used to span the large range in O3 reaction rate constants for sesquiterpene species (10). Reaction rate constants used for TRP1 and the three sesquiterpene classes are given in Table S2, Supporting Information. Assignments of individual sesquiterpene compounds to the three model sesquiterpene classes are given by Sakulyanontvittaya (20). Although isoprene has been suggested as a potentially large source of SOA, the relevant pathways and model approximations remain highly uncertain. Consequently, we did not change the treatment of isoprene in CMAQ, version 4.5; it participates only in gas-phase chemistry.

All three sesquiterpene classes are assumed to produce condensable products through their reactions with ozone, OH, and NO3. Once condensable products are produced through the gas-phase reactions of the sesquiterpenes, they are treated in the CMAQ model as capable of undergoing gas-particle partitioning via an equilibrium absorption model, which uses yields of condensable products and equilibrium partition coefficients derived from smog chamber experiments. The equilibrium partition coefficients used in this study for all the condensable species, including the three added sesquiterpene classes, are shown in Table S3 of the Supporting Information. These parameters were estimated from limited smog chamber data and thus represent a large source of uncertainty.

The Clausius–Clapeyron equation (18, 21) is used to adjust the partition coefficients for temperatures other than the temperatures of the smog chamber experiments from which the coefficients were estimated. Values of the enthalpy of vaporization (ΔH_{vap}) of the condensable products are needed for this calculation. The model is highly sensitive to these values, which are not well-known (3, 6, 13, 22). The reference case in this study uses the ΔH_{vap} values shown in Table S3, Supporting Information. Values for condensable products of anthropogenic VOC and TRP1 are estimated from Takekawa et al. (21). Values for the condensable products of the sesquiterpenes were estimated based on measured values for single-component organic aerosols reported in the literature (23). A simple linear relationship with molecular weight was used to extrapolate the data from these studies to the unknown products of sesquiterpene oxidation (20). With the assumption that the condensable oxidation products of the sesquiterpenes have a molecular weight of 240 g mol⁻¹ (29, 30), the resulting value of ΔH_{vap} for the sesquiterpene condensable products is 163 kJ mol⁻¹. In contrast to the values shown in Table S3, Supporting Information, the original CMAQ, version 4.5, model sets ΔH_{vap} = 156 kJ mol⁻¹ for all condensable products of VOC oxidation, based on Tao and McMurry (23).

Recent studies have suggested oligomers or polymers of organic compounds can form through heterogeneous reactions on particulate matter (e.g., refs 31–33). The standard version of CMAQ, version 4.5, neglects this process. In this study, a preliminary polymerization module was added to CMAQ, version 4.5, for sensitivity analysis purposes. On the basis of the paper by Kalberer et al. (33), we assume polymerization shifts SOA mass from volatile SOA to non-volatile polymerized SOA for all species through a first-order process with a rate constant k_{poly} = 9.627 × 10⁻⁸ s⁻¹, which corresponds to a half-life of 20 h for volatile SOA.

Anthropogenic emissions for the U.S. and meteorological input data for multiweek episodes in July 2001 and January 2002 were obtained from A.G. Russell and his students at the Georgia Institute of Technology. The meteorological inputs were derived from the Fifth Generation Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (MMS), processed with the Meteorology Chemistry Interface Processor, version 2.0. The U.S. anthropogenic emissions were prepared based on the 1999 National Emissions Inventory (NEI) using the Sparse Matrix Operator Kernel Emissions (SMOKE) processor, version 2.0 (34). At the time the model runs were initiated, the most recent anthropogenic emissions available for Mexico and Canada were for 1999 and 1996, respectively. These inventories were downloaded from the EPA Web site and processed with SMOKE, version 2.1. Chemical boundary conditions for July 2001 and January 2002 were obtained from the MOZART global chemical transport model, version 2.2 (35), with SOA in the boundary conditions assumed to originate primarily from monoterpene emissions. New biogenic emissions inventories were developed specifically for this study, as discussed below.

