Model evidence for a significant source of secondary organic aerosol from isoprene

Aaron van Donkelaar[a],[*], Randall V. Martin[a],[b], Rokjin J. Park[c], Colette L. Heald[c], Tzung-May Fu[c], Hong Liao[d], Alex Guenther[e]

[a]*Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada*
[b]*Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*
[c]*Division of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA*
[d]*Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China*
[e]*Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO, USA*

Abstract

We investigate how a recently suggested pathway for production of secondary organic aerosol (SOA) affects the consistency of simulated organic aerosol (OA) mass in a global three-dimensional model of oxidant-aerosol chemistry (GEOS-Chem) versus surface measurements from the interagency monitoring of protected visual environments (IMPROVE) network. Simulations in which isoprene oxidation products contribute to SOA formation, with a yield of 2.0% by mass reduce a model bias versus measured OA surface mass concentrations. The resultant increase in simulated OA mass concentrations during summer of 0.6–$1.0\,\mu g\,m^{-3}$ in the southeastern United States reduces the regional RMSE to $0.88\,\mu g\,m^{-3}$ from $1.26\,\mu g\,m^{-3}$. Spring and fall biases are also reduced, with little change in winter when isoprene emissions are negligible.

1. Introduction

Aerosols influence climate through both direct and indirect means. Direct effects refer to the absorption, scattering, and emission of radiation. Indirect effects such as increased cloud lifetime and smaller cloud droplets are more uncertain, but nonetheless are thought to contribute significantly to the global radiation budget (Lohmann and Feichter, 2005). Accurate simulation of the earth's climate requires a complete representation of processes affecting aerosol abundance.

Organic aerosol (OA) is a major constituent of aerosol mass even outside of biomass burning regions. Airborne measurements off the eastern coast of North America during summer reveal that OA can be the dominant contributor to aerosol optical depth (Hegg et al., 1997). Analysis of springtime airborne measurements over the Northwest Pacific provide evidence that OA is the dominant component of aerosol mass in the free

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*Corresponding author.
E-mail address: kelaar@dal.ca (A. van Donkelaar).

troposphere, a feature that current models fail to capture (Heald et al., 2005).

Atmospheric OA can be divided into two main categories, primary and secondary. Primary OA (POA) refers to OA that has been directly emitted into the atmosphere, often from sources of combustion. Secondary OA (SOA) production occurs within the atmosphere, by condensation of gaseous species. Kanakidou et al. (2005) thoroughly review current understanding of OA sources and sinks.

Global isoprene emissions are approximately $500\,\mathrm{Tg\,C\,yr^{-1}}$, accounting for the majority of non-methane volatile organic emissions (Guenther et al., 2006), implying that even a low-yield pathway could produce a significant amount of SOA. Initial studies attempting to quantify an isoprene-initiated SOA source suggested that isoprene was not a significant precursor of SOA (Pandis et al., 1991). Claeys et al. (2004a, b) recently analyzed aerosols from the Amazonian forest and proposed that isoprene oxidation could provide an additional source of SOA via multiphase acid-catalyzed reactions with hydrogen peroxide. Recent laboratory chamber studies found a yield of 1–2% at high NO_x level (Kroll et al., 2005) and ~3% at low NO_x levels (Kroll et al., 2006). Edney et al. (2005) found little evidence of isoprene-derived SOA formation in high atmospheric NO_x conditions, but found a 2.8% yield in the presence of SO_2. An in-cloud process for SOA formation from isoprene has also been identified (Lim et al., 2005). Field experiments by Matsunaga et al. (2005) provide evidence that the isoprene oxidation products hydroxyacetone, methylglyoxal, and glycoaldehyde annually contribute 10–120 Tg of OA to the atmosphere.

Henze and Seinfeld (2006) recently examined the global implications of SOA formation from isoprene oxidation products and found that the simulated SOA burden doubled. Here we compare surface measurements of OA with simulated OA over the continental United States to quantify how this process affects the comparison.

2. Analysis of IMPROVE measurements of OA

The Interagency Monitoring of Protected Visual Environments (IMPROVE) network was initiated in 1988 to monitor visibility-reducing aerosol species including OA. Daily IMPROVE OA measurements are obtained using two separate methods at each station. The first measurement uses thermal optical reflectance, in which collected samples are heated, causing the emission of CO_2 which is then converted to CH_4 and measured (Chow et al., 1993). The OA mass is determined by multiplying the measured carbon mass by a constant organic carbon factor, which represents the average molecular weight per carbon weight for the OA. A second measurement uses particle-induced X-ray emission and proton elastic scattering analysis to determine the quantities of sulphur and hydrogen; the abundance of OA is inferred by assuming that the measured hydrogen is solely associated with sulphur and OA. OA measurements from the two methods are highly consistent ($r^2 = 0.86$) with a regression line of 0.98 (Malm et al, 1994).

