

Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry

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[1] We implement a new isoprene oxidation mechanism in a global 3-D chemical transport model (GEOS-Chem). Model results are evaluated with observations for ozone, isoprene oxidation products, and related species from the International Consortium for Atmospheric Research on Transport and Transformation aircraft campaign over the eastern United States in summer 2004. The model achieves an unbiased simulation of ozone in the boundary layer and the free troposphere, reflecting canceling effects from recent model updates for isoprene chemistry, bromine chemistry, and HO₂ loss to aerosols. Simulation of the ozone-CO correlation is improved relative to previous versions of the model, and this is attributed to a lower and reversible yield of isoprene nitrates, increasing the ozone production efficiency per unit of nitrogen oxides (NO_x ≡ NO + NO₂). The model successfully reproduces the observed concentrations of organic nitrates (ΣANs) and their correlations with HCHO and ozone. ΣANs in the model is principally composed of secondary isoprene nitrates, including a major contribution from nighttime isoprene oxidation. The correlations of ΣANs with HCHO and ozone then provide sensitive tests of isoprene chemistry and argue in particular against a fast isomerization channel for isoprene peroxy radicals. ΣANs can provide an important reservoir for exporting NO_x from the U.S. boundary layer. We find that the dependence of surface ozone on isoprene emission is positive throughout the U.S., even if NO_x emissions are reduced by a factor of 4. Previous models showed negative dependences that we attribute to erroneous titration of OH by isoprene.

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1. Introduction

[2] Isoprene (2-methyl-1,3-butadiene), the most important nonmethane volatile organic compound (NMVOC) emitted

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by vegetation, affects tropospheric ozone, OH (the main tropospheric oxidant), and aerosols in complex ways. It has a lifetime of about 1 h against oxidation by OH [Atkinson and Arey, 2003]. The resulting oxidation products lead to the formation of ozone, an effective greenhouse gas and air pollutant. Isoprene also reacts with the nitrate radical (NO₃) at night, with important implications for global budget of nitrogen oxides (NO_x ≡ NO + NO₂) and therefore ozone [Brown *et al.*, 2009]. The successive oxidation steps of isoprene produce a range of multifunctional organic compounds that can go on to form secondary organic aerosols (SOA) with implications for climate and public health. The International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) aircraft campaign provided a detailed characterization of boundary layer chemistry across the isoprene-rich eastern U.S. in July–August 2004 [Fehsenfeld *et al.*, 2006; Singh *et al.*, 2006]. We use here aircraft observations from this campaign, interpreted with a global 3-D chemical transport model (GEOS-Chem), to better understand the importance of isoprene chemistry for tropospheric ozone and its precursors.

[3] Daytime oxidation of isoprene is initialized by its reaction with OH, leading to the production of peroxy radicals (ISOP₂). In the presence of NO_x, ISOP₂ reacts with NO

leading to the production of organic nitrates by a minor branch. These nitrates may act as a sink for both HO_x ($\text{HO}_x \equiv \text{H} + \text{OH} + \text{peroxy radicals}$) and NO_x and therefore affect global and regional ozone budgets [Fiore et al., 2005; Horowitz et al., 2007; Ito et al., 2009; Paulot et al., 2012; Perring et al., 2009b; von Kuhlmann et al., 2004; Wu et al., 2007; Xie et al., 2013]. Laboratory data indicate a yield of first-generation organic nitrates from isoprene oxidation ranging from 7% to 12% [Giacopelli et al., 2005; Lockwood et al., 2010; Patchen et al., 2007; Paulot et al., 2009a; Sprengnether et al., 2002]. A model interpretation of the ICARTT data by Horowitz et al. [2007] indicated a smaller yield (4%). Isoprene nitrates are partly recycled back to NO_x upon further oxidation, leading to further complication in their role as a sink or reservoir for NO_x [Horowitz et al., 2007; Ito et al., 2009; Paulot et al., 2012; Paulot et al., 2009a; Perring et al., 2009b]. They may serve as nitrogen reservoir to export boundary layer NO_x to rural and remote atmospheres [Atlas, 1988; Horowitz et al., 1998; Neff et al., 2002].

[4] In the absence of NO_x , ISOPO_2 is assumed in standard mechanisms to be converted to organic hydroxyperoxides ISOPOOH [Jacob and Wofsy, 1988], leading to titration of OH. However, observations from a number of field campaigns show no such OH titration [Carslaw et al., 2001; Hofzumahaus et al., 2009; Lelieveld et al., 2008; Pugh et al., 2010; Ren et al., 2008; Stone et al., 2010; Tan et al., 2001; Thornton et al., 2002; Whalley et al., 2011; Mao et al., 2012]. Several mechanisms have been proposed to explain this discrepancy, including OH regeneration via oxidation of epoxydiols formed from the oxidation of ISOPOOH based on laboratory studies [Paulot et al., 2009b] and fast isomerization of ISOPO_2 based on theoretical studies [Peeters and Müller, 2010; Peeters et al., 2009]. We now define this rate constant determined by these theoretical studies as “fast isomerization rate,” as it is later found to be faster than the laboratory-determined isomerization rate constant [Crouse et al., 2011] by a factor of ~ 50 . Measurements of OH concentrations by the standard laser induced fluorescence technique may be biased high due to internally generated OH from oxidation of biogenic volatile organic compounds (VOCs) [Mao et al., 2012]. After correcting for this effect, Mao et al. [2012] find good agreement between model and observations when OH regeneration from oxidation of epoxydiols [Paulot et al., 2009b] and laboratory-based slow isomerization of ISOPO_2 [Crouse et al., 2011] are included in the model.

[5] Besides daytime oxidation, nighttime oxidation of isoprene by NO_3 contributes significantly to the budget of organic nitrates [Horowitz et al., 2007; von Kuhlmann et al., 2004; Xie et al., 2013]. This pathway is initialized by addition of NO_3 to one of the double bonds of isoprene, followed by production of organic nitrates with high yield (65–85%) [Paulson and Seinfeld, 1992; Perring et al., 2009a; Rollins et al., 2009]. These organic nitrates can degrade in a matter of hours to more stable forms of organic nitrates, leading to the formation of SOA [Rollins et al., 2009].

[6] Isoprene chemistry is of particular importance in affecting summertime ozone over the eastern U.S. [Jacob et al., 1993], with important implications for air quality management. Both global and regional chemical transport models tend to overestimate summertime surface ozone over the eastern U.S. by 10–20 ppb [Fiore et al., 2009; Lin et al., 2008; Murazaki and Hess, 2006; Rasmussen et al., 2012;

Yu et al., 2007; Yu et al., 2010]. Fiore et al. [2005] suggested that this problem might be due to incorrect representation of isoprene sources and chemistry.

[7] The ICARTT aircraft campaign is a unique resource for testing models of isoprene chemistry and the impact of isoprene on ozone. It provided a detailed characterization of boundary layer chemistry across the eastern U.S. in July–August 2004 [Fehsenfeld et al., 2006; Singh et al., 2006]. Two aircraft were deployed with comprehensive chemical payloads, including measurements of isoprene and several of its oxidation products [Fried et al., 2008; Perring et al., 2009b; Warneke et al., 2010]. Previous analyses of isoprene chemistry using ICARTT data have been presented by Horowitz et al. [2007], Perring et al. [2009b], and Xie et al. [2013] with a focus on isoprene nitrates, and by Stavroukou et al. [2010] with a focus on HO_x .