**Biogenic Emissions Inventory.** The biogenic emissions inventory was produced using MEGAN, version 2.02 (8), with chemical speciation and lumping schemes developed for the SAPRC99 mechanism. As described by Sakulyanontvittaya et al. (8), emission factors and coefficients of the exponential temperature dependence relationships used in MEGAN, version 2.02, for monoterpene and sesquiterpene emissions are based on recent enclosure measurements, and emissions factors for sesquiterpene compounds are developed for four PFTs. The emissions were allocated temporally and spatially using hourly solar radiation and ambient temperature data from the same MM5-based meteorological inputs used with CMAQ and information on leaf area index and plant distributions for the same months from MODIS satellite data. All monoterpene and sesquiterpene emissions are assumed to escape from the canopy into the atmosphere. The isoprene emissions factor map described by Guenther et al. (5) was used to estimate isoprene emissions.

Table 1 summarizes the monoterpene, sesquiterpene, and isoprene emissions from MEGAN, version 2.02, used in this study and compares the monoterpene and isoprene estimates to those from the Biogenic Emissions Inventory System, version 3 (BEIS3.0), that have been used in other recent studies (e.g., refs 16 and 34). On a mass basis, sesquiterpene emissions from MEGAN, version 2.02, equal about 16% of monoterpene emissions in July and about 10% of monoterpene emissions in January. As discussed by Sakulyanontvittaya et al. (8), a significant fraction of sesquiterpene

<table>
<thead>
<tr>
<th></th>
<th>isoprene (ton h⁻¹)</th>
<th>monoterpene (ton h⁻¹)</th>
<th>sesquiterpene (ton h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEIS3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>July 2001</td>
<td>7416</td>
<td>2205</td>
<td></td>
</tr>
<tr>
<td>January 2002</td>
<td>170</td>
<td>292</td>
<td></td>
</tr>
<tr>
<td>MEGAN, version 2.02</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>July 2001</td>
<td>12145</td>
<td>1852</td>
<td></td>
</tr>
<tr>
<td>January 2002</td>
<td>356</td>
<td>123</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 1. Emissions for the Contiguous U.S., Northern Mexico, and Southern Canada for Isoprene, Monoterpene, and Sesquiterpenes from BEIS3.0 and MEGAN, version 2.02, for July 2001 and January 2002 (Adapted from Ref 8)**
emissions over the U.S. in the current MEGAN model are associated with the grass-crop PFT. However, sesquiterpene emissions have only been quantified for a small number of plants in this category, making emissions estimates for this PFT especially uncertain and highlighting the need for more measurements. The average monoterpane emission estimates from BEIS3.0 are higher than those given by MEGAN, version 2.02, whereas isoprene emissions from MEGAN are higher than those from BEIS3.0.

**Model Performance Evaluation.** Model performance was investigated using an evaluation tool developed at the University of California at Riverside (UCR MPE Tools Air Quality Model Evaluation Software, version 2.0.1). Using this evaluation tool, CMAQ model output was directly compared to measurements from four networks (see Table S4 of the Supporting Information). Data from these networks for July 2001 and January 2002 were compiled by the CE-CERT Air Quality Group at the University of California at Riverside. Model evaluation results for particle-phase organic material (OM) are presented below. Results for ozone, total PM$_{2.5}$, PM$_{1.0}$, and additional results for OM are presented by Sakulyanontvittaya (20). Mass concentrations of OM estimated with CMAQ are compared with measured organic carbon (OC) concentrations that are multiplied by a factor of 1.4 (36). Note that some references recommend use of OM/OC ratios of up to about 2 for summertime measurements at rural sites (e.g., ref 37).

