

Global modeling of organic aerosol: the importance of reactive nitrogen (NO_x and NO_3)

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Abstract. Reactive nitrogen compounds, specifically NO_x and NO_3 , likely influence global organic aerosol levels. To assess these interactions, GEOS-Chem, a chemical transport model, is updated to include improved biogenic emissions (following MEGAN v2.1/2.04), a new organic aerosol tracer lumping scheme, aerosol from nitrate radical (NO_3) oxidation of isoprene, and NO_x -dependent monoterpene and sesquiterpene aerosol yields. As a result of significant nighttime terpene emissions, fast reaction of monoterpenes with the nitrate radical, and relatively high aerosol yields from NO_3 oxidation, biogenic hydrocarbon- NO_3 reactions are expected to be a major contributor to surface level aerosol concentrations in anthropogenically influenced areas such as the United States. By including aerosol from nitrate radical oxidation in GEOS-Chem, terpene (monoterpene + sesquiterpene) aerosol approximately doubles and isoprene aerosol is enhanced by 30 to 40% in the Southeast United States. In terms of the global budget of organic aerosol, however, aerosol from nitrate radical oxidation is somewhat minor (slightly more than 3 Tg/yr) due to the relatively high volatility of organic- NO_3 oxidation products in the yield parameterization. Globally, 69 to 88 Tg/yr of organic aerosol is predicted to be produced annually, of which 14–15 Tg/yr is from oxidation of monoterpenes and sesquiterpenes and 8–9 Tg/yr from isoprene.

1 Introduction

The aerosol phase is an important intermediate or terminal form for many species in the atmosphere including volatile organic compounds (VOCs) (Goldstein and Galbally, 2007), and understanding aerosol formation is important for assessing the climate change and human health impacts of air pollution. Organic aerosol can result from direct emissions, producing primary organic aerosol (POA), or form in situ from chemical transformation, yielding secondary organic aerosol (SOA). Anthropogenic SOA contributors include light aromatics (aerosol yield about 5 to 40% at an organic aerosol loading of $10 \mu\text{g}/\text{m}^3$, see Table 1) (Ng et al., 2007b), naphthalene (yield about 20 to 70%) (Chan et al., 2009), and alkanes (yields ranging from a few percent to 50%) (Lim and Ziemann, 2005). Low-volatility compounds emitted from sources including diesel combustion and biomass burning also lead to significant amounts of POA and SOA (Robinson et al., 2007). In addition to these hydrocarbons, biogenic compounds such as isoprene (aerosol yield about 4 to 10% depending on oxidant), monoterpenes (yield generally about 10 to 20%), and sesquiterpenes (yield generally higher than 40%) serve as SOA precursors (Hoffmann et al., 1997; Griffin et al., 1999a; Kroll et al., 2006). Chamber studies of these compounds have provided the foundation for organic aerosol parameterizations in global models such as GEOS-Chem (Henze and Seinfeld, 2006; Liao et al., 2007; Henze et al., 2008; Pye and Seinfeld, 2010), NCAR Community Atmospheric Model (CAM3) (Heald et al., 2008), TM3 (Tsigaridis and Kanakidou, 2003), and GISS GCM II-prime (Chung and Seinfeld, 2002).



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A number of issues related to organic aerosol parameterizations remain unresolved. Models often predict organic aerosol levels that are much lower than those observed (Heald et al., 2005; Volkamer et al., 2006; Liao et al., 2007; Pye and Seinfeld, 2010). In addition, organic aerosol even in urban areas tends to contain significant “modern” carbon indicating a biogenic source (Szidat, 2009; Marley et al., 2009; Schichtel et al., 2008) but correlates with anthropogenic tracers (de Gouw et al., 2005; Weber et al., 2007).

Gas-phase VOC-NO_x chemistry represents a potential way for anthropogenic and biogenic systems to interact. NO_x (NO + NO₂) levels have been identified as an important factor in SOA formation from photooxidation and ozonolysis (Presto et al., 2005; Ng et al., 2007a), and both modeling and experimental work indicate that the yield of aerosol is highly sensitive to NO_x, especially for low VOC/NO_x ratios (VOC/NO_x < 1 ppb/ppb) (Ng et al., 2007a; Capouet et al., 2008). Light aromatics (Ng et al., 2007b), polycyclic aromatic hydrocarbons (Chan et al., 2009), and monoterpenes (Presto et al., 2005) are expected to have lower yields under high-NO_x conditions (VOC/NO_x < 0.1 ppb/ppb), in which the peroxy radical from the initial oxidation of the parent hydrocarbon reacts preferentially with NO instead of HO₂. Ng et al. (2007a) examined the monoterpene, α -pinene, and the sesquiterpenes, longifolene and aromdendrene, and found that sesquiterpenes generally exhibit higher yields under high-NO_x conditions as a result of a higher probability of isomerization for RO₂ + NO alkoxy radicals or higher yields of less volatile organic nitrates. For isoprene, yields under high-NO_x conditions are typically lower than under-low NO_x conditions (Kroll et al., 2005, 2006). But, recent work indicates that high-NO_x isoprene oxidation can be just as effective as low-NO_x oxidation in producing SOA (Surratt et al., 2010; Chan et al., 2010). During the night, NO_x emissions in the form of NO₂ can react with O₃ to produce nitrate radicals (NO₃). Monoterpenes have a very short lifetime against reaction with NO₃ (Fry et al., 2009), and the yield of aerosol from reaction with NO₃ is generally higher than the yield from photooxidation (Griffin et al., 1999a; Ng et al., 2008).

In this work, updated biogenic emissions are incorporated with a new lumping scheme to simulate organic aerosol in the global chemical transport model GEOS-Chem. Possible interactions between anthropogenic and biogenic emissions, in terms of SOA formation, are investigated for the United States. New processes represented in GEOS-Chem include aerosol from nitrate radical oxidation of isoprene and NO_x-dependent terpene (monoterpene and sesquiterpene) aerosol yields. Section 2 describes the updated emissions and SOA parameterization. The Results section is devoted to examining the global organic aerosol (OA) budget and surface concentrations over the US.

2 Model description

2.1 Global model

Present-day (year 2000) organic aerosol is simulated in the global chemical transport model, GEOS-Chem (version 8-01-04, <http://acmg.seas.harvard.edu/geos/>). Simulations are performed at 2° latitude by 2.5° longitude horizontal resolution using GEOS-4 assimilated meteorology with 30 vertical layers up to 0.01 hPa. Simulations include fully-coupled ozone-NO_x-hydrocarbon chemistry (Bey et al., 2001). Updates to GEOS-Chem version 8-01-04 are discussed in the later sections.

A GEOS-Chem simulation using nonvolatile POA was found to have a mean bias of $-0.56 \mu\text{g}/\text{m}^3$ or -34% compared to the Interagency Monitoring of Protected Visual Environments (IMPROVE) observations over the United States (Liao et al., 2007). The bias tends to become even larger when semivolatile POA is implemented (Pye and Seinfeld, 2010). As a result, two types of simulations are performed in this work: a “traditional” POA simulation and a semivolatile POA simulation. The nonvolatile (traditional) POA simulation, which uses nonvolatile POA and does not consider SOA from intermediate volatility compounds, is used for some sensitivity simulations to compensate for the fact that the semivolatile POA model predicts aerosol levels that are too low. The traditional GEOS-Chem simulation has also been extensively compared to observations in the work of Park et al. (2003, 2006), Heald et al. (2005), and Liao et al. (2007). The semivolatile POA simulation (Pye and Seinfeld, 2010) replaces nonvolatile POA with a pool of primary semivolatile organic compounds (SVOCs) that immediately partition between the gas and aerosol phases as well as react in the gas phase. The semivolatile POA simulation also includes intermediate volatility organic compounds (IVOCs, saturation concentration about $10^5 \mu\text{g}/\text{m}^3$) which are emitted entirely in the gas phase but are assumed to behave like naphthalene in terms of SOA yields (Pye and Seinfeld, 2010).

Semivolatile organic species are removed from the atmosphere by wet and dry deposition as in previous work (Chung and Seinfeld, 2002; Pye and Seinfeld, 2010). Dry deposition follows a resistance in series method (Wesely, 1989; Zhang et al., 2001), and gas-phase secondary organic species are assumed to be hydrophilic with a Henry’s Law coefficient of $10^5 \text{ M}/\text{atm}$ (Chung and Seinfeld, 2002). Primary organic aerosol is treated as hydrophobic in the semivolatile POA simulation or emitted as half hydrophobic and half hydrophilic in the nonvolatile POA simulation.

2.2 Emissions

SOA precursor emissions include biogenic hydrocarbons, benzene, toluene, xylene, intermediate volatility compounds, and semivolatile organic compounds or primary organic aerosol. The light aromatic, IVOC, and POA/SVOC

Table 1. SOA Yield Parameterizations at 298 K.