[8] A number of previous studies have applied GEOS-Chem to simulation of the ICARTT data, including evaluation with observations of NO_x and ozone [Hudman et al., 2009; Hudman et al., 2007; Liang et al., 2007], CO [Hudman et al., 2008; Turquety et al., 2007], HCHO [Millet et al., 2006], and aerosols [Drury et al., 2010; Fu et al., 2009; Heald et al., 2006]. In particular, Hudman et al. [2007] found that the lightning NO_x source inferred from the ICARTT data was much larger than expected, and Hudman et al. [2008] found the need for a 60% reduction in CO emissions relative to the National Emission Inventory (NEI 99) from the U.S. Environmental Protection Agency (EPA). Hudman et al. [2009] indicated no significant bias in their simulation of ozone over the eastern U.S. after the lightning correction, and neither did a subsequent GEOS-Chem study by Zhang et al. [2011]. However, those model versions assumed an unreasonably high yield of isoprene nitrates (18%) and that isoprene nitrates behaved like a terminal sink for NO_x .

[9] Here we implement in GEOS-Chem a state-of-science isoprene chemistry mechanism based on Paulot et al. [2009a] and Paulot et al. [2009b], along with other updates, and evaluate the simulation of ozone, isoprene oxidation products, and related chemical correlations during ICARTT. From there we gain insights into the organic nitrates produced from isoprene oxidation and their role in ozone chemistry, and we discuss the sensitivity of summertime surface ozone to isoprene emissions.

2. GEOS-Chem Model

2.1. General Description

[10] GEOS-Chem is a global 3-D chemical transport model driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS-5) of the NASA Global Modeling and Assimilation Office [Bey et al., 2001]. We apply here GEOS-Chem version 9-01-03 (<http://www.geos-chem.org>) to simulation of the ICARTT period (1 July to 15 August 2004). The GEOS-5 meteorological data have 6 h temporal resolution (3 h for surface variables and mixing depths) with $0.5^\circ \times 0.667^\circ$ horizontal resolution and 72 vertical layers from the surface to 0.01 hPa. We regrid here the meteorological data to $2^\circ \times 2.5^\circ$ for input to GEOS-Chem. The model is initialized with a 1 year simulation from June 2003 to June 2004 with $4^\circ \times 5^\circ$ resolution and from June 2004 with $2^\circ \times 2.5^\circ$ resolution. Boundary layer mixing in GEOS-Chem uses the nonlocal scheme [Holtslag and Boville, 1993] implemented by Lin and McElroy [2010]. Stratospheric ozone

is simulated with a linearized ozone (Linoz) algorithm described by *McLinden et al.* [2000].

[11] Biogenic emission of isoprene follows the process-based Model of Emissions of Gases and Aerosols from Nature (MEGAN) inventory [*Barkley et al.*, 2011; *Guenther et al.*, 2006; *Millet et al.*, 2008] with monthly mean leaf area index from the Moderate Resolution Imaging Spectroradiometer satellite instrument [*Myneni et al.*, 2007]. The resulting North American isoprene emission is 10.2 TgC for June–August 2004 (65°W to 130°W, 20°N to 50°N), in line with an independent estimate of 7.1–11.6 TgC inferred from satellite data for formaldehyde [*Millet et al.*, 2008].

[12] Anthropogenic emission inventories in GEOS-Chem include EPA NEI-05 for the U.S., Criteria Air Contaminants (CAC) for Canada (http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), Big Bend Regional Aerosol and Visibility Observational (BRAVO) for Mexico [*Kuhns et al.*, 2005], Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) for Europe [*Vestreng and Klein*, 2002], and *Streets et al.* [2006] for East Asia. We reduce CO emissions in the NEI-05 inventory by 53% following *Hudman et al.* [2008]. This reduction is consistent with other estimates of U.S. CO emissions based on atmospheric observations [*LaFranchi et al.*, 2013; *Miller et al.*, 2012; *Miller et al.*, 2008; *Parrish*, 2006]. For the rest of the world we use the Emissions Database for Global Atmospheric Research (EDGAR) emission inventory for CO, NO_x, and SO₂ [*Olivier and Berdowski*, 2001] and the Reanalysis of the Tropospheric chemical composition (RETRO) emission inventory for volatile organic compounds (VOCs) [*Schultz et al.*, 2007]. All anthropogenic emissions are scaled to 2004 based on the changes in total CO₂ emissions, which are obtained from the Carbon Dioxide Information Analysis Center [*van Donkelaar et al.*, 2008].

[13] Lightning NO_x emissions are calculated as a function of GEOS-5 cloud top height and rescaled to match the Optical Transient Detector (OTD) and Lightning Imaging Sensor (LIS) climatological observations [*Murray et al.*, 2012]. The global lightning source is imposed to be 6 TgN yr⁻¹ [*Martin et al.*, 2007], with higher NO_x yields per flash at midlatitudes than in the tropics [*Hudman et al.*, 2007]. We use monthly biomass burning emissions from the Global Fire Emission Database version 3 [*van der Werf et al.*, 2010]. Forest fire plumes transported from Alaska and western Canada were important in the free troposphere during ICARTT [*Pfister et al.*, 2008; *Turquety et al.*, 2007]. Soil NO_x emissions are computed using a modified version of the *Yienger and Levy* [1995] algorithm with canopy reduction factors as described in *Wang et al.* [1998].

[14] Dry deposition in GEOS-Chem is calculated using a standard resistance-in-series model [*Wesely*, 1989], in which the surface resistances for gases are determined by their Henry's law constants and surface reactivities. We revised the reactivity of all oxygenated VOCs including ketones, aldehydes, organic peroxides and organic nitrates to be the same as ozone following *Karl et al.* [2010]. We also include wet and dry deposition of isoprene hydroperoxide and epoxydiols with Henry's law constants of 1.7×10^6 and 1.3×10^8 M atm⁻¹ following *Marais et al.* [2012]. Wet deposition is described by *Liu et al.* [2001] for water-soluble aerosols and by *Amos et al.* [2012] for gases. It includes wet scavenging in convective updrafts as well as grid-resolved first-order rainout and washout.

[15] The standard GEOS-Chem simulation of ozone-NO_x-HO_x-VOC chemistry is described by *Mao et al.* [2010], with more recent implementation of bromine chemistry [*Parrella et al.*, 2012]. The chemical mechanism includes updated recommendations from the Jet Propulsion Laboratory [*Sander et al.*, 2011] and the International Union of Pure and Applied Chemistry (<http://www.iupac-kinetic.ch.cam.ac.uk>). In addition, we included an improved HO₂ aerosol reactive uptake with $\gamma(\text{HO}_2) = 1$ producing H₂O, suggested by *Mao et al.* [2013]. We also increased the NO₃ aerosol reactive uptake coefficient γ from 1×10^{-4} [*Jacob*, 2000] to 0.1 with HNO₃ as product. This reflects recent measurements of high $\gamma(\text{NO}_3)$ on soot [*Karagulian and Rossi*, 2007], dust [*Karagulian and Rossi*, 2005], dry salts [*Seisel et al.*, 1999], organic aerosols [*Brown and Stutz*, 2012; *Fry et al.*, 2011; *Lee et al.*, 2013], and ambient urban aerosols [*Tang et al.*, 2010]. Modeled ozone and organic nitrates appear to be insensitive to the choice of $\gamma(\text{NO}_3)$ in the range of 1×10^{-4} to 0.1. The treatment of isoprene oxidation is described in the following subsection.