**Simulation Cases.** Four model simulation cases were examined (Table 2). The reference case for this analysis (labeled SQT) uses the modified version of CMAQ, version 4.5, with updated $\Delta H_{\text{vap}}$ values and without polymerization of SOA, and includes sesquiterpene and other MEGAN2.02 BVOC emissions. The case labeled NSQT uses identical inputs of SOA, and includes sesquiterpene and other MEGAN2.02 BVOC emissions. The case labeled SQT/PLMZ includes sesquiterpene emissions and treats all SOA as capable of undergoing polymerization. Finally, the case labeled SQT/ETHP includes sesquiterpene emissions, without polymerization, and using the CMAQ default value of $\Delta H_{\text{vap}}$ (156 kJ mol$^{-1}$) for all SOA precursors (SQT/ETHP), July average total SOA concentrations in the eastern US range from about 0.3 to 1.3 µg m$^{-3}$. As shown in Table 1, emissions of monoterpenes and sesquiterpenes are more than an order of magnitude lower in January than in July. Modeled SOA concentrations are also lower in January than in July but are not reduced as sharply as the emissions because lower winter temperatures favor partitioning of condensable monoterpane and sesquiterpane reaction products to the aerosol phase (Figure S1 in the Supporting Information). In January, average total SOA concentrations in the eastern US range from about 0.05 to 0.25 µg m$^{-3}$ in the SQT and NSQT cases and from about 0.05 to 0.3 µg m$^{-3}$ in the SQT/ETHP case. The use of $\Delta H_{\text{vap}}$ = 156 kJ mol$^{-1}$ for all SOA precursors and including sesquiterpenes but not polymerization (SQT/ETHP) produces somewhat higher SOA concentrations in January, with monthly average concentrations in the eastern U.S. ranging from about 0.15 to 0.6 µg m$^{-3}$. The regions with the highest total SOA predicted by the model for January are the southeastern U.S., California, and northwestern Mexico (Figure S1, Supporting Information).

In the reference SQT case in July, the quantities of SOA attributable to sesquiterpenes (Figure 2) and monoterpenes (Figure S2, Supporting Information) are similar; both are substantially higher than the contribution from anthropogenic VOC (Figure S3, Supporting Information), which is typically less than 10%. Sesquiterpene and monoterpane yields similar quantities of SOA in the SQT case, despite the fact that domain-wide mass emissions of monoterpane are approximately six times greater than sesquiterpane emissions. Kleinidist et al. (38) also found similar SOA contributions from monoterpenes and sesquiterpenes (about 1 µg m$^{-3}$ each) in midsummer using organic tracer measurements from a forested site in North Carolina. Including polymerization of SOA (SQT/PLMZ case) increases the SOA contribution from sesquiterpenes by roughly 50% and increases the contribution from monoterpenes by more than a factor of 2. In the SQT/PLMZ case, half of the SOA at the boundaries was assumed to be polymerized SOA. The amount of polymerized SOA from monoterpenes is influenced by these boundary conditions, as evidenced by the non-negligible SOA concentrations over the Pacific Ocean shown in Figure S2, Supporting Information.

The use of $\Delta H_{\text{vap}}$ = 156 kJ mol$^{-1}$ for all SOA precursors (SQT/ETHP case) results in a slight increase in the SOA concentrations produced from sesquiterpenes and a much more substantial increase in SOA from monoterpenes (Figures 2 and S2, Supporting Information). In this case, monoterpane emissions contribute about half the total SOA, while sesquiterpane and anthropogenic VOC emissions each contribute about a fourth of the total. SOA formation from monoterpenes and anthropogenic VOC is higher in the SQT/ETHP case because the $\Delta H_{\text{vap}}$ values used for their condensable products are much higher than in the SQT case. In

**TABLE 2. Configuration of CMAQ Used in the Reference Case (SQT) and Three Sensitivity Cases**

<table>
<thead>
<tr>
<th>configuration</th>
<th>SQT</th>
<th>NSQT</th>
<th>SQT/PLMZ</th>
<th>SQT/ETHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>sesquiterpene emissions</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>monoterpenes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>polymerization</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>enthalpy of vaporization</td>
<td>83.1 kJ mol$^{-1}$</td>
<td>83.1 kJ mol$^{-1}$</td>
<td>83.1 kJ mol$^{-1}$</td>
<td>156.0 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>sesquiterpenes</td>
<td>163.0 kJ mol$^{-1}$</td>
<td>163.0 kJ mol$^{-1}$</td>
<td>163.0 kJ mol$^{-1}$</td>
<td>163.0 kJ mol$^{-1}$</td>
</tr>
</tbody>
</table>