Parent HC	Oxidant	α for C* (C* in $\mu\text{g}/\text{m}^3$)					RMSE ^a [$\mu\text{g}/\mu\text{g}$]	Yield at 10 $\mu\text{g}/\text{m}^3$	Data
		nonvolatile	0.1	1	10	100			
Monoterpenes and sesquiterpenes									
LIMO	OH, O ₃ ; NO	0	0	0.474	0.117	1.419	0.145	0.62	dark high-NO _x limonene ozonolysis (Zhang et al., 2006), refit using a density of 1.3 g/cm ³
MTPA/O	OH, O ₃ ; NO	0	0.04	0.0095	0.09	0.015	NA	0.09	based on low-NO _x fit, adjusted for NO _x based on Ng et al. (2007a) and Pathak et al. (2007)
SESQ	OH, O ₃ ; NO	0	0	0.000	1.146	2.981	NA	0.84	based on low-NO _x fit, adjusted for NO _x based on Ng et al. (2007a)
LIMO	OH, O ₃ ; HO ₂	0	0	0.366	0.321	0.817	0.068	0.57	dark low-NO _x limonene ozonolysis (Zhang et al., 2006), refit using a density of 1.3 g/cm ³
MTPA/O	OH, O ₃ ; HO ₂	0	0.08	0.019	0.18	0.03	0.016	0.19	dark α -pinene ozonolysis (Shilling et al., 2008), not wall loss corrected
SESQ	OH, O ₃ ; HO ₂	0	0	0.000	0.574	1.489	0.037	0.42	β -caryophyllene and α -humulene [VOC/NO _x] > 3ppbC/ppb (Griffin et al., 1999a), fit using a density of 1.3 g/cm ³
all terpenes	NO ₃	0	0	0.000	0.321	1.083	0.057	0.26	β -pinene+NO ₃ (Griffin et al., 1999a), fit using a density of 1.3 g/cm ³
Isoprene									
ISOP	NO ₃	0	0	0.000	0.217	0.092	0.023	0.12	Ng et al. (2008)
ISOP	OH	0	0	0.031	0.000	0.095	0.003	0.04	low-NO _x photooxidation (Kroll et al., 2006)
Aromatics									
BENZ	OH; NO	0	0	0.078	0.000	0.793	0.005	0.14	benzene high-NO _x photooxidation (Ng et al., 2007b)
TOLU	OH; NO	0	0	0.032	0.094	0.080	0.001	0.08	toluene high-NO _x photooxidation (Ng et al., 2007b)
XYLE	OH; NO	0	0	0.025	0.036	0.090	0.002	0.05	xylene high-NO _x photooxidation (Ng et al., 2007b)
BENZ	OH; HO ₂	0.37	0	0	0	0	NA	0.37	benzene low-NO _x photooxidation (Ng et al., 2007b)
TOLU	OH; HO ₂	0.36	0	0	0	0	NA	0.36	toluene low-NO _x photooxidation (Ng et al., 2007b)
XYLE	OH; HO ₂	0.30	0	0	0	0	NA	0.30	xylene low-NO _x photooxidation (Ng et al., 2007b)
IVOCs									
NAP	OH; NO	0	0	0.039	0.296	0.235	0.036	0.20	naphthalene high-NO _x photooxidation (Chan et al., 2009)
NAP	OH; HO ₂	0.73	0	0	0	0	NA	0.73	naphthalene low-NO _x photooxidation (Chan et al., 2009)

^a Root mean square error of the fit in mass of SOA per mass of parent hydrocarbon reacted. See Supplement for plots of the raw data.

emissions are the same as in previous work (Henze et al., 2008; Pye and Seinfeld, 2010). Briefly, benzene, toluene, and xylene are emitted from biomass burning, biofuel burning, and other anthropogenic sources based on their emission ratios relative to CO (for biomass and biofuel burning) and emissions described by the Emission Database for Global Atmospheric Research (EDGAR V2.0). IVOCs are spatially distributed like naphthalene from biomass burning, biofuel burning, and other anthropogenic sources and scaled up to represent all intermediate volatility organic compounds as described by Pye and Seinfeld (2010). The traditional POA emission inventory is described by Park et al. (2003, 2006) and is used as a surrogate for SVOC emissions. When POA is treated as semivolatile (i.e. POA is replaced by SVOCs), the traditional POA inventory is scaled up 27% (Schauer et al., 2001; Pye and Seinfeld, 2010) to account for SVOCs that are emitted entirely in the gas-phase.

Biogenic emissions of isoprene and seven major monoterpenes (α -pinene, β -pinene, limonene, myrcene, sabinene, Δ 3-carene and ocimene), are updated to follow the Model of Emissions of Gases and Aerosols from Nature (MEGAN) v2.1 (Guenther et al., 2006) as implemented in GEOS-Chem

version 8-02-04. Other monoterpene and sesquiterpene (farnesene, β -caryophyllene, and other sesquiterpenes) emissions are added based on MEGAN v2.1 plant functional types and MEGAN v2.04 emission factors and parameters. Emissions are modeled as a species specific emission rate at standard conditions (ϵ) and corrected using emission activity factors for leaf age (γ_{Age}), temperature (γ_T), leaf area index (γ_{LAI}), and light (γ_P) (Guenther et al., 2006; Sakulyanontvittaya et al., 2008):

$$E = \epsilon \gamma_{\text{Age}} \gamma_T \gamma_{\text{LAI}} [\gamma_P \text{LDF} + (1 - \text{LDF})] \quad (1)$$

Included in the emissions updates (standard in GEOS-Chem version 8-02-04) are the use of monthly MODIS data instead of the AVHRR product for the leaf area index used to calculate γ_{Age} and γ_{LAI} . The temperature adjustment (γ_T) is computed as a function both of the current temperature and the average temperature over the previous 10 days for isoprene (Guenther et al., 2006). For monoterpenes and sesquiterpenes, γ_T is computed as an exponential function of current temperature (Sakulyanontvittaya et al., 2008). Unlike isoprene emissions which are 100% light-dependent, only a fraction of the monoterpene and sesquiterpene

emissions are light-dependent. The light-dependence fraction (LDF) is around 5 to 10% for most monoterpenes (except ocimene) and 50% for sesquiterpenes (Sakulyanontvitaya et al., 2008). The light activity factor (γ_P) uses the parameterized canopy environment emission activity (PCEEA) algorithm of Guenther et al. (2006). The effects of soil moisture and production or loss within the canopy are ignored.

Emissions of monoterpenes are grouped into three tracers: MTPA, LIMO, and MTPO (Fig. 1). MTPA (α -pinene and similar monoterpenes) consists of the bicyclic monoterpenes α -pinene, β -pinene, sabinene, and Δ^3 -carene. Limonene (LIMO) is not lumped with any other species since its aerosol yields tend to be much higher than other monoterpenes. MTPO (other monoterpenes) consists of myrcene, ocimene, terpinene, terpinolene, and other terpenoid compounds such as alcohols and ketones. MTPO is the equivalent of the MEGAN myrcene, ocimene, and other monoterpene categories.

2.3 SOA parameterization

The yield of aerosol from a given hydrocarbon/oxidant pair can be parameterized using a volatility basis set (VBS) (Donahue et al., 2006) or an Odum 2-product approach (Odum et al., 1996). Both methods adequately describe most chamber conditions because of the limited range of organic loadings examined (on the order of one to several hundred $\mu\text{g}/\text{m}^3$). The Odum model is computationally advantageous since it requires only two (or one) surrogate species per parent hydrocarbon. However, lumping multiple parent hydrocarbon systems together requires approximation (Bian and Bowman, 2002). The VBS requires more semivolatile surrogates (generally four) (Pathak et al., 2007; Lane et al., 2008b) per parent hydrocarbon/oxidant system, but combining different systems is more straightforward.

The organic aerosols in this work are lumped into five aerosol systems based on the parent hydrocarbons treated: terpenes (monoterpenes + sesquiterpenes), isoprene, light aromatics and IVOCs, primary SVOCs, and oxidized SVOCs (Fig. 1). Each aerosol system is represented with either a unique VBS (for systems with multiple parent hydrocarbons and/or multiple aerosol forming pathways) or Odum 2-product fit (for systems in which there is essentially one parent hydrocarbon). The lumping was chosen to maximize the amount of parent hydrocarbon information while maintaining a limited number of tracers. The terpene system (TSOA/G) includes semivolatile aerosol formed from photooxidation, ozonolysis, and nitrate radical oxidation of monoterpenes and sesquiterpenes. The isoprene system (ISOA/G) contains semivolatile aerosol from photooxidation and nitrate radical oxidation. The photooxidation aerosol from light aromatics and the naphthalene-like IVOC surrogate (ASOA/G) are lumped together since they have similar behavior under high and low- NO_x conditions. SVOCs are emitted as two semivolatile species (POA/G1-2)

in roughly equal amounts based on an Odum 2-product fit to wood burning emissions (Shrivastava et al., 2006), and each of the primary SVOCs can oxidize in the gas phase to form lower volatility species (OPOA/G) (Pye and Seinfeld, 2010). The aerosol treatment with semivolatile POA requires 14 semivolatile gas-phase species, 14 semivolatile aerosol-phase species, 1 nonvolatile species, and 7 gas-phase precursors (excluding isoprene) for a total of 36 tracers (indicated by red outlined boxes in Fig. 1) in addition to the standard gas-phase simulation tracers. Except for isoprene and light aromatics, which are a part of the gas-phase chemical mechanism, SOA precursor oxidation is performed offline (see Sect. 4.2 for more information). The partitioning equations are the same as those in the work of Chung and Seinfeld (2002).