2.2. Chemical Mechanism for Isoprene Oxidation

[16] A focus of this work is to use the ICARTT observations to test our model mechanism for isoprene chemistry. This new mechanism differs significantly from the original isoprene oxidation mechanism in GEOS-Chem described in *Horowitz et al.* [1998]. The full mechanism is described at http://wiki.seas.harvard.edu/geos-chem/index.php/New_isoprene_scheme. Figure 1 illustrates the treatment of first-generation isoprene oxidation by OH. Oxidation under the high-NO_x regime mainly follows *Paulot et al.* [2009a]. It is initialized by OH addition at 1 and 4 positions, resulting in a pool of β and δ -hydroxyl peroxy radicals (ISOPO₂) with yields of 71% and 29%, respectively. In the presence of NO_x, the degradation of β -hydroxyl ISOPO₂ leads to the production of HCHO (66%), methylvinylketone (MVK) (40%), and methacrolein (MACR) (26%) with a small yield of β -hydroxyl isoprene nitrates (ISOPNB) (6.7%). Reaction of δ -hydroxyl ISOPO₂ with NO leads to the formation of δ -hydroxyl isoprene nitrates (ISOPND) (24%). The total first-generation isoprene nitrate yield (11.7%) from ISOPND (7.0%) and ISOPNB (4.7%), respectively, is in line with other laboratory studies as described above. The fates of ISOPNB and ISOPND are discussed below.

[17] Under low-NO_x conditions, ISOPO₂ can follow either of two pathways. One is to react with HO₂ to form isoprene hydroperoxides (ISOPOOH) with a small production of HCHO, MVK, and MACR (4.7%, 7.3%, and 12%, respectively) [*Paulot et al.*, 2009b], largely consistent with a recent study by *Liu et al.* [2013]. Most of ISOPOOH reacts with OH to produce epoxydiols and quantitatively regenerate OH [*Paulot et al.*, 2009b]. Another pathway is the unimolecular isomerization of ISOPO₂ (1,6-H shift) [*Peeters and Müller*, 2010; *Peeters et al.*, 2009], leading to the production of hydroperoxyaldehydes (HPALDs). The subsequent fate of HPALDs is dominated by photolysis, with a 100% yield of OH [*Wolfe et al.*, 2012]. We do not consider the 1,5-H shift as it is expected to be unimportant [*Crouse et al.*, 2011; *Da Silva et al.*, 2010]. The rate constant of 1,6-H shift isomerization is still under debate [*Archibald et al.*, 2010; *Crouse et al.*, 2011; *Karl et al.*, 2009; *Peeters and Müller*, 2010; *Peeters et al.*, 2009]. We adopt the rate constant from *Crouse et al.* [2011], which is lower than the original one

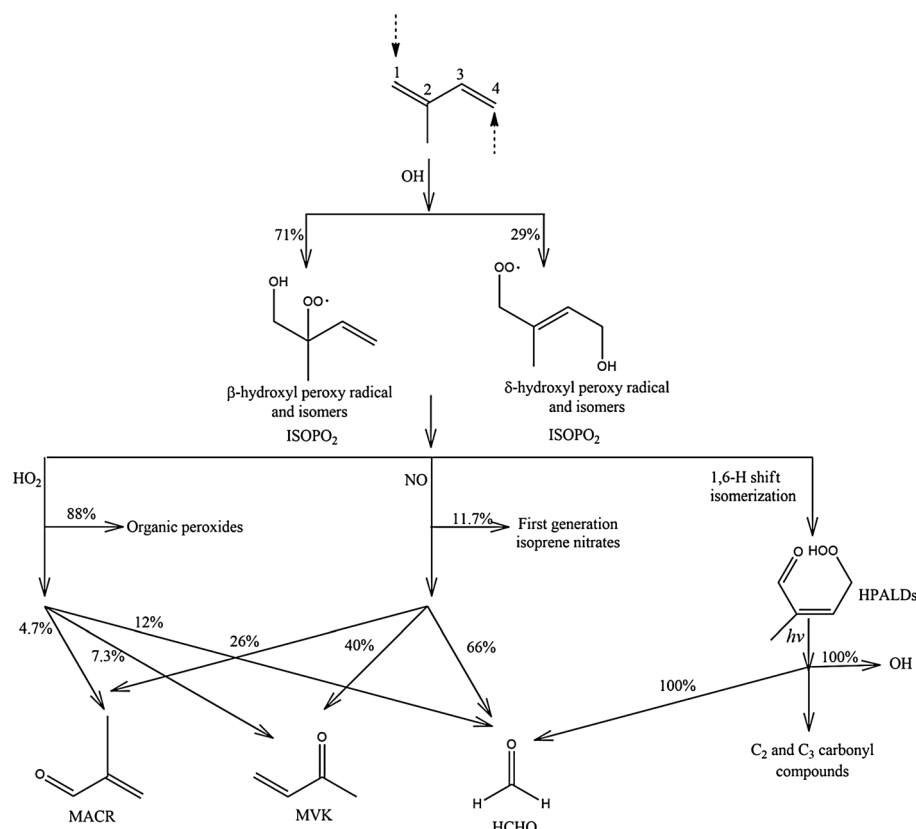


Figure 1. Schematic of the first stage of the isoprene oxidation mechanism initiated by OH.

from Peeters et al. [Peeters and Müller, 2010; Peeters et al., 2009] by a factor of ~ 50 . As we will see in section 4, the lower rate constant affords a better simulation of organic nitrate measurements in ICARTT.

[18] The subsequent fate of ISOPND and ISOPNB is mainly via reactions with OH and ozone because of the remaining C=C bond. The degradation of ISOPND and ISOPNB is assumed to return NO_x with a weighted average yield of 55% [Paulot et al., 2009a]. Paulot et al. [2009a] suggested that ISOPND and ISOPNB have photochemical lifetimes against oxidation by OH of 1 and 7 h, respectively ($\text{OH} = 3 \times 10^6 \text{ molecules cm}^{-3}$ at 298 K). Lockwood et al. [2010] suggested photochemical lifetimes against oxidation by ozone of 2 and 4 h, respectively (ozone = 60 ppbv), which is 5–10 times shorter than the previous value suggested by Giacomelli et al. [2005]. As a result, these nitrates are degraded in a matter of hours, leading to the formation of a series of secondary organic nitrates, including methylvinylketone nitrates (MVKN), methacrolein nitrates (MACRN), ethanal nitrate (ETHLN), and propanone nitrate (PROPNN), as shown in Figure 2. Reactions of ISOPND and ISOPNB with ozone can also produce these secondary organic nitrates, and this is mainly from the decomposition of primary ozonides that are initially formed by the addition of ozone across the C=C bond [Baker et al., 2002]. These secondary organic nitrates are more stable than the primary ones due to the lack of a C=C bond. MVKN, MACRN, and ETHLN have lifetimes of 17, 2, and 9 h against oxidation by OH ($\text{OH} = 3 \times 10^6 \text{ molecules cm}^{-3}$ at 298 K), and PROPNN is mainly lost through photolysis with a global mean lifetime of 13 days in GEOS-Chem.