Fig. 1 shows seasonal averages of IMPROVE-measured OA. Maximum concentrations are found in the southeast United States during summer and fall, associated with enhanced biogenic emissions of SOA precursors (Malm et al., 2004). However, considerable uncertainty remains in the processes affecting SOA production (Kavouras et al., 1998). Several large-scale fire events that occurred during September and October in eastern and southern regions contribute to the heightened OA concentrations during fall of this year. Abnormally high OA concentrations in excess of $40\,\mu\mathrm{g\,m^{-3}}$ are found in the Great Smoky Mountains National Park, NC from November 12–18, 2001 due to an arson event.

Here we interpret the IMPROVE measurements using the GEOS-Chem chemical transport model (Bey et al., 2001; Park et al., 2003, 2004). Park et al. (2003) previously compared the GEOS-Chem OA simulation with IMPROVE measurements during 1998, when North American biomass burning emissions of OA were a factor of two higher than the long-term mean. We extend the work of Park et al. (2003) by focusing on SOA production during 2001 when biomass burning emissions are within 10% of the long-term mean. We exclude measured values during the Great Smoky Mountains arson event from subsequent comparisons to reduce uncertainty in our analysis of OA as this occurred near to the IMPROVE instrument.

The GEOS-Chem model (http://www.as.harvard.edu/chemistry/trop/geos/index.html) is driven by assimilated meteorological data from the goddard earth observing system (GEOS-3) at the NASA global modeling assimilation office (GMAO). Meteorological fields include surface properties, humidity, temperature, winds, cloud properties, heat flux, and precipitation. The first five levels in the model are centered at approximately 10, 50, 100,
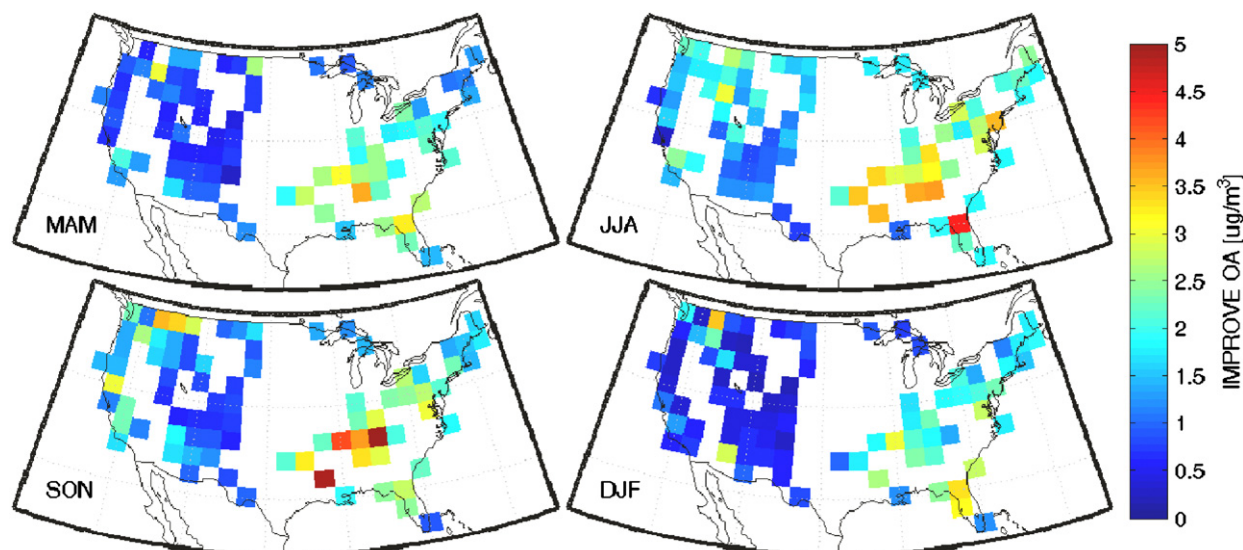
Fig. 1. Seasonal average of surface OA measurements as part of the IMPROVE network for March–May 2001 (MAM), June–August 2001 (JJA), September–November 2001 (SON), and December 2001, January 2002 and February 2001 (DJF) at $2° \times 2.5°$ resolution. White spaces show locations without measurements.