2.3.1 Aerosol yields

Table 1 shows the VBS fits for the aerosol forming pathways. Following the work of Stanier et al. (2008), mass-based stoichiometric coefficients, α , for each parent hydrocarbon/oxidant system are obtained by minimizing the difference between modeled and observed yields. Most systems are fit with a VBS using saturation concentrations, C^* , of 1, 10, and 100 $\mu\text{g}/\text{m}^3$ at 298 K. If yields are not available at the reference temperature, an enthalpy of vaporization of 42 kJ/mol is used in the fitting procedure to adjust C^* (Chung and Seinfeld, 2002). The same enthalpy is also used for temperature adjustments online in GEOS-Chem. Figures showing the fits and data on which they were based is available as a Supplement.

The terpene aerosol parameterization in GEOS-Chem, based on the work of Chung and Seinfeld (2002), is updated to reflect NO_x -dependent yields, a more realistic aerosol density, and new experimental results. The behavior of the lumped monoterpenes, MTPA and MTPO, under low- NO_x conditions, is modeled based on the dark α -pinene ozonolysis fit by Shilling et al. (2008). Shilling et al. (2008) were able to obtain very low organic aerosol loading (less than 1 $\mu\text{g}/\text{m}^3$) and thus the saturation concentration of 0.1 $\mu\text{g}/\text{m}^3$ is included in the fit. Using α -pinene ozonolysis yields for all photooxidation and ozonolysis conditions for MTPO and MTPA is an approximation. This yield might overestimate the amount of aerosol formed since photooxidation pathways often have a lower yield than ozonolysis pathways (Griffin et al., 1999a), α -pinene has one of the highest ozonolysis aerosol yields of the bicyclic monoterpenes (Griffin et al., 1999a), and UV light should suppress SOA (Pathak et al., 2007). However, the Shilling et al. (2008) parameterization may underestimate yields since not all monoterpenes behave like α -pinene; for example, monoterpenes with two double bonds (like terpinene and to a certain extent myrcene) appear to have higher aerosol yields than those with one double bond under photooxidation (Griffin et al., 1999a). In addition, species like β -pinene and sabinene have higher yields under photooxidation

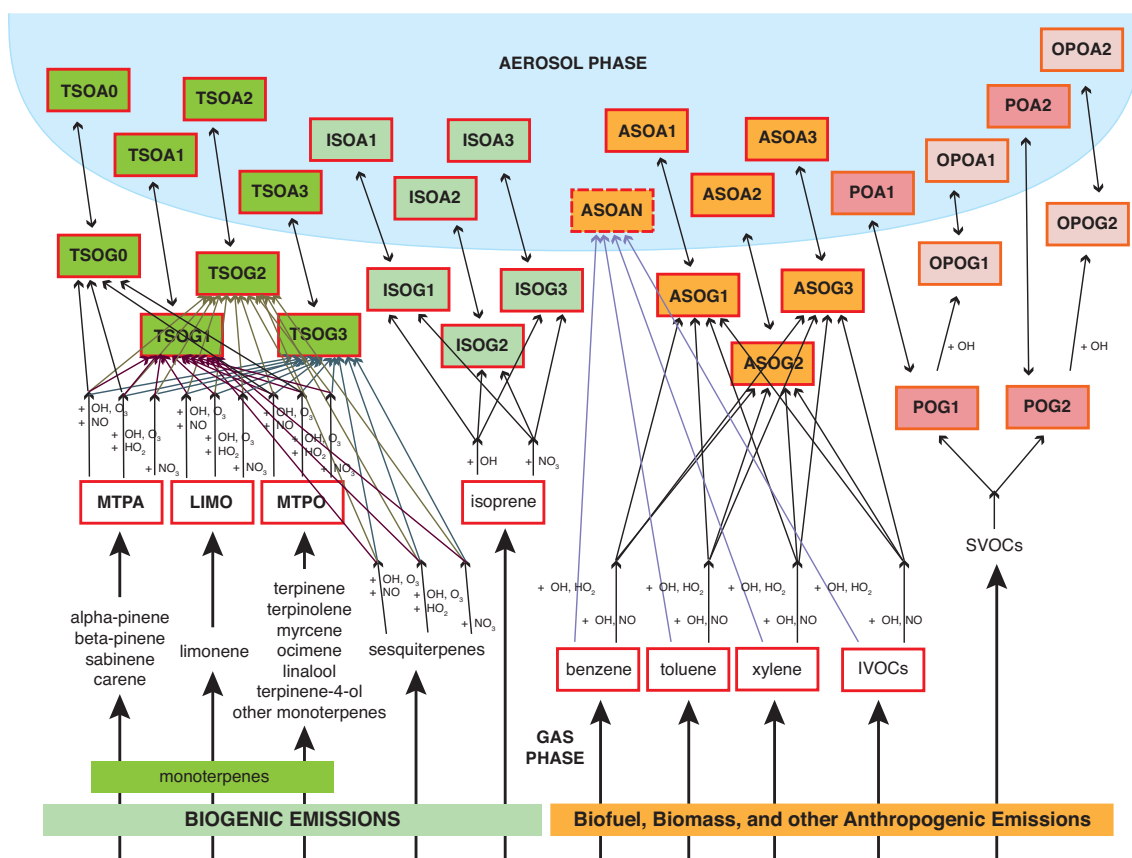


Fig. 1. Schematic of SOA model. Species appearing in boxes are tracers. A bidirectional arrow across the aerosol/gas interface indicates a semivolatile species. ASOAN is nonvolatile. SOA/G0-3 species have saturation concentrations of 0.1, 1, 10, 100 $\mu\text{g}/\text{m}^3$. SVOCs are represented using an Odum 2-product fit. Yield parameters are shown in Table 1. For a traditional simulation, IVOCs are not emitted and nonvolatile POA replaces the SVOCs.

than ozonolysis (Griffin et al., 1999a), and investigations by Ng et al. (2007a) indicate that if NO_x is absent (or extremely low), α -pinene photooxidation can produce very high yields. The yield may also be underestimated since the fit from Shilling et al. (2008) was not corrected for wall loss, and as a result, the authors estimate the yields could be 30 to 60% higher than those captured by the fit. The MTPA/MTPO fit for high- NO_x photooxidation and ozonolysis is obtained by reducing the low- NO_x yield, and thus α , by 50% for a given loading based on work by Ng et al. (2007a) and Pathak et al. (2007). The yield of aerosol from limonene under high and low- NO_x conditions is based on data from Zhang et al. (2006) using a density of $1.3 \text{ g}/\text{cm}^3$ (Ng et al., 2007a). The Zhang et al. (2006) experiments show a very mild dependence on NO_x level with slightly higher yields under high- NO_x conditions at low loadings. The sesquiterpene yields are based on the same underlying data as previous GEOS-Chem simulations; the yield data for β -caryophyllene and α -humulene from Griffin et al. (1999a) with a $[\text{VOC}]/[\text{NO}_x]$ ratio greater than 3 ppbC/ppb are used to obtain a low- NO_x fit. The high- NO_x yield curve is obtained by doubling the

yield for a given loading based on Ng et al. (2007a). All terpene (monoterpene and sesquiterpene) aerosol from the nitrate oxidation pathway is represented based on β -pinene experiments by Griffin et al. (1999a). Aerosol from the isoprene + NO_3 pathway is added to GEOS-Chem based on experiments by Ng et al. (2008).

SOA from photooxidation of isoprene (Henze and Seinfeld, 2006), light aromatics (Henze et al., 2008), and a naphthalene-like IVOC (Pye and Seinfeld, 2010) is essentially the same as previous work. The underlying data from previous GEOS-Chem aerosol studies for isoprene, light aromatics, and IVOCs are refit to a VBS with saturation concentrations of 1, 10, and 100 $\mu\text{g}/\text{m}^3$. Although high- NO_x conditions have traditionally been thought to suppress isoprene aerosol (Carlton et al., 2009), recent work shows high- NO_x isoprene aerosol yields can be similar to the low- NO_x yields at atmospherically relevant NO_2/NO ratios (Chan et al., 2010). As in previous versions of GEOS-Chem, isoprene photooxidation aerosol follows low- NO_x behavior based on Kroll et al. (2006) regardless of the NO_x level (Henze and Seinfeld, 2006).