[19] Nighttime isoprene oxidation is updated from Xie et al. [2013], which is largely based on the chamber study by Rollins et al. [2009]. This new treatment assumes 70% yield of first-generation carbonyl nitrates from the isoprene + NO_3 reaction. These nitrates can be further oxidized by NO_3 , leading to the formation of secondary organic nitrates (Figure 3). For simplification, we lump here all secondary organic nitrates from nighttime isoprene oxidation into one lumped alkyl nitrate (R_4N_2), which has a global mean lifetime of 5 days against OH oxidation and photolysis in GEOS-Chem. The relatively long lifetime of R_4N_2 is largely based upon the nighttime oxidation product that is derived from Xie et al. [2013] and shows a similar structure to PROPNN.

[20] Several additional updates are included in this new mechanism. First, we implemented the isomerization of methacrolein peroxy radicals (MACRO_2) based on experiments by Crouse et al. [2012]. Second, we updated the reaction rate of HO_2 with $> \text{C}_2$ peroxy radicals to the expression in Saunders et al. [2003], leading to an increase of factor 2 for $\text{HO}_2 + \text{ISOPO}_2$ at 298 K. Third, we updated OH regeneration for the reactions of HO_2 with acetyl peroxy ($\text{CH}_3\text{C}(\text{O})\text{O}_2$) and acetyl peroxy ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$) radicals based on laboratory measurements [Dillon and Crowley, 2008; Hasson et al., 2004; Jenkin et al., 2007]. Fourth, the reaction of isoprene with ozone was modified following the Master Chemical Mechanism v3.2 [Jenkin et al., 1997; Saunders et al., 2003].

3. Simulation of Ozone and Related Species

[21] Here we use the ICARTT observations to evaluate our new isoprene oxidation mechanism implemented in GEOS-Chem.

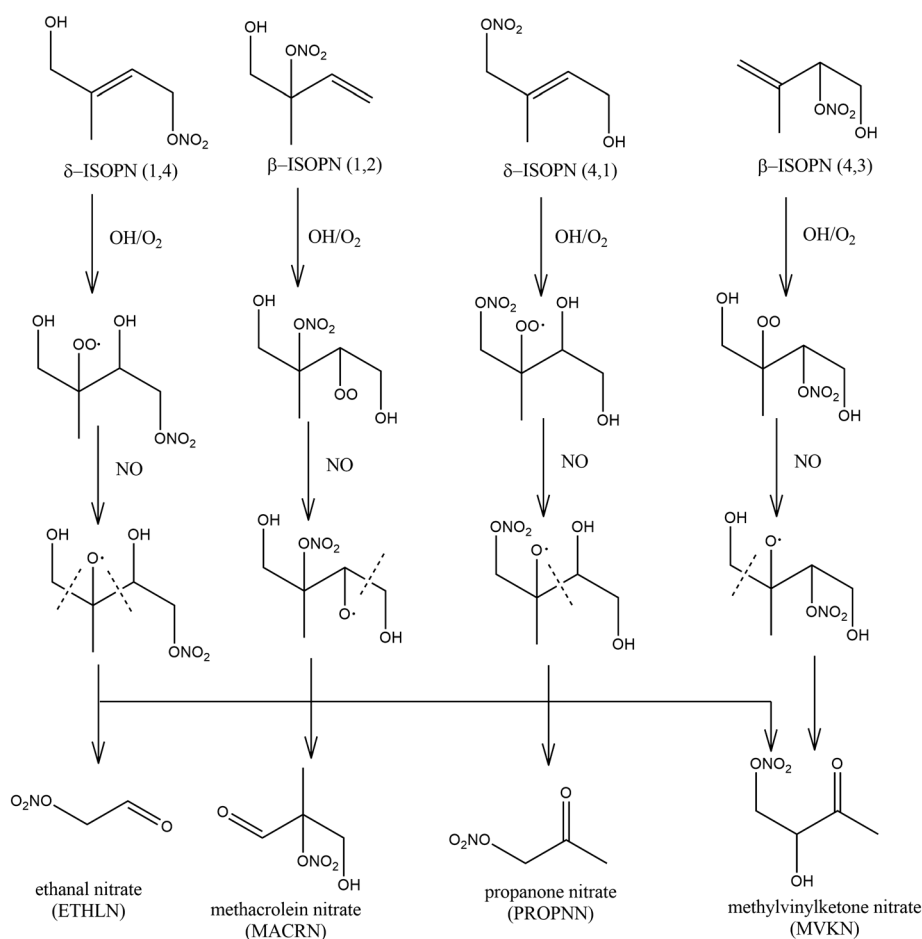


Figure 2. Schematic of the oxidation of isoprene nitrates by OH following *Paulot et al.* [2009a].

There were two aircraft in the field, the NASA DC-8 and the NOAA WP-3D [Fehsenfeld *et al.*, 2006; Singh *et al.*, 2006]. We mostly focus on data from the DC-8, which provided regional coverage over the eastern U.S., whereas the WP-3D often targeted urban plumes in the Northeast [Warneke *et al.*, 2007]. However, we use the MVK + MACR observations from the WP-3D as these measurements were not made on the DC-8. We exclude biomass burning and urban plumes ($\text{CH}_3\text{CN} > 225$ ppt or $\text{HCN} > 425$ ppt or $\text{NO}_2 > 4$ ppb or $\text{NO}_x/\text{NO}_y > 0.4$ mol mol⁻¹), which would not be represented properly on the scale of the model [Hudman *et al.*, 2007]. We also exclude stratospheric air as diagnosed by $\text{O}_3/\text{CO} > 1.25$ mol mol⁻¹. All comparisons between model and observations use model output sampled along the flight tracks and at the flight time with 15 min time resolution. Ninety-six percent of all data points (DC8) were collected between 08:00 and 18:00 local time.

[22] Figure 4 (top) compares observed and simulated mean ozone concentrations in the boundary layer (0–1.5 km). A regression for the ensemble of the data shows no significant bias (bottom left). The model largely captures the spatial pattern of boundary layer ozone but with a relatively low correlation, likely due to the uncertainties in MEGAN biogenic emissions [Millet *et al.*, 2008]. The model overestimates boundary layer ozone in the Southeast U.S. by 3–5 ppbv but has no bias over the Northeast. The small ozone bias over the Southeast could be due to several factors including

excessive convection in the model over the Gulf of Mexico [Fiore *et al.*, 2002] and omission of terpene compounds that may act as additional NO_x sinks through formation of organic nitrates [Browne and Cohen, 2012; Pratt *et al.*, 2012].

[23] In the analysis that follows we mainly focus on the data collected over land. Figure 5 shows the mean 0–4 km vertical profiles of ozone, isoprene, CO, HCHO, peroxyacetyl nitrate (PAN), HNO₃, NO_x, and MVK + MACR concentrations measured by the aircraft and simulated by the model. The spatial distributions of summertime HCHO, CO, and NO_y over the eastern U.S. during ICARTT have been examined in previous GEOS-Chem studies [Hudman *et al.*, 2008; Hudman *et al.*, 2007; Millet *et al.*, 2006]. As shown in Figure 5, the vertical gradient of ozone between the boundary layer and the free troposphere is well reproduced by the model. CO is also well simulated, reflecting the adjustment of anthropogenic emissions as recommended by Hudman *et al.* [2008]. We discuss the other species below.