200, and 300 m. We use $2° \times 2.5°$ resolution with 50 tracers based upon GEOS-Chem v7-02-04 with additional updates as described below.

The GEOS-Chem aerosol simulation includes the sulphate–nitrate–ammonium system, carbonaceous aerosols, mineral dust, and sea-salt. The aerosol and oxidant simulations are coupled through formation of sulphate and nitrate (Park et al., 2004), heterogeneous chemistry (Jacob, 2000), aerosol effects on photolysis rates (Martin et al., 2003), and SOA formation as discussed below. GEOS-Chem POA industrial emission inventories are from Cooke et al. (1999). Seasonally varying biomass burning inventories are from Duncan et al. (2003). In the standard GEOS-Chem algorithm, all POA emissions are scaled based on an inversion with IMPROVE observations using GEOS-Chem v4.23, as described in Park et al. (2003); we remove the results of their inversion to identify biases in the OA simulation versus bottom-up inventories.

Isoprene emissions in our simulation are taken from the MEGAN inventory (Guenther et al., 2006), which exhibits strong coherence with GOME HCHO-derived isoprene emissions (Palmer et al., 2006). Most other biogenic emissions, including monoterpenes, are based upon Guenther et al. (2000) and extended to global scales using the driving variables described by Guenther et al.

(2006), with the exception of sesquiterpenes, which are treated as 5% of the other biogenic reactive volatile organic carbon emissions from the GEIA inventory (Griffin et al., 1999a; Guenther et al., 1995). POA emissions are assumed to be 50% hydrophilic, while SOA are assumed to be 80% hydrophilic. The simulation includes wet and dry deposition based upon Liu et al. (2001), including both washout and rainout of hydrophilic carbonaceous species. Extension to moderately soluble gases with low retention efficiencies is as described by Park et al. (2004).

SOA chemistry is based upon Chung and Seinfeld (2002). Hydrocarbons oxidize with O_3, OH, and NO_3 to produce semi-volatile products, which are partitioned between the gas and aerosol phase based upon equilibrium partition coefficients. Chung and Seinfeld (2002) divide reactive biogenic hydrocarbons into five classes, as shown in Table 1. Emissions of each class are determined from total monoterpene emissions based upon their relative global abundance as presented in Griffin et al. (1999a). Rate constants and aerosol yield parameters are calculated by arithmetic average of species values contained within each class obtained from smog chamber data by Griffin et al. (1999a, b).

The domination of a small subset of biogenic hydrocarbon species is a potential source of error in

the SOA algorithm since an arithmetic mean would no longer be representative of overall species class properties. Speciation of monoterpenes varies greatly according to plant type and conditions (Guenther et al., 1996), suggesting that a more regional approach to biogenic hydrocarbon emissions may be necessary. We implement a monoterpene speciation and apply weighted-mean rate constants representative of mean continental United States values using national monoterpene speciation data presented in Geron et al. (2000). This correction produces a typical decrease of only 5% (0.1–0.2 μg m^{-3} OA) relative to the standard simulation in the southeast United States during summer.

SOA yield is typically treated as a function of existing aerosol mass concentration (Yamasaki et al., 1982; Pankow, 1994), which includes both POA and SOA mass. GEOS-Chem POA is simulated by the multiplication of carbon mass with an organic carbon factor of 1.4, which is below the range of recommended values (Turpin and Lim, 2001), but is used here for consistency with IMPROVE.

Fig. 2 compares seasonally averaged IMPROVE measurements of dry OA mass with GEOS-Chem model calculations. Annual average concentrations for 2001 are generally consistent ($r^2 = 0.62$, $N = 79$, slope = 1.42). However, simulated OA concentrations are underestimated during non-winter months in the southeast United States by 1.5–2.5 μg m^{-3} and along the western United States-Canadian border during summer and fall by 2.0–3.0 μg m^{-3}. The bias in the northwestern United States is readily explained by biomass burning not captured in the model, as concluded from a similar bias in black carbon. The discrepancy with IMPROVE in the Florida region results from excessive model precipitation (Park et al., 2006), which produces enhanced wet scavenging and is consistent with an observed under-prediction of black carbon concentrations. We focus our attention on the remaining region of the southeast United States, north of Florida, which is not explained by the previously mentioned mechanisms. Radiocarbon measurements from summer 1999 suggest that 51–73% of total carbonaceous aerosol is of biogenic origin in Nashville, TN (Lewis et al., 2004), well above the value of 43% in our standard simulation for

Table 1
Reactive terpene groups included in Chung and Seinfeld (2002) and used by GEOS-Chem

