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

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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 ICARTT 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 HO$_2$ 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 (OPE) per unit of nitrogen oxides (NO$_x$ ≡ NO + NO$_2$). The model successfully reproduces the observed concentrations of organic nitrates ($\Sigma$ANs) and their correlations with HCHO and ozone. $\Sigma$ANs in the model is principally composed of secondary isoprene nitrates, including a major contribution from nighttime isoprene oxidation. The correlations of $\Sigma$ANs with HCHO and ozone then provide sensitive tests of isoprene chemistry and argue in particular against a fast isomerization channel for isoprene peroxy radicals. $\Sigma$ANs can provide an important reservoir for exporting NO$_x$ from the US boundary layer. We find that the dependence of surface ozone on isoprene emission is positive throughout the US, 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.
1. Introduction

Isoprene (2-methyl-1,3-butadiene), the most important nonmethane volatile organic compound (NMVOC) emitted by vegetation, affects tropospheric ozone, OH (the main tropospheric oxidant), and aerosols in complex ways. It has a lifetime of about one hour against oxidation by OH. The resulting oxidation products lead to the formation of ozone, an effective greenhouse gas and air pollutant. Isoprene also reacts with the nitrate radical (NO$_3$) at night, with important implications for global budget of nitrogen oxides (NO$_x$ = NO + NO$_2$) and therefore ozone. 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 ICARTT aircraft campaign provided a detailed characterization of boundary layer chemistry across the isoprene-rich eastern US 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 SOA precursors.

Daytime oxidation of isoprene is initialized by its reaction with OH, leading to the production of peroxy radicals (ISOPO$_2$). In the presence of NO$_x$, ISOPO$_2$ reacts with NO leading to the production of organic nitrates by a minor branch. These nitrates may act as a sink for both HO$_x$ (HO$_x$ = H + OH + peroxy radicals) and NO$_x$, and therefore affect global and regional ozone budgets (von Kuhlmann et al., 2004; Fiore et al., 2005; Horowitz et al., 2007; Wu et al., 2007; Ito et al., 2009; Perring et al., 2009a; Paulot et al., 2012; Xie et al., 2012). Laboratory data indicate a yield of first-generation organic nitrates from isoprene oxidation ranging from 7% to 12% (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\textsubscript{x} upon further oxidation, leading to further complication in their role as a sink or reservoir for NO\textsubscript{x} (Horowitz et al., 2007; Ito et al., 2009; Paulot et al., 2009a; Perring et al., 2009a; Paulot et al., 2012). They may serve as nitrogen reservoir to export boundary layer NO\textsubscript{x} to rural and remote atmospheres (Atlas, 1988; Horowitz et al., 1998; Neff et al., 2002).

In the absence of NO\textsubscript{x}, ISOPO\textsubscript{2} is assumed in standard mechanisms to be converted to organic hydroxperoxides 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; Tan et al., 2001; Thornton et al., 2002; Lelieveld et al., 2008; Ren et al., 2008; Hofzumahaus et al., 2009; Pugh et al., 2010; Stone et al., 2010; Whalley et al., 2011). 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\textsubscript{2} based on theoretical studies (Peeters et al., 2009; Peeters and Müller, 2010). Measurements of OH concentrations by the standard Laser Induced Fluorescence (LIF) technique may be biased high due to internally generated OH from oxidation of biogenic 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\textsubscript{2} (Crounse et al., 2011) are included in the model.
Besides daytime oxidation, nighttime oxidation of isoprene by NO$_3$ contributes significantly to the budget of organic nitrates (von Kuhlmann et al., 2004; Horowitz et al., 2007; Xie et al., 2012). 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., 2009b; 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).

Isoprene chemistry is of particular importance in affecting summertime ozone over the eastern US (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 US by 10-20 ppb (Murazaki and Hess, 2006; Yu et al., 2007; Lin et al., 2008; Fiore et al., 2009; Yu et al., 2010; Rasmussen et al., 2012). Fiore et al. (2005) suggested that this problem might be due to incorrect representation of isoprene sources and chemistry.

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 US 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., 2009a; Warneke et al., 2010). Previous analyses of isoprene chemistry using ICARTT data have been presented by Horowitz et al. (2007), Perring et al. (2009a), and Xie et al. (2012) with a focus on isoprene nitrates, and by Stavrakou et al. (2010) with a focus on HO$_x$. 
A number of previous studies have applied GEOS-Chem to simulation of the ICARTT data, including evaluation with observations of NO\textsubscript{x} and ozone (Hudman et al., 2007; Liang et al., 2007; Hudman et al., 2009), CO (Turquety et al., 2007; Hudman et al., 2008), HCHO (Millet et al., 2006) and aerosols (Heald et al., 2006; Fu et al., 2009; Drury et al., 2010). In particular, Hudman et al. (2007) found that the lightning NO\textsubscript{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 US Environmental Protection Agency (EPA). Hudman et al. (2009) indicated no significant bias in their simulation of ozone over the eastern US 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\textsubscript{x}.