4.5, with updated (labeled SQT) uses the modified version of CMAQ, version 2.02, whereas isoprene emissions from MEGAN, version 2.02, are compared with measured concentrations in the eastern U.S. range from about 0.2 to 0.8 µg m$^{-3}$. Treating all SOA as capable of undergoing polymerization further increases SOA concentrations; in this case (SQT/PLMZ), July average SOA concentrations in the eastern U.S. range from about 0.4 to 1.2 µg m$^{-3}$. Finally, with sesquiterpene emissions, without polymerization, and using the CMAQ default value of $\Delta H_{\text{vap}}$ (156 kJ mol$^{-1}$) for all SOA precursors (SQT/ETHP), July average total SOA concentrations in the eastern US range from about 0.3 to 1.3 µg m$^{-3}$.

Figure 1 shows the monthly average distribution of SOA in the surface layer for July 2001 for each of the four cases. The SOA concentrations represent the sum of the Aitken and accumulation modes in CMAQ. The regions most influenced by SOA in July are the eastern U.S., California, western Oregon, and northern Idaho and correspond with areas of elevated precursor emissions, including sesquiterpenes (8). Figure 1 shows that with updated values for $\Delta H_{\text{vap}}$ and without sesquiterpene emissions (NSQT case), little SOA is produced. This result has been noted previously by Zhang et al. (22). Inclusion of sesquiterpenes roughly doubles the surface SOA concentrations; in the SQT case, July average total SOA concentrations in the eastern U.S. range from about 0.2 to 0.8 µg m$^{-3}$. Treating all SOA as capable of undergoing polymerization further increases SOA concentrations; in this case (SQT/PLMZ), July average SOA concentrations in the eastern U.S. range from about 0.4 to 1.2 µg m$^{-3}$. Finally, with sesquiterpene emissions, without polymerization, and using the CMAQ default value of $\Delta H_{\text{vap}}$ (156 kJ mol$^{-1}$) for all SOA precursors (SQT/ETHP), July average total SOA concentrations in the eastern US range from about 0.3 to 1.3 µg m$^{-3}$.

As shown in Table 1, emissions of monoterpenes and sesquiterpenes are more than an order of magnitude lower in January than in July. Modeled SOA concentrations are also lower in January than in July but are not reduced as sharply as the emissions because lower winter temperatures favor partitioning of condensable monoterpane and sesquiterpane reaction products to the aerosol phase (Figure S1 in the Supporting Information). In January, average total SOA concentrations in the eastern US range from about 0.05 to 0.25 µg m$^{-3}$ in the SQT and NSQT cases and from about 0.05 to 0.3 µg m$^{-3}$ in the SQT/ETHP case. The use of $\Delta H_{\text{vap}}$ = 156 kJ mol$^{-1}$ for all SOA precursors and including sesquiterpenes but not polymerization (SQT/ETHP) produces somewhat higher SOA concentrations in January, with monthly average concentrations in the eastern U.S. ranging from about 0.15 to 0.6 µg m$^{-3}$. The regions with the highest total SOA predicted by the model for January are the southeastern U.S., California, and northwestern Mexico (Figure S1, Supporting Information).

In the reference SQT case in July, the quantities of SOA attributable to sesquiterpenes (Figure 2) and monoterpenes (Figure S2, Supporting Information) are similar; both are substantially higher than the contribution from anthropogenic VOC (Figure S3, Supporting Information), which is typically less than 10%. Sesquiterpene and monoterpane yields similar quantities of SOA in the SQT case, despite the fact that domain-wide mass emissions of monoterpane are approximately six times greater than sesquiterpane emissions. Kleinidist et al. (38) also found similar SOA contributions from monoterpenes and sesquiterpenes (about 1 µg m$^{-3}$ each) in midsummer using organic tracer measurements from a forested site in North Carolina. Including polymerization of SOA (SQT/PLMZ case) increases the SOA contribution from sesquiterpenes by roughly 50% and increases the contribution from monoterpenes by more than a factor of 2. In the SQT/PLMZ case, half of the SOA at the boundaries was assumed to be polymerized SOA. The amount of polymerized SOA from monoterpenes is influenced by these boundary conditions, as evidenced by the non-negligible SOA concentrations over the Pacific Ocean shown in Figure S2, Supporting Information.