Primary SVOCs from biomass burning, biofuel burning, and other anthropogenic sources are represented using an Odum 2-product fit based on the work of Shrivastava et al. (2006), as implemented by Pye and Seinfeld (2010). SVOCs are emitted as two species with saturation concentrations of 1600 and 20 $\mu\text{g}/\text{m}^3$ at 300 K. As the gas-phase SVOCs react with OH, the volatility of the reaction products decreases by a factor of 100 to form oxidized SVOCs (Grieshop et al., 2009). The oxidized SVOCs remain semivolatile but more efficiently partition to the aerosol phase than the primary SVOC emissions. More information about the SVOC and IVOC simulation can be found in the work of Pye and Seinfeld (2010).

2.3.2 Implementation of NO_x -dependent yields

The difference in yield between high- and low- NO_x conditions for photooxidation and ozonolysis is assumed to result from competition between the NO and HO_2 reactions of the peroxy radical (Presto et al., 2005). Following the approach used in GEOS-Chem for light aromatics and intermediate volatility compounds (Henze et al., 2008; Pye and Seinfeld, 2010), the amount of parent hydrocarbon reaction through each pathway is calculated. The amount of hydrocarbon reacting through the high- NO_x , $\text{RO}_2 + \text{NO}$ pathway, ($\Delta\text{HC}_{\text{NO},i,j}$) is computed as:

$$\Delta\text{HC}_{\text{NO},i,j} = \beta \Delta\text{HC}_{i,j} \quad (2)$$

where β is the fraction of peroxy radicals reacting with NO and ΔHC is the amount of parent hydrocarbon i reacted with oxidant j . The amount of hydrocarbon reacting through the low- NO_x , $\text{RO}_2 + \text{HO}_2$ pathway, ($\Delta\text{HC}_{\text{HO}_2,i,j}$) is computed as:

$$\Delta\text{HC}_{\text{HO}_2,i,j} = (1 - \beta) \Delta\text{HC}_{i,j} \quad (3)$$

Equations (2) and (3) assume $\text{RO}_2 + \text{RO}_2$ reactions are negligible in the atmosphere and reaction of the parent hydrocarbon with OH or ozone is the rate-limiting step for aerosol formation. The branching ratio, β , is computed from:

$$\beta = \frac{k_{\text{RO}_2+\text{NO}}[\text{NO}]}{k_{\text{RO}_2+\text{NO}}[\text{NO}] + k_{\text{RO}_2+\text{HO}_2}[\text{HO}_2]} \quad (4)$$

where $k_{\text{RO}_2+\text{NO}}$ and $k_{\text{RO}_2+\text{HO}_2}$ are the rate constants for reaction of the peroxy radical with NO and HO_2 , respectively. Due to limited information about reaction rates, all peroxy radicals resulting in SOA are assumed to have the same $\text{RO}_2 + \text{NO}$ and $\text{RO}_2 + \text{HO}_2$ rate constants (Henze et al., 2008).

3 Results and discussion

3.1 Emissions

Table 2 shows the global, annually averaged emission rates of POA and SOA precursors. Compared to standard GEOS-

Table 2. SOA precursor emissions. Emissions are for year 2000 using GEOS-4 assimilated meteorology at 2° latitude by 2.5° longitude horizontal resolution.

Species	Global Emissions [Tg C/yr]
α -pinene	34
β -pinene	16
sabinene	8
Δ 3-carene	6
limonene	9
myrcene	3
ocimene	14
other monoterpenes	12
sesquiterpenes	12
isoprene	449
benzene	5
toluene	7
xylene	5
IVOCs ^a	15
traditional POA ^a	29
SVOCs ^a	37

^a Either POA is emitted as non-volatile at the rate specified (for traditional, non-volatile POA simulations) or IVOCs and SVOCs are emitted at the rates specified (for a semivolatile POA simulation). For more information on the IVOC and SVOC emissions, see Pye and Seinfeld (2010).

Chem version 8-01-04 (which uses MEGAN v2.0 and Griffin et al. (1999b) speciation), the bicyclic monoterpene (α -pinene, β -pinene, sabinene, and Δ 3-carene) emission rate is relatively unchanged. Ocimene emissions, however, are about a factor of 6 higher than previously estimated, and limonene emissions are about 60% lower. Global sesquiterpene emissions differ by less than 10% different from previous estimates based on the other reactive volatile organic compound (ORVOC) inventory of Guenther et al. (1995) and the speciation of Griffin et al. (1999b). Isoprene emissions are about 14% larger than MEGAN v2.0 as implemented in GEOS-Chem. One of the largest differences between previous GEOS-Chem studies (e.g. Henze and Seinfeld, 2006 or Pye and Seinfeld, 2010) and this work is the significantly reduced terpenoid ketone and terpenoid alcohol emissions. All relevant terpenoid ketone and alcohol emissions (previously estimated at 43 Tg/yr) are assumed to be a subset of the MEGANv2.04 other monoterpene category which is predicted to have emissions of about 14 Tg/yr. The net result is that global monoterpene + sesquiterpene emissions are about 20% lower than previous model estimates. Regional differences may be much higher, and the diurnal variation is often significantly different (for example: sesquiterpenes were treated as 100% light dependent in previous work, but now are only 50% light dependent).

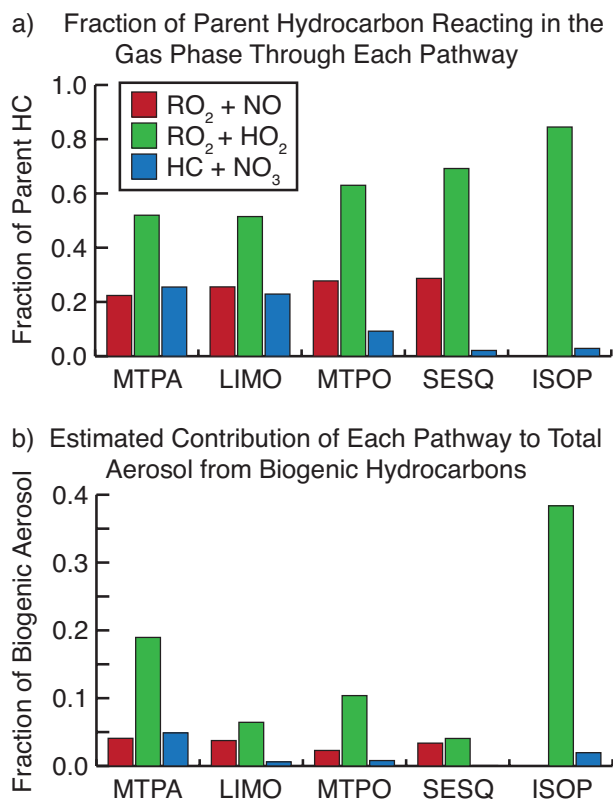


Fig. 2. Fraction of parent hydrocarbon reacting through each SOA-forming pathway globally and annually averaged (a). All isoprene photooxidation is labeled as low- NO_x ($\text{RO}_2 + \text{HO}_2$) since the aerosol yields are representative of those conditions. Isoprene (ISOP) reaction with ozone is not shown since it does not produce aerosol. Panel (b) shows the estimated contribution of each parent hydrocarbon-oxidant pathway to total biogenic aerosol globally and annually averaged. Panel (b) is estimated using the aerosol yield for each system at an organic loading of $1.5 \mu\text{g}/\text{m}^3$.

3.2 Global budget

Figure 2a shows the fraction of each lumped parent hydrocarbon reacting under high- NO_x ($\text{RO}_2 + \text{NO}$), low- NO_x ($\text{RO}_2 + \text{HO}_2$), and nitrate radical oxidation pathways. All pathways sum to one for each parent hydrocarbon except for isoprene which also reacts with ozone but does not produce aerosol from that pathway. All isoprene photooxidation is shown as “low NO_x ” since the aerosol yield is representative of those conditions. About 22, 52, and 26% of the lumped bicyclic monoterpenes, MTPA, react under high- NO_x , low- NO_x , and nitrate radical conditions, respectively. The rate constant for MTPO ozonolysis is slightly higher than the MTPA ozonolysis rate constant and consequently, the nitrate oxidation is less important, but still significant, for MTPO. In contrast, only 2% of the sesquiterpenes (SESQ), with their much stronger dependence on light and temperature for emission and relatively fast reaction with ozone, re-

act with the nitrate radical. Isoprene is emitted only during the daytime, and less than 3% is predicted to react with the nitrate radical. Note that for all monoterpenes and sesquiterpenes, the low- NO_x pathway is globally dominant, reflecting where biogenic compounds are emitted and the branching ratio, β , in those locations (Fig. 3).