[24] Isoprene measured by the DC-8 decreases from 500 pptv near the surface to 20 pptv at 3 km, reflecting its short photochemical lifetime. Values measured by the WP-3D are lower, reflecting the northeast sampling bias. As MVK, MACR, and HCHO are major first-generation products from isoprene oxidation under high-NO_x conditions (Figure 1), they all show a rapid decrease from boundary layer to 3 km, consistent with isoprene. Millet *et al.* [2006] previously showed that isoprene was the dominant source of HCHO variability during ICARTT. The model provides

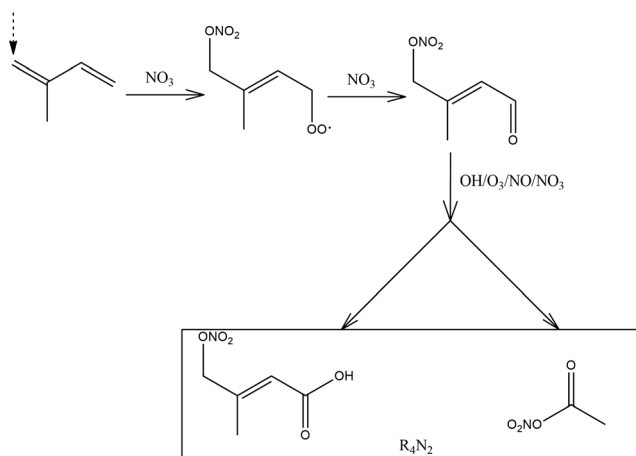


Figure 3. Partial schematic of isoprene oxidation by NO_3 following *Rollins et al.* [2009] and *Xie et al.* [2013]. For simplification, we lump here all secondary organic nitrates from nighttime isoprene oxidation into one lumped alkyl nitrate (R_4N_2).

overall a good simulation of the observed mean profiles. The yield of HCHO from isoprene oxidation appears to be relatively insensitive to the choice of mechanism [*Marais et al.*, 2012], but the yield of MVK+MACR is sensitive to the rate constant of ISOPO_2 isomerization, as MVK and MACR are not produced by that pathway (Figure 1). In a sensitivity simulation using the fast isomerization of

ISOPO_2 [*Peeters and Müller, 2010; Peeters et al., 2009*] we find mean MVK+MACR concentrations of 100 pptv in the boundary layer, leading to an even lower underestimate of MVK+MACR.

[25] Mean observed NO_x decreases from 700 pptv near the surface to 50 pptv at 3 km. The model agrees with observations within 30%. Oxidation of NO_x produces HNO_3 , PAN, and other organic nitrates (to be discussed in section 4). Simulated HNO_3 in the free troposphere is too high, which could reflect insufficient scavenging. PAN is simulated without bias. We find that isoprene is the main VOC precursor for PAN, consistent with previous model studies for the eastern U.S. [*Horowitz et al., 1998*] as well as observed correlations with other peroxyacylnitrates [*Williams et al., 1997*].

[26] The most recent previous evaluation of the GEOS-Chem ozone simulation over the U.S. was by *Zhang et al.* [2011], who also found no significant bias. That simulation used v8-02-03 of GEOS-Chem. Since then, several objective improvements have been made to GEOS-Chem that have had significant consequences for the ozone simulation (<http://www.geos-chem.org>): (1) decrease in isoprene nitrate yield (from 18% to 11.7%) and partial recycling of NO_x (section 2.2), (2) inclusion of tropospheric bromine chemistry [*Parrella et al., 2012*], (3) heterogeneous loss of HO_x radicals [*Mao et al., 2013*], and (4) correction of the diurnal cycle of NO_x emissions by shifting emissions peaks by 6 h to reflect the proper timing of local transportation. For the eastern U.S. boundary layer and free troposphere in summer, (1) causes a

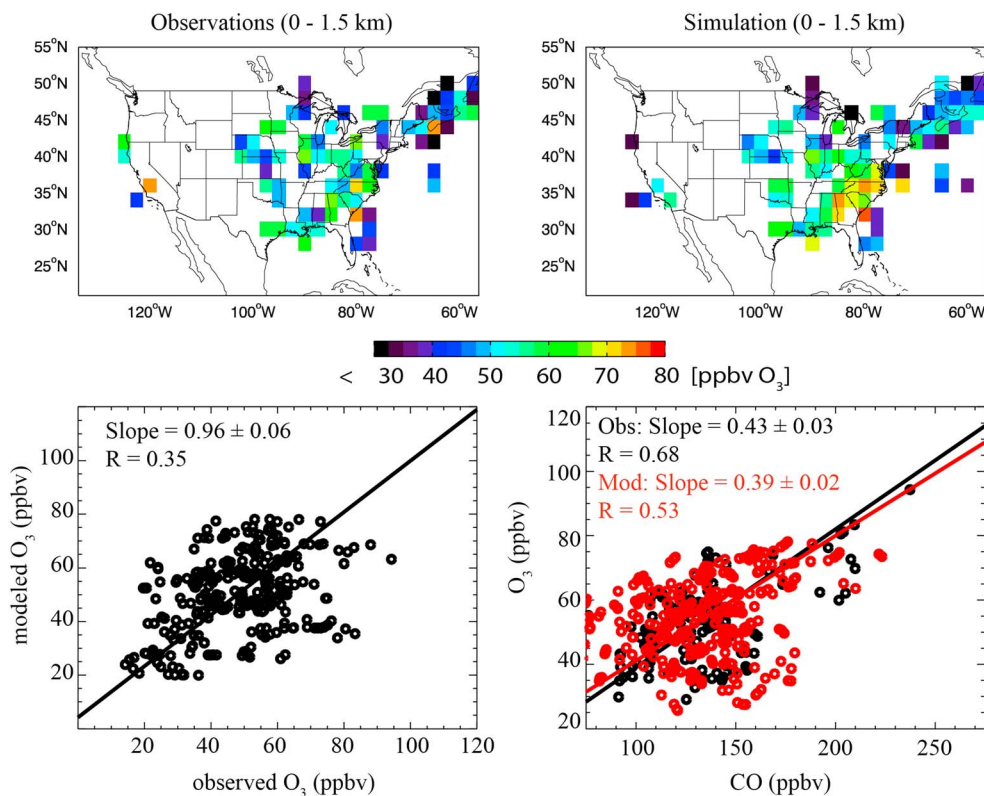


Figure 4. Ozone concentrations and ozone-CO correlations in the boundary layer (0–1.5 km) during ICARTT (1 July to 15 August 2004). (top) Observed and simulated values averaged over the $2^\circ \times 2.5^\circ$ GEOS-Chem grid. (bottom left) A model versus observed scatterplot of these values. (bottom right) The ozone-CO correlations in the observations (black) and in the model (red). Regression slopes are from a reduced-major-axis regression with errors determined by nonparametric bootstrap resampling.