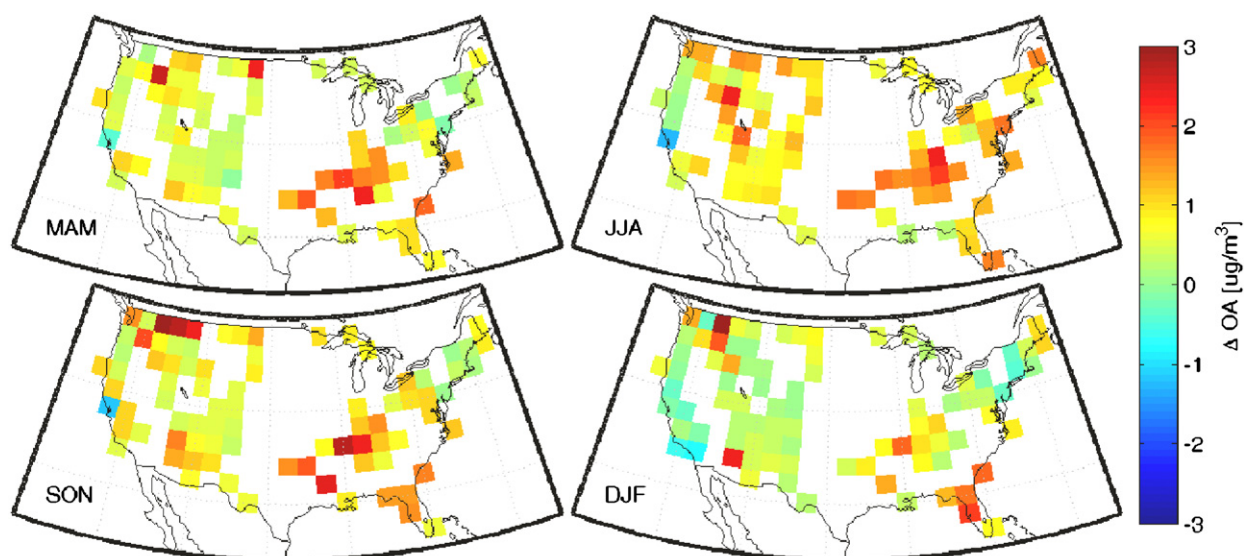| Hydrocarbon class	Constituents
I	α-pinene, β-pinene, sabinene, career terpenoid ketones
II	Limonene
III	α-terpinene, γ-terpinene, terpinolene
IV	Myrcene, terpenoid alcohols,ocimene
V	Sesquiterpenes

Fig. 2. Seasonal average of IMPROVE OA minus simulated GEOS-Chem OA over February 2001–January 2002.
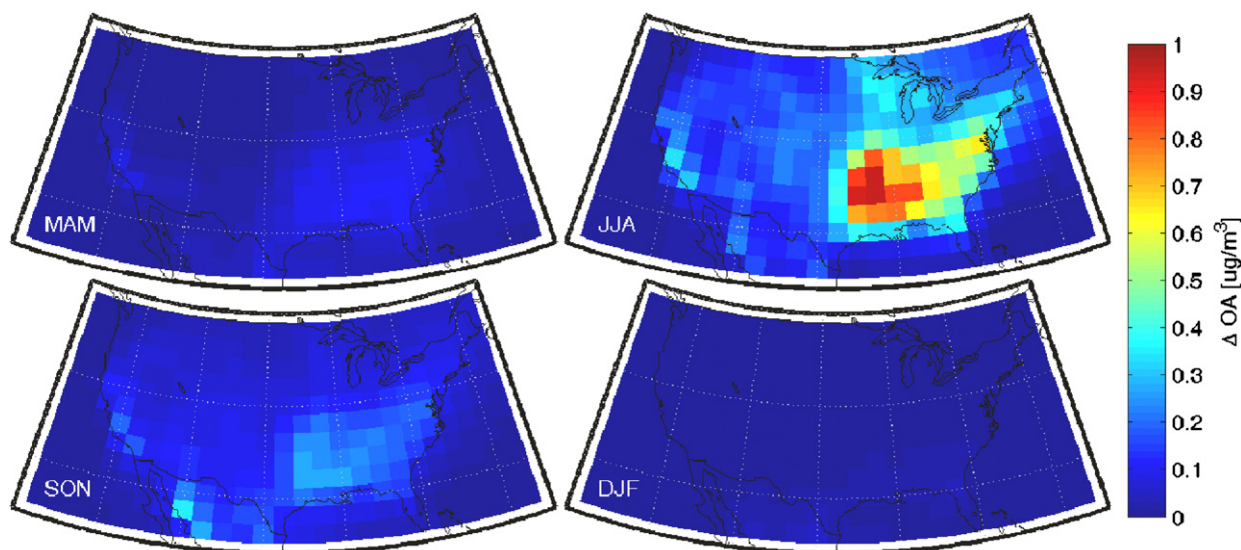
Fig. 3. Seasonal average of the simulated contribution of isoprene oxidation products to OA for a 2.0% yield by mass over February 2001–January 2002.