The bottom of Fig. 2 shows the predicted contribution of each reaction pathway to net biogenic aerosol production (all pathways shown sum to one). These global values were calculated using the aerosol yield at an organic loading of $1.5 \mu\text{g}/\text{m}^3$ which was found to approximately reproduce the lumped global net aerosol production rate in GEOS-Chem which considers the partitioning of all individual semivolatile species based on their yields and saturation concentrations. The loading of $1.5 \mu\text{g}/\text{m}^3$ is thus a fitted value used for illustration purposes since all monoterpene and sesquiterpene aerosol is lumped by volatility instead of parent hydrocarbon, and aerosol yields are regionally variable as a result of the semivolatile nature of most SOA. On a global, annually averaged basis, isoprene photooxidation is the largest single parent hydrocarbon-oxidant contributor to biogenic organic aerosol. The second largest source of biogenic OA is low- NO_x oxidation of monoterpenes. For the lumped monoterpenes, MTPA and MTPO, the low- NO_x pathway is even more important relative to the high- NO_x pathways in terms of net aerosol production than would be estimated based on gas-phase oxidation since the low- NO_x yield is about double the yield under high- NO_x conditions. For limonene, the high- NO_x pathway becomes relatively more important for aerosol production. For sesquiterpenes, a similar amount of net aerosol production is predicted to result from the high and low- NO_x pathways since the aerosol yield is about double under high- NO_x conditions compared to low- NO_x conditions. For all monoterpenes and sesquiterpenes, the nitrate radical reaction contributes less to global net aerosol production than it contributes to gas-phase oxidation. Since very little isoprene reacts with nitrate, the majority of the isoprene aerosol comes from the photooxidation path, even though the yield of aerosol from the nitrate radical path can be substantially higher. A discussion on possible model biases is presented in Sect. 4.

Table 3 shows the predicted net production of SOA for year 2000. Despite the fact that the simulated monoterpene emissions have decreased substantially (about 20% globally) since the work of Pye and Seinfeld (2010), the amount of SOA predicted to form from terpenes has increased to 14–15 Tg/yr and isoprene SOA has decreased slightly to 8–9 Tg/yr. A traditional simulation in the work of Pye and Seinfeld (2010) (year 2000, GEOS-Chem v8-01-04, 2° by 2.5° horizontal resolution), predicted 10 Tg/yr of monoterpene + sesquiterpene SOA and 12 Tg/yr of isoprene SOA. Previous work by Henze et al. (2008) (year 2004, GEOS-Chem v7-04-11, 2° by 2.5° horizontal resolution), predicted 12 and 14 Tg/yr and work by Farina et al. (2010) (year 1980, Unified GISS-II', 4° by 5° horizontal resolution) predicted

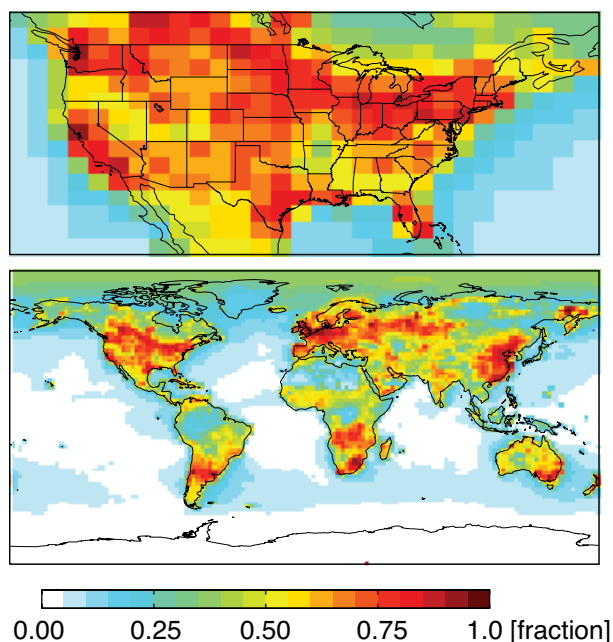


Fig. 3. Fraction of peroxy radical species reacting with NO, β , averaged for the month of August 2000 at the surface (model level 1) for the United States and globally.

21 and 6 Tg/yr from terpenes and isoprene, respectively. Increased terpene SOA production in the present work compared to Pye and Seinfeld (2010) is a result of higher aerosol yields from monoterpene and sesquiterpene oxidation. At low loadings (about $1 \mu\text{g}/\text{m}^3$), the yield of aerosol from low- NO_x monoterpene (MTPA/O) oxidation is about $5\times$ the yield using older parameterizations (Griffin et al., 1999a; Chung and Seinfeld, 2002). The high- NO_x sesquiterpene yield implemented in this work also results in significantly more aerosol from sesquiterpenes. Limonene yields (Zhang et al., 2006) at low loadings are about a factor of 10 higher than previous work using data from Griffin et al. (1999a), however limonene emissions are substantially lower. The nitrate radical oxidation yield is also slightly higher as a result of the density correction. At higher organic aerosol loadings, like those typical of summertime conditions in the southeast US (about $10 \mu\text{g}/\text{m}^3$), yields are generally higher than in previous work, but generally no more than about double (except for limonene). The yield of aerosol from isoprene photooxidation is within 10% of that using the Odum 2-product fit of Henze and Seinfeld (2006) at low loadings since it is based on the same underlying data (Kroll et al., 2006). The addition of isoprene from the NO_3 pathway contributes a small amount of aerosol since relatively little of the parent hydrocarbon reacts through that pathway. Changes in the estimated aerosol production rate from isoprene compared to previous work (Henze and Seinfeld, 2006; Henze et al., 2008; Pye and Seinfeld, 2010) are likely due to differences in the emissions and an improved tracer lumping scheme.

Table 3. Global net production of SOA (GEOS-Chem 2° latitude by 2.5° longitude horizontal resolution with GEOS-4 meteorology).

Precursor	Traditional Simulation [Tg/yr]	Semivolatile POA and IVOCs [Tg/yr]
Terpenes	15.1	13.7
Isoprene	8.6	7.9
Aromatics+IVOCs	3.2	8.5
SVOCs	61.2 ^a	0.7
Oxidized SVOCs	0.0	38.5
Total OA	88.2	69.3

^a POA emission rate in a traditional simulation with nonvolatile POA using an OM/OC ratio of 2.1.

The preceding discussion focused on the global net aerosol production which is the sum of production and evaporation. Figure 4 shows the fraction of mass that partitions to the aerosol phase but later evaporates. Mass partitions to the aerosol phase in locations with high loadings (such as anthropogenic source regions) or low temperatures and evaporates when loadings becomes lower (such as in outflow regions) or temperatures increase (for example due to diurnal temperature variation). For the terpene SOA species with a saturation concentration of $0.1 \mu\text{g}/\text{m}^3$, about 24% of the mass that partitions to the aerosol phase eventually evaporates. For a species with a C^* of $10 \mu\text{g}/\text{m}^3$, about 80% eventually evaporates. The fit in Fig. 4 was obtained by modeling the fraction evaporated (F_E) for a species emitted in a location with an initial loading of $M_{o,i}$ and transported to an area with a loading of $M_{o,f}$:

$$F_E = 1 - \frac{1 + C^*/M_{o,i}}{1 + C^*/M_{o,f}} \quad (5)$$

Equation (5) neglects losses in the gas or aerosol phases which leads to some of the discrepancy between the fitted curve and data. The fitted $M_{o,i}$ and $M_{o,f}$ were determined to be 2.56 and $0.33 \mu\text{g}/\text{m}^3$. Transfer of mass between the gas and aerosol phases is driven by deviations from equilibrium. The semivolatile organic species are always assumed to be at equilibrium during the partitioning routine. Deviations from equilibrium occur as species are dry deposited, wet deposited, and gas-phase chemical reactions produce more (or less) of the semivolatile species. For all secondary semivolatiles, the only gas-phase removal process is dry and wet deposition. For the primary semivolatiles, reaction in the gas-phase to produce lower volatility species is an additional removal process that will tend to force primary semivolatiles out of the particle phase. Since secondary semivolatiles do not experience this same loss process, the primary semivolatiles were not included in the secondary semivolatile fit of Fig. 4.

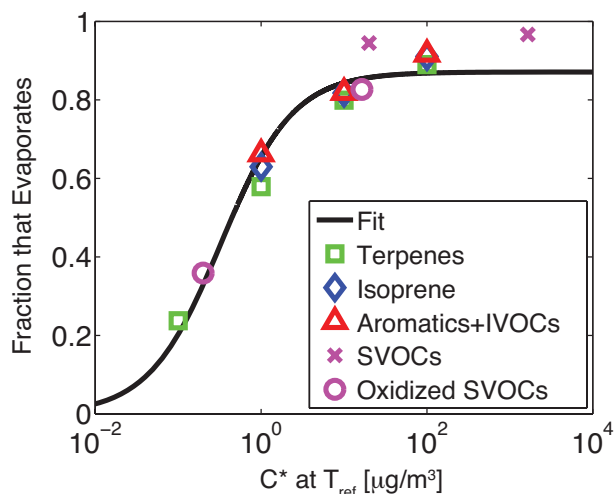


Fig. 4. Fraction of semivolatile mass that partitions to the aerosol phase but later evaporates globally and annually averaged as a function of saturation concentration at the reference temperature. The fit corresponds to a semivolatile that is emitted in region with a loading of $2.6 \mu\text{g}/\text{m}^3$ and travels to a region with a loading of $0.3 \mu\text{g}/\text{m}^3$ without any losses. T_{ref} is 298 K for all semivolatile species except primary SVOCs and oxidized SVOCs which use 300 K.