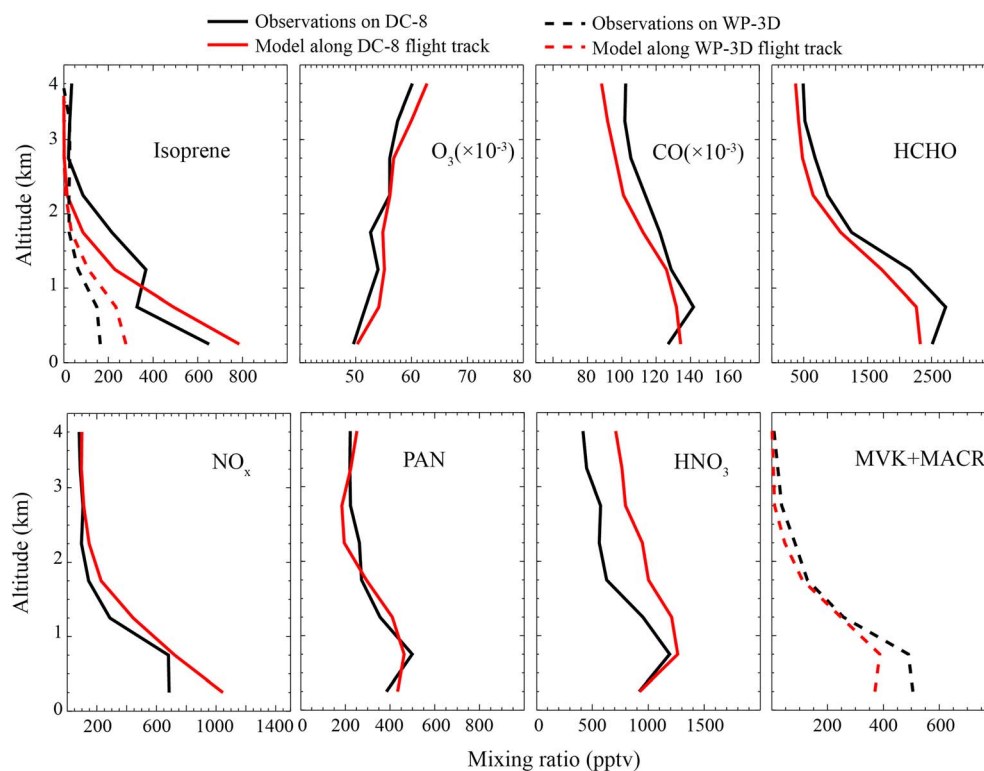


Figure 5. Mean vertical profiles of species concentrations during ICARTT (1 July to 15 August 2004) over land (Figure 4). Measurements are from the DC-8 aircraft except for MVK+MACR which was only measured aboard the WP-3D aircraft (we also show isoprene from the WP-3D aircraft).

3–5 ppbv increase in ozone in the model. However, the resulting positive bias is effectively corrected by (2)–(4), each of which decreases ozone in the above conditions by 1–3 ppbv, as shown in Figure S1 (supporting information). This highlights the importance of canceling errors in model simulations of ozone. Further constraints can be obtained by correlations of ozone with related species, as discussed below.

4. Organic Nitrates and Relationship With HCHO and Ozone

[27] *Perring et al.* [2009b] made measurements of total organic nitrates other than peroxyacetyl nitrates (RONO₂, hereinafter Σ ANs) aboard the DC-8 during ICARTT. As Σ ANs is mainly expected to include isoprene nitrates under the ICARTT conditions [*Beaver et al.*, 2012], this provides an opportunity to evaluate the simulation of isoprene nitrates in GEOS-Chem. Analysis of the ICARTT Σ ANs data has been presented previously in several studies. *Perring et al.* [2009b] found good correlation between observed HCHO and Σ ANs in the boundary layer. *Horowitz et al.* [2007] found that the vertical profile of Σ ANs and the ozone- Σ ANs correlation could be best reproduced by a 4% yield of isoprene nitrates with 40% recycling efficiency. *Xie et al.* [2013] applied the treatment of isoprene nitrates from *Paulot et al.* [2009a] to the Community Multiscale Air Quality (CMAQ) regional air quality model, but they find an overestimate of Σ ANs by 30% in their model. We here examine organic nitrates and their relationship with HCHO and ozone in GEOS-Chem.

[28] Figure 6 shows the mean vertical profile of Σ ANs during ICARTT. Concentrations decrease from 200 pptv near the surface layer to 50–100 pptv in the free troposphere, both in observations and in the model. In contrast to *Xie et al.* [2013], we show very little overestimation of Σ ANs in the model. This is likely due to different treatment of organic nitrates produced from NMVOCs other than isoprene, as they find that only 60% of Σ ANs is from isoprene oxidation in their model, in contrast to more than 90% in our model. We also find that the vertical profile of Σ ANs is insensitive to the deposition rates of ISOPND and ISOPNB because of their short photochemical lifetimes. A sensitivity simulation using slower reaction rates with ozone [*Giacopelli et al.*, 2005] shows little difference in the vertical profile of Σ ANs, as ISOPND is mainly oxidized by OH. A sensitivity simulation using the fast isomerization of ISOPO₂ [*Peeters and Müller*, 2010; *Peeters et al.*, 2009] produces less than 100 pptv Σ ANs in the boundary layer.

[29] We see from Figure 6 that Σ ANs in the model is mainly contributed by the second generation of isoprene nitrates, i.e., PROPNN, MVKN+MACRN, and R₄N₂ (Figure 2). In particular, R₄N₂ and PROPNN contribute to 44% and 21% of Σ ANs in the boundary layer. This reflects the short lifetime of the first-generation isoprene nitrates against oxidation by OH and ozone. For the same reason, MVKN+MACRN decline rapidly in the free troposphere where most of Σ ANs is contributed by the longer-lived R₄N₂ and PROPNN species. Oxidation of isoprene by NO₃ accounts for 80% of R₄N₂ in the model, emphasizing the need for better understanding of this chemistry [*Beaver*

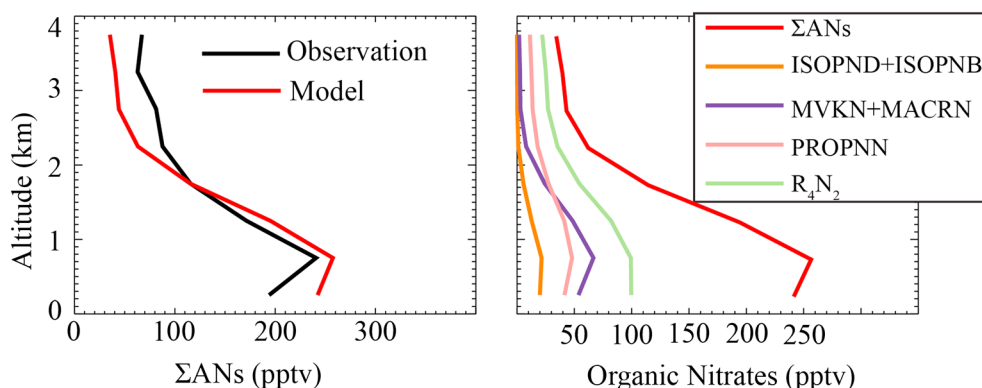


Figure 6. (left) Mean vertical profiles of total organic nitrates excluding peroxyacynitrates (Σ ANs) during ICARTT (1 July to 15 August 2004) over land (Figure 4). Observations (black) are compared to GEOS-Chem (red). (right) contributions of individual species to mean Σ ANs in GEOS-Chem including β -hydroxyl isoprene nitrates (ISOPNB), δ -hydroxyl isoprene nitrates (ISOPND), methacrolein nitrates (MACRN), methylvinylketone nitrates (MVKN), propanone nitrate (PROPNN), and a lumped organic nitrate (R_4N_2). R_4N_2 is produced from nighttime isoprene oxidation as well as oxidation of $\geq C_3$ ketones, and $\geq C_4$ alkanes.

et al., 2012; Brown *et al.*, 2009; Grossenbacher *et al.*, 2001; Kwan *et al.*, 2012].