The use of $\Delta H_{\text{vap}}$ = 156 kJ mol$^{-1}$ for all SOA precursors (SQT/ETHP case) results in a slight increase in the SOA concentrations produced from sesquiterpenes and a much more substantial increase in SOA from monoterpenes (Figures 2 and S2, Supporting Information). In this case, monoterpane emissions contribute about half the total SOA, while sesquiterpane and anthropogenic VOC emissions each contribute about a fourth of the total. SOA formation from monoterpenes and anthropogenic VOC is higher in the SQT/ETHP case because the $\Delta H_{\text{vap}}$ values used for their condensable products are much higher than in the SQT case. In
contrast, the $\Delta H_{vap}$ value for condensable products of sesquiterpenes is reduced from 163 kJ mol$^{-1}$ in the SQT case to 156 kJ mol$^{-1}$ in the SQT/ETHP case. Although this change alone would reduce SOA production from sesquiterpenes, increasing the $\Delta H_{vap}$ values for the other SOA precursors makes additional condensed phase organic matter available to absorb condensable sesquiterpene reaction products, so SOA formation from sesquiterpenes is also slightly higher in the SQT/ETHP case. In all three cases with sesquiterpene emissions, the spatial distribution of SOA from sesquiterpenes is similar to that from monoterpenes.

In January (results not shown) as in July, sesquiterpenes and monoterpenes contribute similar quantities of SOA in the reference SQT case. In the SQT/ETHP case, the SOA contribution from monoterpenes in January is increased by about a factor of 5 and from anthropogenic VOC emissions by almost a factor of 10 compared to the SQT case, whereas the contribution from sesquiterpenes is increased only modestly. In the SQT/ETHP case in January, sesquiterpenes contribute less than 10% of the SOA, monoterpenes about 40%, and anthropogenic VOC emissions about 50%.

Surface-level SOA concentrations modeled in this study are comparable to those Andersson-Skold and Simpson (13) estimated for terpenes in northern Europe, which ranged from 0.2 to 1.4 $\mu g$ m$^{-3}$ for July and 0.08 to 0.6 $\mu g$ m$^{-3}$ for January, and to those Liao et al. (4) estimated for BVOC (sesquiterpenes, monoterpenes, and isoprene), which for the southeastern U.S. ranged from 0.5 to 1.5 $\mu g$ m$^{-3}$ in summer and were less than 0.5 $\mu g$ m$^{-3}$ in the winter. However, the fraction of the SOA contributed by sesquiterpenes differs between the studies, in part because of differences in emissions and partitioning parameters, as well as the inclusion of isoprene by Liao et al. (4). Across their domain and on an annual basis, Andersson-Skold and Simpson (13) estimated sesquiterpenes contributed about 12% of the SOA from all terpenes. On an annual basis for the U.S., Liao et al. (4) estimated sesquiterpenes contribute about 6% of SOA from BVOC including isoprene. Our study found higher fractional contributions from sesquiterpene emissions, in part, because our estimated sesquiterpene emissions represent a greater fraction of terpene emissions than did either of the earlier studies. In addition, in the SQT case in this study, condensable products of sesquiterpene oxidation are more likely to be found in the particle phase than those of monoterpenes, because our estimated sesquiterpene emissions represent a greater fraction of terpene emissions than did either of the earlier studies. In addition, in the SQT case in this study, condensable products of sesquiterpene oxidation are more likely to be found in the particle phase than those of monoterpenes because of the difference in the $\Delta H_{vap}$ values we used for the two BVOC classes. In contrast, Andersson-Skold and Simpson (13) used a single $\Delta H_{vap}$ value of 80 kJ mol$^{-1}$, and Liao et al. (4) a single value of 42 kJ mol$^{-1}$, with no differentiation across product classes.
Vertical and Temporal Variations of SOA. To illustrate the vertical distribution of SOA from monoterpenes and sesquiterpenes, Figure S4, Supporting Information, presents total biogenic SOA concentrations from the SQT case for the nine layers in the model, plotted as a function of time for the grid cell corresponding to the Jefferson Street monitoring site in Atlanta, GA, which is part of the SEARCH monitoring network. To understand the source of SOA concentrations aloft, the precursor gases, condensable product concentrations, and ambient temperature were also plotted as time series of vertical profiles. The results (not shown) indicate the precursor gases are reacted completely within the lowest 1 km above ground level (AGL). In particular, the sesquiterpenes are largely reacted within the first 100 m AGL. However, the condensable products are transported up to 10 km AGL in July (and to 3 km AGL in January), where temperatures are colder and favor partitioning to the particulate phase.