3.3 Surface level aerosol over the United States

The global budget is heavily influenced by remote areas where biogenic emissions are high and NO levels are low (e.g. the Amazon basin). Biogenic hydrocarbons may behave differently when emitted in a location with significant anthropogenic emissions. In this section, the United States is used as a case study for aerosol formation in an anthropogenically influenced area.

3.3.1 Fate of the peroxy radical

NO_x levels influence the yield of aerosol through the rate of peroxy radical reaction with either NO or HO_2 . Over the US, the $\text{RO}_2 + \text{NO}$ reaction usually dominates over the $\text{RO}_2 + \text{HO}_2$ reaction, particularly in the Northeast (Fig. 3) and during the winter when HO_x levels are lower (Henze et al., 2008). Even in the summer in the Southeast, more than 50% of the RO_2 is predicted to react with NO (Fig. 3). The effect of NO_x on light aromatic and IVOC SOA in a global model has been investigated previously (Henze et al., 2008; Pye and Seinfeld, 2010).

Figure 5 shows the predicted surface level organic aerosol from terpenes, isoprene, aromatics, and nonvolatile POA (a traditional simulation) during August 2000. High loadings occur in areas such as Idaho as a result of biomass burning. The second panel shows the fraction of that organic aerosol from oxidation of a biogenic parent hydrocarbon (monoterpene, sesquiterpene, or isoprene). Compared to a semivolatile POA simulation in which a large fraction of the

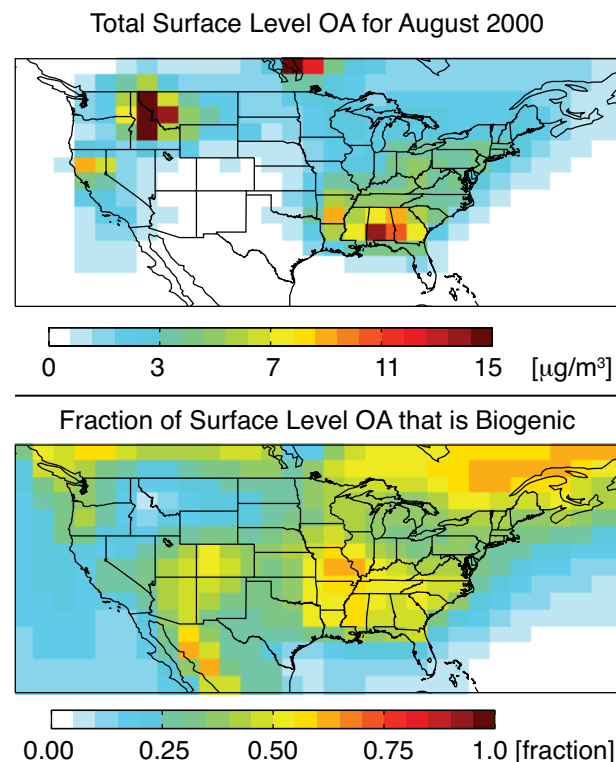


Fig. 5. Surface level organic aerosol from monoterpenes, sesquiterpenes, isoprene, benzene, toluene, xylene, and primary organic aerosol from a traditional, non-volatile POA simulation during August 2000. The biomass burning event near Idaho is saturated on the colorbar. Bottom panel is the fraction of aerosol in the top panel that comes from monoterpenes, sesquiterpenes, and isoprene. POA is assumed to be non-volatile and IVOCs do not form aerosol.

POA evaporates (Pye and Seinfeld, 2010), biogenic aerosol contributes less but still significant amounts of the aerosol in the southeast US (about 50%). Compared to previous work, summertime aerosol is up to $2.6 \mu\text{g}/\text{m}^3$ lower in the Southeast and up to $0.66 \mu\text{g}/\text{m}^3$ lower in the Northeast.

Increased reaction of the peroxy radical with NO leads to both increased and decreased aerosol. More reaction through the high- NO_x pathway reduces the yield of aerosol from monoterpenes and light aromatics but increases the yield from sesquiterpenes. Figure 6 shows the effect on surface level organic aerosol (OA) of forcing the aerosol yield through the low- NO_x ($\beta = 0$) or high- NO_x ($\beta = 1$) path as compared to a simulation using the model calculated β for a traditional POA simulation (reference simulation is depicted in Figs. 3 and 5). The northeast US is dominated by the response of monoterpenes and light aromatics which produce more aerosol in the low- NO_x simulation and less in the high- NO_x simulation. The difference between the standard simulation and the low- NO_x simulation is greater than the difference between the standard simulation and the high- NO_x simulation since model calculated NO_x levels are already

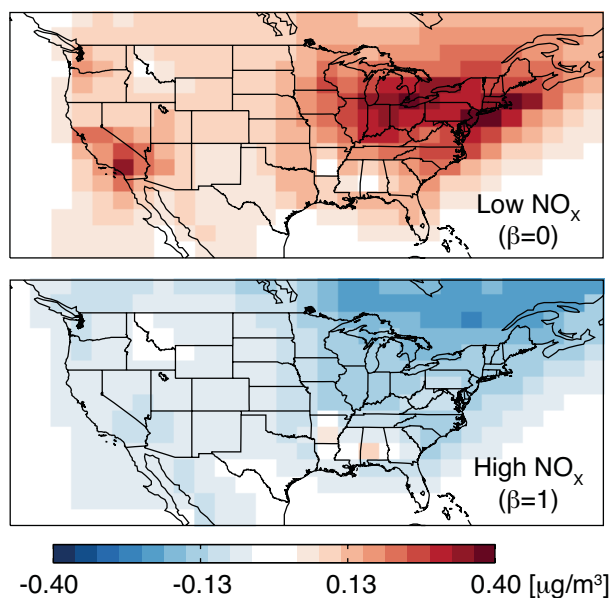


Fig. 6. The change in surface concentration of total OA (August 2000) compared to concentrations in Fig. 5 as a result of forcing photooxidation and ozonolysis through either the low- NO_x ($\beta=0$) or high- NO_x ($\beta=1$) yields. POA is assumed to be non-volatile and IVOCs do not form aerosol (traditional simulation).

sufficiently high to force most of the peroxy radical through the high- NO_x pathway. In the Southeast, the model response is dampened and shows an opposite trend for the high- NO_x simulation. This response occurs as a result of significant aerosol that is not dependent on the RO_2 branching ratio (POA, isoprene aerosol, and nitrate radical aerosol from terpenes) and sesquiterpene aerosol that has higher yields in the $\beta=1$ than in the $\beta=0$ simulation. While the branching of the peroxy radical reaction between high- NO_x and low- NO_x pathways has an influence on surface concentrations, the effect is generally small (OA levels are within about 10% of the levels using the model calculated β).

3.3.2 SOA from nitrate radical oxidation

With roughly 30 to 40% of the monoterpene emissions and 20 to 30% of the sesquiterpene emissions occurring at night, aerosol from the nitrate oxidation pathway is predicted to be significant. Aerosol formed from nitrate radical oxidation of terpenes and isoprene contributes up to $3.35 \mu\text{g}/\text{m}^3$ of organic aerosol during August over the US. The nitrate pathway has the largest effect on terpene (mono- and sesquiterpene) aerosol followed by isoprene. Aerosol production from the nitrate pathway increases terpene aerosol by up to $2.76 \mu\text{g}/\text{m}^3$ (generally $1.5 \mu\text{g}/\text{m}^3$ or more in the Southeast) and isoprene aerosol by about 0.4 to $0.6 \mu\text{g}/\text{m}^3$. Figure 7 shows the percent increase in aerosol from terpenes, isoprene, and all sources compared to a simulation in which the nitrate pathway does not produce aerosol (all simulations use