[30] Perring *et al.* [2009b] pointed out that the observed HCHO- Σ ANs correlation provides an additional constraint on the bulk yield of isoprene nitrates, due to the coproduction of HCHO and Σ ANs from isoprene oxidation under the high- NO_x regime (Figure 1). As shown in Figure 7, the model reproduces successfully the observed continental boundary layer correlation in ICARTT. Fast isomerization of ISOPO₂ [Peeters *et al.*, 2009] underestimates the Σ ANs yield. Despite the large fraction of R_4N_2 in Σ ANs, we find that the variability of Σ ANs in the boundary layer is largely determined by the daytime products of isoprene oxidation, partly attributed to the short lifetimes in both Σ ANs and HCHO.

[31] Σ ANs and ozone are coproduced from $RO_2 + NO$ reactions, so that one would expect a strong correlation between the two [Flocke *et al.*, 1991; Horowitz *et al.*, 2007; Ito *et al.*, 2009]. This correlation has been used to constrain

ozone production efficiency and photochemical aging in urban conditions [Farmer *et al.*, 2011; Perring *et al.*, 2010; Rosen *et al.*, 2004]. We find that the observed correlation in ICARTT (Figure 7) is reproduced by GEOS-Chem. Similar to Σ ANs versus HCHO, this correlation (slope = 82.0 ± 9.0) cannot be reproduced by the model using the fast isomerization of ISOPO₂ (slope = 154.0 ± 6.0).

[32] The yield of first-generation nitrates (11.7%) in our mechanism is considerably higher than the yield derived by Horowitz *et al.* [2007]. Using the same observational data set, they found that Σ ANs versus ozone correlation can best match their model with 4% yield of isoprene nitrates. With 8% yield, they overestimated boundary layer Σ ANs by 40%. This can be attributed to their assumption that secondary organic nitrates are inert and the slow $RO_2 + HO_2$ rate used. In fact, a large fraction of secondary nitrates in our model, such as ETHLN and MACRN (Figure 3), can degrade in a matter of hours returning NO_x , with little contribution to Σ ANs.

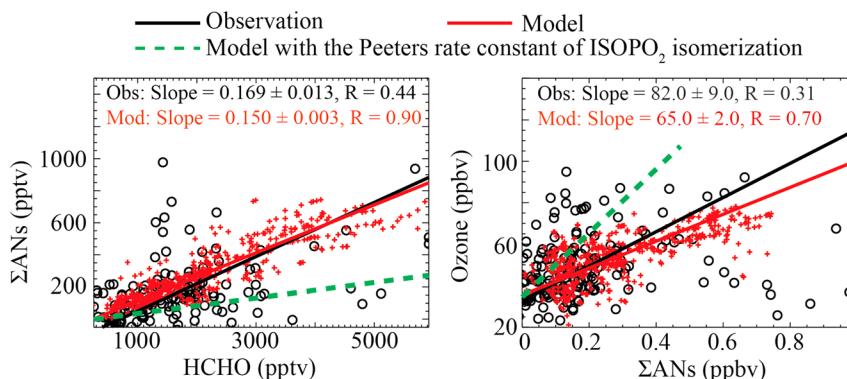


Figure 7. (left) Σ ANs versus HCHO and (right) ozone versus Σ ANs correlations in the continental boundary layer (<1.5 km) during ICARTT. Model results (red) are compared to observations from the DC-8 aircraft (black). Solid lines are the reduced major axis regression lines. Also shown is the model with a higher rate constant for ISOPO₂ isomerization following Peeters *et al.* [2009] (green dashed lines).

Table 1. NO_y Budget in Eastern U.S. Boundary Layer for July 2004^a

Species	Emission	Chemical (P-L)	Dry Deposition	Wet Deposition	Net Export
NO_x	386	-337	44	-	5
PANs ^b		24	13	-	11
ΣANs					
ANs ^c		18	7.4	3.6	7
R_4N_2 ^d		10	0.5	-	10
HNO_3		277	180	110	-3

^aWe define the eastern U. S. boundary layer as 62.5°–97.5°W, 24°–52°N and from the surface to approximately 1.8 km altitude (below 800 hPa). Budget terms are in Gg N.

^bPANs include peroxyacetyl nitrate (PAN), peroxyacetyl nitrate (PMN), and peroxypropionyl nitrate (PPN).

^cANs include δ -hydroxyl isoprene nitrates (ISOPND), β -hydroxyl isoprene nitrates (ISOPNB), methacrolein nitrates (MACRN), methylvinylketone nitrates (MVKN), propanone nitrate (PROPNN), and ethanal nitrate (ETHLN).

^dNighttime isoprene oxidation contributes to 80% of R_4N_2 production.

[33] Secondary organic nitrates from daytime and nighttime isoprene oxidation provide an important mechanism for exporting NO_x from the U.S. boundary layer. We show in Table 1 that nitrogen is more efficiently exported as ΣANs than as PAN, partly due to their longer photochemical lifetimes. The chemical lifetime of some speciated alkyl nitrates (such as ETHLN, PROPNN, MVKN, MACRN) are largely dependent on one chamber study from *Paulot et al.* [2009a], while others (such as R_4N_2) are highly simplified into one lumped species as very few experimental data are

available on the degradation of nighttime isoprene oxidation products. Further experimental work is warranted on both daytime and nighttime organic nitrates.

5. Ozone-CO Correlation

[34] Observations in polluted regions show positive ozone-CO correlations in summer, and these correlations can be related to the ozone production efficiency per unit NO_x emitted (OPE) through the NO_x/CO emission ratio [*Horowitz et al.*,