In the SQT/ETHP case using the CMAQ default value of $\Delta H_{\text{vap}}$ (156 kJ mol$^{-1}$), SOA concentrations are roughly uniformly increased in comparison with the SQT case. Consequently, the vertical distributions show little difference between these two cases. However, the vertical distribution changes more markedly in the case with polymerization (SQT/PLMZ), where elevated biogenic SOA concentrations extend further into the upper layers of the model, making the vertical distribution more uniform than in the SQT case (Figure S5, Supporting Information).

Model Performance. The monthly average distributions of modeled fine particulate OM in the surface layer for July 2001 and January 2002 are shown in Figures S6 and S7 of the Supporting Information. For July 2001, modeled OM concentrations over most of the southeastern U.S. range from about 0.5 to 2 $\mu$g m$^{-3}$ in the SQT case and from about 1 to 3 $\mu$g m$^{-3}$ in the SQT/PLMZ and SQT/ETHP cases. For January, the corresponding concentration range is from about 0.5 to 3 $\mu$g m$^{-3}$ in all three of these cases. The normalized mean bias (see Table S4 of Supporting Information) is negative for all cases, ranging from about $-40\%$ to $-70\%$, and the magnitude of bias is similar to the magnitude of the error, indicating the model consistently underpredicts surface OM concentrations. The model’s underestimation bias would be greater if actual OM/OC ratios are larger than the ratio of 1.4 we used to convert the measured OC concentrations (37).

Compared to the case without sesquiterpene emissions (NSQT) the model performance improves when sesquiterpene emissions are added (SQT) and further improves when polymerization is considered (SQT/PLMZ) or when the default $\Delta H_{\text{vap}}$ value is used (SQT/ETHP) (Figure S8, Supporting Information). The differences in performance between the four cases are more pronounced for July than for January, reflecting the greater influence in July of SOA as...
compared to primary organic aerosol (POA). Even in the best performing cases, however, the model still strongly underestimates surface OM concentrations in comparison with the observations, and the correlation between predictions and observations is low. This highlights our lack of understanding of the processes that control SOA concentrations.

The underestimation bias observed here has also been noted in other recent studies that have applied the CMAQ model (34, 39). Two recent studies that used CMAQ, version 4.4, with the CBIV mechanism, anthropogenic emissions from the 2001 NEI, and biogenic emissions from BEIS3.12 obtained much smaller bias in particle-phase organic concentrations but still saw large absolute errors (22, 40). These studies both neglected sesquiterpene emissions but apparently used higher estimates of POA emissions than used in this work (41). In their initial simulations using CMAQ, version 4.4, with the CBIV mechanism, Morris et al. (16) originally greatly underestimated OC concentrations in July 2002 in the southeastern U.S. They found that inclusion of SOA polymerization and SOA formation from both sesquiterpenes and isoprene significantly reduced the bias in their results. However, their sesquiterpene emissions estimates were simply derived as a fixed fraction of the monoterpene emissions from BEIS and appear to be overestimated (8). Additional studies are needed to constrain total emissions of biogenic SOA precursors and determine the relative contribution of individual biogenic SOA precursors, including isoprene as well as monoterpenes and sesquiterpenes. Comparisons of spatial and temporal variations in SOA precursors and OM distributions and the identification of unique marker compounds (e.g., refs. 38 and 42) are promising approaches for improving regional OM estimates.

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Supporting Information Available
Detailed information about the model configuration and performance and additional figures that show the simulated aerosol concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
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