summer 2001. Radiocarbon measurements by Lemire et al. (2002) found a large biogenic SOA component of OA in southeast Texas, again not captures within the standard simulation.

Given the large uncertainty in the chemical mechanism for SOA production from isoprene oxidation products, we conduct a simple sensitivity study in which isoprene is allowed to directly contribute to SOA production. We adopt a 2.0% yield by mass, within the range of previous studies. Fig. 3 shows the seasonal change in simulated OA concentrations. Simulated OA mass concentrations increase by 0.6–1.0 μg m^{-3} over the southeast United States during summer with a spatial pattern equivalent to isoprene emissions. SOA from isoprene contributes 10–50% of total OA in summer in the United States, with the higher percentages in the Midwest where total OA concentrations are lower. Biogenic SOA in this simulation is within the range of radiocarbon measurements in Nashville (Lewis et al., 2004) and southeast Texas (Lewis et al., 2004). The regional model bias in the standard simulation during summer in the eastern United States (RMSE = 1.26 μg m^{-3}) is reduced to a RMSE of 0.88 μg m^{-3}. Other seasons also show improvement, with the RMSE in spring reduced from 1.11 to 1.04 μg m^{-3} and in fall from 1.24 to 1.11 μg m^{-3}. Negligible SOA is produced from isoprene during winter. A SOA yield of up to 5.0% by mass reduces the average of seasonal RMSE relative to the

standard simulation. This is not meant to suggest that SOA formation from isoprene occurs at such high rates, but does show that this process can be readily accommodated within the current bias in modeled OA concentrations.

OA formation is an active area of ongoing research. Other processes not represented in our simulation likely contribute to the remaining bias between observed and modeled OA. POA derived from cellulose and plant debris could represent a significant source of OA, especially in spring and fall (Puxbaum and Tenze-Kunit, 2003; Womiloju et al., 2003). In-situ airborne measurements in plumes and chamber studies provide evidence that inorganic aerosol may promote SOA formation (Jang and Kamens, 2001; Jang et al., 2002; Brock et al., 2003; Czoschke et al., 2003; Gao et al., 2004) or decrease SOA yields in the case of α-pinene (Crocker et al., 2001). In-cloud oxidation of isoprene through cloud processing could also contribute a SOA yield of up to 0.3% by mass (Lim et al., 2005).

3. Conclusions

We have compared surface measurements of OA mass from the IMPROVE network with simulations in a global three-dimensional model of oxidant-aerosol chemistry (GEOS-Chem) to assess the

implications of SOA formation from isoprene oxidation products.

We found a seasonally varying negative bias of $1.5–3\,\mu g\,m^{-3}$ in simulated versus measured OA in the southeastern United States during spring through fall, and in the western United States during summer and fall. The underestimate in the western United States was readily explained by POA from biomass burning. A regional bias in the southeastern United States, not explained by other recognized model limitations, occurs in an area of intense isoprene production and was the focus of this work.

Recent field and laboratory measurements provided evidence that SOA is formed from isoprene oxidation products. Given the large uncertainty in this particular chemical mechanism, we conducted a simple sensitivity study in which isoprene is allowed to directly contribute to SOA production. We adopted a yield of 2% by mass, within the range of previous studies. This sensitivity study increased simulated SOA mass by $0.6–1\,\mu g\,m^{-3}$ over the southeast United States during summer, reducing the regional RMSE from 1.26 to $0.88\,\mu g\,m^{-3}$. In summary, SOA production from isoprene oxidation products was not only accommodated by current OA simulations, but improved the model simulation versus OA measurements.

Limitations of this work include the simple treatment of SOA production from isoprene oxidation products as well as uncertainty in the model simulation of both POA and SOA. Additional guidance from laboratory and field measurements on the chemical mechanism for SOA formation, and its dependence upon ambient trace gases, would improve the analysis here. Future work should continue developing OA mechanisms to account for other processes, such as cellulose and plant debris, that could explain the remaining underestimate in simulated OA over the southeastern United States.

Acknowledgments

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