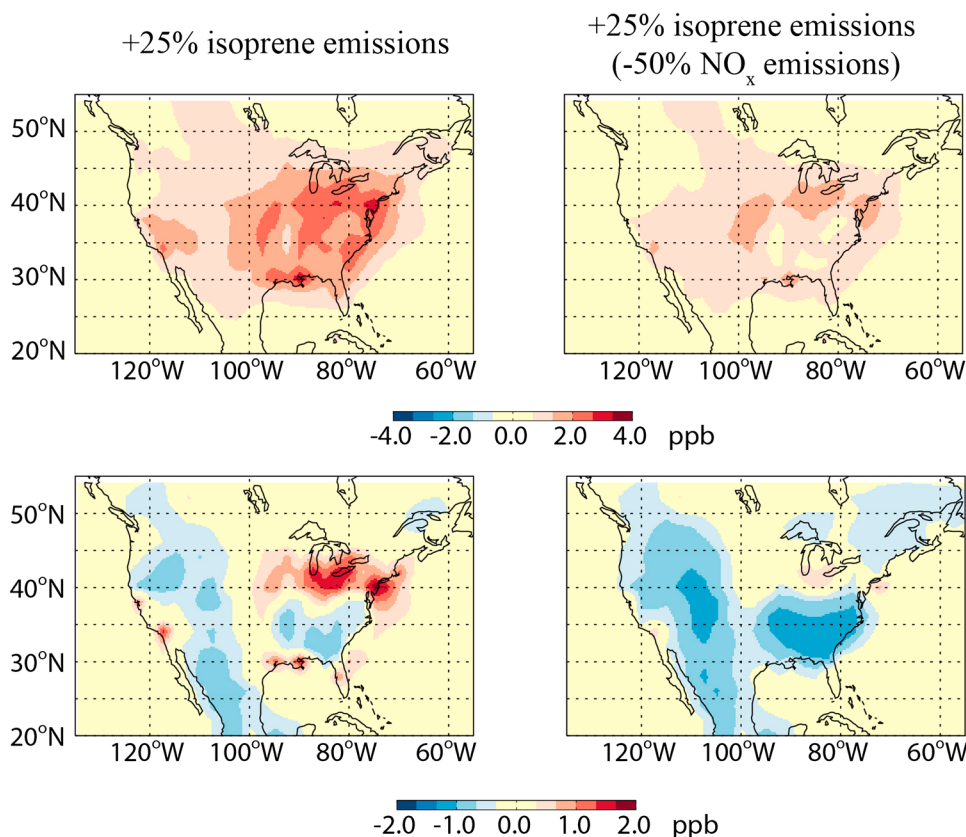


Figure 8. Computed change of mean afternoon (1300–1700 LT) surface ozone concentrations during July 2004 as a result of increasing isoprene emissions by 25% at different levels of anthropogenic NO_x emissions. The top row uses the isoprene oxidation mechanism in this work, and the bottom row uses the isoprene chemistry applied in *Zhang et al.* [2011] that assumed a high yield of isoprene nitrates (18%) without recycling of NO_x . The base simulations for the left column are for the model simulation at current level of anthropogenic NO_x emissions, and the base simulations for the right column are for the model simulation with 50% reduction of current anthropogenic NO_x emissions.

1998; Hudman *et al.*, 2009]. Chin *et al.* [1994] reported a regression slope (dO_3/dCO) of 0.28–0.32 mol mol⁻¹ at three eastern U.S. sites in 1988–1992. Parrish *et al.* [1998] reported dO_3/dCO of 0.28–0.40 for 1991–1994 at four sites in Atlantic Canada. Hudman *et al.* [2009] found higher observed dO_3/dCO of 0.41–0.46 in the continental boundary layer during ICARTT, reflecting decadal changes in U.S. CO and NO_x emissions as well as an apparent increase in the OPE. Their GEOS-Chem simulation indicated a smaller dO_3/dCO (0.34–0.36), likely due to an excessive yield of isoprene nitrates as discussed above.

[35] Figure 4 (bottom right) shows our simulated ozone-CO correlations for the boundary layer DC-8 aircraft flight tracks (0–1.5 km altitude) in the afternoon (1100–1700 LT) compared to observations. The dO_3/dCO value is determined by the slope of the reduced-major-axis regression line, with errors determined by nonparametric bootstrap resampling. The observations indicate $dO_3/dCO = 0.43 \pm 0.03$, as previously reported by Hudman *et al.* [2009], but here the relationship is better reproduced by the model (0.39 ± 0.02), reflecting the new isoprene mechanism as well as HO₂ aerosol uptake (lowering OH and thus increasing the lifetime of NO_x). The slope degrades to 0.33 in a sensitivity simulation using the Peeters *et al.* [2009] rate constant of ISOPO₂ isomerization, mainly due to a faster oxidation of NO_x through higher OH.

6. Sensitivity of Surface Ozone to Isoprene Emissions

[36] Isoprene emissions may change rapidly on decadal time scales due to ecosystem evolution and changes in forestry practices [Guenther *et al.*, 2006; Heald *et al.*, 2009; Purves *et al.*, 2004; Wu *et al.*, 2012]. Understanding the effect of these changes in isoprene emission is critical for air quality management. Models disagree even in the sign of the response of summertime surface ozone in the eastern U.S. to isoprene emissions, varying from a decrease [Fiore *et al.*, 2005; Wu *et al.*, 2012; Wu *et al.*, 2008] to an increase [Horowitz *et al.*, 1998; Sanderson *et al.*, 2003]. This has been attributed to the discrepancies between models in the yield of isoprene nitrates [Wu *et al.*, 2007], NO_x recycling efficiency from isoprene nitrates [Ito *et al.*, 2009], and the relative magnitude of isoprene and NO_x emissions [Fiore *et al.*, 2005].

[37] Figure 8 shows our computed change of mean afternoon (1300–1700 LT) surface ozone concentrations during July 2004 as a result of increasing current isoprene emissions by 25% in the model. At current level of anthropogenic NO_x emissions (for the year of 2004), we find an ozone increase of 2–4 ppbv with the new implemented isoprene mechanism (top left). When anthropogenic NO_x emissions are reduced to 50% of current level, we find that the sensitivity of ozone to increasing isoprene emissions is reduced by about a factor of 2 (top right). Reduction of NO_x emission to 25% of current level shows further decrease of the ozone sensitivity to isoprene emission (not shown), although the sensitivity does not become negative. With the isoprene chemistry applied in Zhang *et al.* [2011] that assumed a high yield of isoprene nitrates (18%) without recycling of NO_x, we find similar negative sensitivity of ozone to isoprene emissions (Figure 8, bottom), consistent with previous model studies as described above. This reflects in part the importance of isoprene ozonolysis as a sink for ozone under low-NO_x

conditions because of OH titration [Fiore *et al.*, 2005; Mickley *et al.*, 2001]. As pointed out above, such OH titration by isoprene in models appears inconsistent with observations. Nevertheless, our work indicates that reducing anthropogenic NO_x emissions to improve ozone air quality significantly reduces the sensitivity of ozone to isoprene emissions.

7. Conclusions

[38] We implemented a state-of-science isoprene chemistry mechanism in GEOS-Chem, based on Paulot *et al.* [2009a, 2009b], along with other updates. This mechanism was evaluated with observations from the NASA DC8 and NOAA WP3D aircraft during the ICARTT campaign over the eastern U.S. in the summer of 2004.

[39] Models have a general tendency to overestimate surface ozone in the eastern U.S. [Fiore *et al.*, 2009]. The previous GEOS-Chem simulation of Zhang *et al.* [2011] was unbiased relative to observations, but it assumed an excessive yield of isoprene nitrates serving as terminal sinks for NO_x. Our improved representation of isoprene chemistry increases ozone over the eastern U.S. by 3–5 ppbv, and this is compensated by other model improvements including bromine chemistry and HO₂ loss to aerosols. Thus, the GEOS-Chem ozone simulation remains unbiased relative to observations, in the boundary layer as well as in the free troposphere. Simulation of the observed ozone-CO correlation is improved relative to previous versions of GEOS-Chem, and this is attributed to the reduced yield of isoprene nitrates.

[40] ICARTT observations of total organic nitrates other than PANs (Σ ANs) are well reproduced in the model, including vertical profiles and correlations with HCHO and ozone. This provides a sensitive test of the isoprene oxidation mechanism and argues in particular against a fast isomerization pathway for the ISOPO₂ radical. Σ ANs in the model is mainly composed of secondary organic nitrates, including a large fraction from nighttime oxidation of isoprene. These secondary nitrates provide an important pathway for exporting NO_x from the U.S. boundary layer, exceeding the export of PANs. Better understanding of nighttime oxidation of isoprene and of the fate of the resulting organic nitrates is needed.

[41] Our improved representation of isoprene chemistry yields a positive dependence of ozone on isoprene emissions throughout the U.S., in contrast to previous model studies that found a negative dependence particularly in the southeastern U.S. We attribute this difference to OH titration by isoprene in previous models, promoting ozone loss by isoprene ozonolysis. Our new mechanism avoids this OH titration, for which observations show no evidence. Nevertheless, we find that the sensitivity of ozone to isoprene emissions decreases as NO_x emissions decrease. This may have important implications for air quality management as well as for understanding ozone concentrations in the preindustrial atmosphere.

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