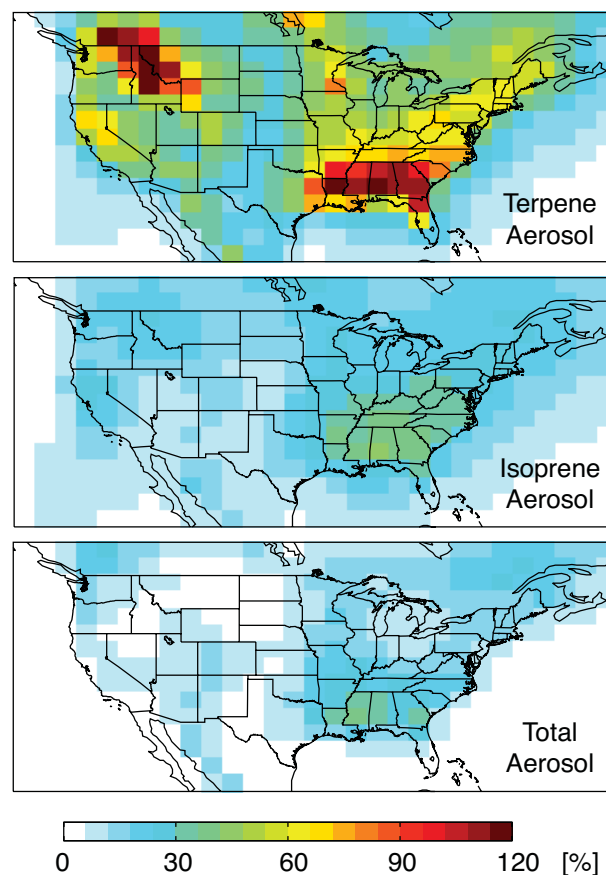


Fig. 7. Enhancement in surface-level August 2000 aerosol from terpenes (monoterpenes and sesquiterpenes), isoprene, and all sources due to aerosol from the nitrate oxidation pathway. The change is relative to a simulation with yields set to zero for the nitrate oxidation pathway. POA is assumed to be non-volatile and IVOCs do not form aerosol (traditional simulation).

traditional POA). An enhancement of 100%, as in the case for terpene OA, indicates that the aerosol level doubles when the nitrate pathway is included. Terpenes are predicted to be the largest contributor to biogenic aerosol in the Southeast, and total organic aerosol is enhanced slightly more than 30% over a wide area as a result of nitrate oxidation aerosol.

Since the terpene + NO_3 aerosol yield data upon which the model parameterization is based contains information at relatively high loadings, aerosol loadings must be significant for organic nitrate aerosol to contribute to surface level OA. The yield of aerosol from the nitrate pathway for terpenes is 4% at $1 \mu\text{g}/\text{m}^3$ (less than the yield from photooxidation and ozonolysis of monoterpenes and sesquiterpenes) and 26% at $10 \mu\text{g}/\text{m}^3$ (more than the yield from photooxidation and ozonolysis of monoterpenes, see Table 1). So although nitrate oxidation enhances aerosol across the US, it is most pronounced in the Southeast where aerosol loadings are higher.

In terms of global budgets, the NO_3 pathway plays a modest role increasing net production of aerosol from terpenes (3 Tg/yr, 20% increase) and isoprene (1 Tg/yr, 10% increase). This lesser role in net global production compared to surface concentrations is due to the relatively low aerosol yield at low loadings and expected evaporation of 80% or more of the organic nitrate aerosol due to its relatively high volatility and the reduced importance of NO_3 reaction in the tropics where NO_x levels are low (see Table 1 for the volatility and Fig. 4 for the expected evaporation).

4 Considerations

In this section, we provide cautionary notes for the implications of our results in terms of emission controls, possible reasons results may be biased, the potential influences of errors in isoprene chemistry, and comments about extrapolating chamber data to the atmosphere.

4.1 Dependence of SOA formation on NO_x level

Simulations presented in Sect. 3.3.1 indicate that the $\text{RO}_2 + \text{NO}$ vs. $\text{RO}_2 + \text{HO}_2$ branching of aromatic and terpene peroxy radicals does not exert a large control on organic aerosol concentrations. Caution should be used when extrapolating these results to implications for air quality management since there are other ways in which NO_x may influence organic aerosol concentrations that have not been examined or implemented in the model.

Another NO_x control on terpene SOA is through the gas-phase oxidants such as the hydroxyl radical, ozone, and nitrate radicals and previous modeling work indicates that changes in gas-phase oxidants may be the primary anthropogenic control on SOA. Simulations by Carlton et al. (2010) indicate that half of biogenic SOA can be controlled, and work by Lane et al. (2008a) indicates that reductions in NO_x emissions are likely to lead to decreased SOA concentrations as a result of lower oxidant concentrations, despite the fact that monoterpene SOA yields are predicted to be higher under low- NO_x conditions. However, the global α -pinene study of Capouet et al. (2008) indicates that the presence of NO_x increases OH and NO_3 levels relative to O_3 levels. As a result, the expected role of the high-yield terpene ozonolysis pathway is diminished and less aerosol results. Thus, a study looking at the implications of NO_x emission reductions may need to parameterize SOA based on gas-phase oxidant (OH vs. O_3) as well as NO_x level and examine the effects of NO_x reductions on oxidant levels.

Our simulations do indicate that the fate of the peroxy radical (reaction with NO or HO_2) is likely not the missing anthropogenic control on organic aerosol especially since increasing β tends to reduce OA concentrations (except in the southeast US) based on current experimental results. Our simulations also indicate that NO_x -dependent monoterpene

and sesquiterpene photooxidation and ozonolysis yields may lead to a more accurate simulation in the northeast US where concentrations are more sensitive to the branching ratio.

4.2 Modeled importance of organic nitrate aerosol

Aerosol from nitrate radical oxidation of biogenic hydrocarbons has been included in previous global modeling work (Chung and Seinfeld, 2002; Farina et al., 2010) but its contribution to aerosol production not separately assessed. Experimental studies have been extrapolated to the global atmosphere and estimated 5 Tg/yr of aerosol from monoterpenes + NO_3 (Fry et al., 2009) and 2–3 Tg/yr from isoprene + NO_3 (Ng et al., 2008). Both of these estimates are about double the values presented in this work. However, our work highlights the potential for NO_3 produced aerosol to have a very large regional effect.

Observations indicate support for a large source of organic compounds from reaction of biogenic VOCs with nitrate radicals. Hennigan et al. (2009) monitored water soluble organic compounds (WSOC) in the gas and aerosol phases during summer in Atlanta and found a pronounced nighttime maximum in gas-phase WSOC likely due to products of nitrate oxidation but no similar maximum in nighttime particulate WSOC. Measurements near the northeast US during the 2002 and 2004 New England Air Quality Studies also indicate a strong interaction between biogenic VOCs and nitrate. Isoprene emitted in the afternoon when OH levels are declining persists long enough to be oxidized by NO_3 . The anticorrelation between α -pinene and NO_3 (Warneke et al., 2004) and isoprene and NO_3 (Brown et al., 2009) indicates that biogenic VOC + NO_3 reactions can be an important sink for both NO_3 and VOCs. Averaged over the entire 2002 campaign, terrestrial biogenic VOCs were estimated to be responsible for 19% of the combined NO_3 and N_2O_5 loss measured offshore (Aldener et al., 2006).

As mentioned previously, the oxidation of monoterpenes and sesquiterpenes by OH, O_3 , and NO_3 is an offline calculation. For each timestep, the gas-phase OH, O_3 , and NO_3 levels are saved from the chemistry solver and used offline in the aerosol routines to determine how much of a given terpene should react with the oxidant during that timestep. Thus, monoterpene and sesquiterpene chemistry does not directly affect OH, O_3 , and NO_3 levels. As a consequence of this offline oxidation calculation, the current version of GEOS-Chem essentially assumes oxidants such as OH, NO, HO_2 , O_3 , and NO_3 are 100% recycled when they react with monoterpenes and sesquiterpenes. Recycling of the oxidants is recommended when only a limited amount of the parent hydrocarbon gas-phase oxidation is represented and later generation products may release oxidants, but this approach may cause the model to overestimate the potential importance of aerosol from nitrate pathways since NO_3 levels may be artificially high.

The yield of organic nitrate can provide an estimate of how much nitrate may be removed from the system or sequestered for later release. Several studies have looked at the yield of organic nitrate from isoprene + NO₃ systems (treated online in the model). Isoprene + NO₃ is expected to yield 65 to 70% organic nitrate (Perring et al., 2009; Rollins et al., 2009), and first generation nitrate products may react with NO₃ again to produce secondary dinitrates (Rollins et al., 2009). The organic nitrates themselves may or may not release NO_x (Perring et al., 2009). This implies recycling no higher than 35% for the isoprene + NO₃ system. Recycling of reactive nitrogen may be higher in monoterpene systems than isoprene systems. The work of Fry et al. (2009) indicates that the yield of organic nitrates from β-pinene + NO₃ is about 40 to 45%, so 55 to 60% of the reacted NO₃ could be immediately recycled as NO₂ or some other reactive nitrogen species (Fry et al. (2009) were unable to detect the recycled species).

To gain insight into the potential role of monoterpene + nitrate reactions and possible depletion of nitrate, one grid cell in the Southeast US (85° W, 32° N) is examined at the beginning of September using a coarse resolution simulation (4° × 5°). Based on the predicted NO₃ and monoterpene levels, even for fairly aggressive levels of reactive nitrogen recycling (perhaps >75%), NO₃ will likely be tritrated in the early evening when isoprene is still present and NO₃ levels are lower. Later during the night, when NO₃ levels are higher, nitrate would likely be in excess. Following the analysis of Brown et al. (2009), we can assume nitrate radicals are at a pseudo steady state as they are formed from:



and removed by reaction with a hydrocarbon, HC:



Reaction with the hydrocarbon is shown to recycle a fraction of the NO₃, *R*. The fractional loss of nitrate due to Reaction (R2), divided by all losses, including N₂O₅ hydrolysis, is:

$$\phi' = (1 - R) \frac{k_{\text{HC}+\text{NO}_3} [\text{NO}_3][\text{HC}]}{k_{\text{NO}_2+\text{O}_3} [\text{NO}_2][\text{O}_3]} = (1 - R)\phi \quad (6)$$

For a simulation with 100% recycling (*R* = 1), ϕ for the lumped monoterpene MTPA is calculated to be approximately 1–2. Thus for any recycling less than 50 to 75%, reaction with the HC could be the dominant removal mechanism for NO₃. Future work using online monoterpene and sesquiterpene oxidation can more carefully examine the interactions between biogenic VOCs and nitrate including the degree to which NO₃ may be titrated and aerosol concentrations lower than predicted in this work.

The amount of aerosol from the NO₃ pathway may also be underestimated by this work since NO₃ SOA-forming pathways of SVOCs and IVOCs have not yet been studied experimentally. SVOCs are globally the largest contributor to

net aerosol production and since yields are generally higher for NO₃ oxidation compared to photooxidation and ozonolysis (for moderate loadings), SVOC reaction with NO₃ could be a substantial method of aerosol production on regional and/or global scales. However, a significant fraction of the SVOC and IVOC emissions are anthropogenic, and reaction with the nitrate radical is expected to be a minor removal process for many anthropogenic species such as alkanes and light aromatics (Warneke et al., 2004; Atkinson and Arey, 2003).

4.3 Uncertainties in isoprene chemistry

In remote areas with little anthropogenic influence (such as the Amazon basin), oxidation of isoprene as represented in the model tends to deplete OH levels to an extent greater than expected based on field measurements (Lelieveld et al., 2008; Butler et al., 2008; Archibald et al., 2010). This falsely low OH can have several effects on organic aerosol levels. Reduced OH can lead to less isoprene, monoterpene, and sesquiterpene reaction with OH and therefore reduce the amount of photooxidation aerosol that forms. The isoprene (or terpene) that is not reacted may be transported to other regions where formation of aerosol is less favorable (for example due to low organic aerosol loadings) or more favorable (for example due to low temperatures and/or reduced deposition aloft), but in either case, the aerosol will be shifted away from where it would have normally formed. Depressed reaction of biogenic hydrocarbons with OH may also lead to an overestimate in the amount of hydrocarbon reacting with nitrate radicals. Isoprene and monoterpenes emitted during the daytime should react primarily with OH and ozone, but if OH levels are abnormally low, a large pool of biogenics may be left to react during the night. Figure 2 indicates that 3% of the daytime isoprene is oxidized at night by NO₃ (isoprene is only emitted during the day), and coarse resolution simulations predict that 10% or less of the monoterpenes emitted during the daytime react with NO₃. Observations do indicate that a certain amount of daytime emissions should be oxidized at night (Warneke et al., 2004). Even if the predicted amount of nitrate reaction is too high, it is likely to have only a small effect on net global production of aerosol since only about 3 Tg/yr of SOA (15% of the biogenic SOA production) is expected to come from nitrate oxidation. Aerosol levels over the Amazon, however, may be significantly overestimated. Issues related to isoprene-OH recycling are not expected to be as important for the simulations over the US where NO_x levels are relatively high.

4.4 Extrapolation of chamber studies

The most representative chamber aerosol yields are those that occur when the fate of the RO₂ radical (reaction with RO₂, HO₂, NO, or NO₃) is the same in chamber studies and the atmosphere. Work by Ng et al. (2008) indicates that the aerosol

from reaction of isoprene with NO_3 results from $\text{RO}_2 + \text{RO}_2$ reactions although aerosol from the $\text{RO}_2 + \text{NO}_3$ pathway may contribute as well (Ng et al., 2008; Rollins et al., 2009). This information raises the question of the applicability of the nitrate oxidation yields to the global atmosphere where parent hydrocarbon concentrations are much lower and $\text{RO}_2 + \text{RO}_2$ should be less important.

Modeling errors can also result when chamber studies do not constrain yields at atmospherically relevant loadings. The SOA yields for monoterpene and sesquiterpene + NO_3 reactions are based on data collected by Griffin et al. (1999a). After correcting for density, the loadings in the chamber range from about 40 to $600 \mu\text{g}/\text{m}^3$. Although the fit shows a low root mean square error (RMSE, 5.7%, Table 1) the fit is unconstrained over the most atmospherically relevant loadings ($1\text{--}10 \mu\text{g}/\text{m}^3$) which could lead to over-predictions or under-predictions of the importance of terpene + NO_3 aerosol.

5 Conclusions

The global chemical transport model, GEOS-Chem, has been used to simulate global organic aerosol from monoterpenes, sesquiterpenes, isoprene, benzene, toluene, xylene, intermediate volatility compounds, and semivolatile organic compounds as well as traditional (nonvolatile) primary organic aerosol with a focus on biogenic aerosol. Models have historically under-predicted organic aerosol levels, and semivolatile POA causes even lower concentrations due to evaporation of a significant fraction of the emissions (Pye and Seinfeld, 2010). The semivolatile POA simulation should become more accurate as additional processes, such as partitioning into aerosol water (Pankow, 2010), are captured and new mechanisms of aerosol formation are elucidated. New terpene emissions used in this work are about 20% lower than previous GEOS-Chem estimates, potentially leading to even lower simulated aerosol concentrations.

Part of the expected decrease in surface concentrations and global production of aerosol in the model is offset by updating the SOA yields to some of the highest values currently supported by chamber experiments. A new lumping scheme is introduced that maintains a reasonable level of parent hydrocarbon identity while ensuring that species of different volatilities remain distinct. As part of the new framework, NO_x -dependent photooxidation and ozonolysis yields are implemented for monoterpene and sesquiterpene aerosol to complement those previously implemented for NO_x -dependent light aromatic SOA (Henze et al., 2008). The α -pinene dark ozonolysis experiments of Shilling et al. (2008) are used to represent low- NO_x monoterpene oxidation and form significant SOA, particularly at low loadings. The yield of aerosol from sesquiterpenes under high- NO_x and limonene under high- and low- NO_x conditions is also signif-

icantly larger than in previous NO_x -independent implementations. Isoprene, light aromatic, and intermediate volatility compound aerosol is refit using a 3-product volatility basis set, and aerosol from nitrate oxidation of isoprene is added.

Changing the photooxidation and ozonolysis of terpenes and light aromatics to use high- NO_x ($\text{RO}_2 + \text{NO}$) vs. low- NO_x ($\text{RO}_2 + \text{HO}_2$) yields leads to relatively small changes in surface concentrations as a result of competing effects of sesquiterpene aerosol (which is enhanced under high- NO_x conditions) and monoterpene/light aromatic aerosol (which is enhanced under low- NO_x conditions). Surface concentrations are more sensitive to the peroxy radical branching ratio ($\text{RO}_2 + \text{NO}$ vs. $\text{RO}_2 + \text{HO}_2$) in the northeast than in the southeast US where aerosol from isoprene, sesquiterpenes, primary emissions, and nitrate radical oxidation, which are independent of the RO_2 branching, dampen the model response.

Globally, 14–15 Tg/yr of SOA is predicted to form from terpenes and 8–9 Tg/yr from isoprene for 22–24 Tg/yr total of biogenic aerosol. Although nitrate radical generated aerosol contributes a small amount to the global burden as a result of its relatively high volatility, it can be very important on a regional level. Aerosol from NO_3 oxidation is predicted to be potentially very important in the Southeast US where it enhances terpene (monoterpene + sesquiterpene) SOA by about 100% or more and total aerosol concentrations by more than 30%. Model estimates of organic nitrate aerosol can be refined by better addressing recycling of nitrate for the terpene + nitrate reactions, and by obtaining better estimates (at low loadings and for multiple terpenes) of the nitrate + terpene SOA yield.

More work is needed to resolve the apparent contradiction that organic aerosol is dominated by modern carbon yet correlates with anthropogenic tracers. Simulations over the US suggest that higher NO_x levels will generally suppress SOA since monoterpenes and light aromatics will generally have a lower yield of aerosol when NO levels are higher. However the impact of reduced NO_x emissions on OH and ozone oxidant levels was not examined and the effect of the RO_2 branching between NO and HO_2 on SOA levels is generally small. Thus far, GEOS-Chem model results have indicated two possible candidates for production of aerosol from modern carbon that would correlate with anthropogenic tracers: the nitrate radical oxidation of terpenes and isoprene and oxidation of semivolatile organic compounds from biofuel burning (Pye and Seinfeld, 2010). Additional theories that need further examination are the possible implications of acidity, sulfate, or NO_2 enhanced production of biogenic aerosol (Surratt et al., 2007, 2010; Eddingsaas et al., 2010; Chan et al., 2010).

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/10/11261/2010/acp-10-11261-2010-supplement.pdf>

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