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

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 (GMAO) (Bey et al., 2001). We apply here GEOS-Chem version 9-01-03 (http://www.geos-chem.org) to simulation of the ICARTT period (July 1st - Aug 15th 2004). The GEOS-5 meteorological data have 6-h temporal resolution (3-h for surface variables and mixing depths) with 0.5° × 0.667° horizontal resolution and 72 vertical layers from the surface to 0.01 hPa. We regrid here the meteorological data to 2° × 2.5° for input to GEOS-Chem. The model is initialized with a 1-year simulation from June 2003 to June 2004 with 4° × 5° resolution, and from June 2004 on with 2° × 2.5° resolution. Boundary layer mixing in GEOS-Chem uses the non-local 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).

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

Anthropogenic emission inventories in GEOS-Chem include EPA NEI-05 for the US, CAC for Canada (http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), BRAVO for Mexico (Kuhns et al., 2005), 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 US...
CO emissions based on atmospheric observations (Parrish, 2006; Miller et al., 2008; Miller et al., 2012; LaFranchi et al., 2013). For the rest of the world we use the EDGAR emission inventory for CO, NO\textsubscript{x}, and SO\textsubscript{2} (Olivier and Berdowski, 2001), and the RETRO emission inventory for volatile organic compounds (VOCs) (Schultz et al., 2007). All anthropogenic emissions are scaled to 2004 based on energy statistics (van Donkelaar et al., 2008).

Lightning NO\textsubscript{x} emissions are calculated as a function of GEOS-5 cloud top height and rescaled to match OTD/LIS climatological observations (Murray et al., 2012). The global lightning source is imposed to be 6 Tg N yr\textsuperscript{-1} (Martin et al., 2007), with higher NO\textsubscript{x} yields per flash at mid-latitudes than in the tropics (Hudman et al., 2007). We use monthly biomass burning emissions from the Global Fire Emission Database version 3 (GFED-v3) (van der Werf et al., 2010). Forest fire plumes transported from Alaska and western Canada were important in the free troposphere during ICARTT (Turquety et al., 2007; Pfister et al., 2008). Soil NO\textsubscript{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).

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 $1.7 \times 10^{6}$ M atm\textsuperscript{-1} and $1.3 \times 10^{8}$ M atm\textsuperscript{-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.

The standard GEOS-Chem simulation of ozone-NOx-HOx-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 suggested by Mao et al. (2013). We also increased the NO3 aerosol reactive uptake coefficient $\gamma$ from $1 \times 10^{-4}$ (Jacob, 2000) to 0.1, as suggested by recent laboratory and field studies (Gross et al., 2009; Tang et al., 2010; Fry et al., 2011; Brown and Stutz, 2012; Lee et al., 2013). The treatment of isoprene oxidation is described in the following subsection.

2.2 Chemical mechanism for isoprene oxidation

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-NOx regime mainly follows Paulot et al. (2009a). It is initialized by OH addition at 1 and 4 positions, resulting in a pool of $\beta$ and $\delta$-hydroxyl peroxy radicals (ISOPO2) with yields of 71% and
29% respectively. In the presence of NO\textsubscript{x}, the degradation of $\beta$-hydroxyl ISOPO\textsubscript{2} leads to the production of HCHO (66%), methylvinylketone (MVK) (40%) and methacrolein (MACR) (26%) with a small yield of $\beta$-hydroxyl isoprene nitrates (ISOPNB) (6.7%). Reaction of $\delta$-hydroxyl ISOPO\textsubscript{2} with NO leads to the formation of $\delta$-hydroxyl isoprene nitrates (ISOPND) (24%). The total first-generation isoprene nitrates 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.

Under low NO\textsubscript{x} conditions, ISOPO\textsubscript{2} can follow either of two pathways. One is to react with HO\textsubscript{2} to form isoprene hydroxyperoxides (ISOPOOH) with a small production of HCHO, MVK and MACR (4.7%, 7.3%, 12% respectively) (Paulot et al., 2009b), largely consistent with a recent study by Liu et al. (2012). Most of ISOPOOH reacts with OH to produce epoxidiols and quantitatively regenerate OH (Paulot et al., 2009b). Another pathway is the unimolecular isomerization of ISOPO\textsubscript{2} (1,6-H shift) (Peeters et al., 2009; Peeters and Müller, 2010), 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 (Da Silva et al., 2010; Crounse et al., 2011). The rate constant of 1,6-H shift isomerization is still under debate (Peeters et al., 2009; Peeters and Müller, 2010; Crounse et al., 2011). We adopt the rate constant from Crounse et al. (2011), which is lower than the original one from Peeters et al. (Peeters et al., 2009; Peeters and Müller, 2010) 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.
The subsequent fate of ISOPND and ISOPNB is mainly via reactions with OH and ozone because of the remaining C=C bond. Paulot (2009a) suggested that ISOPND and ISOPNB have photochemical lifetimes against oxidation by OH of 1h and 7h respectively (OH=3×10^6 molecule cm^{-3} at 298 K). Lockwood et al. (2010) suggested photochemical lifetimes against oxidation by ozone of 2h and 4h respectively (ozone = 60 ppbv), which is 5-10 times shorter than the previous value suggested by Giacopelli 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 h, 2 h, 9 h against oxidation by OH (OH=3×10^6 molecule cm^{-3} at 298 K), and PROPNN is mainly lost through photolysis with a global mean lifetime of 13 d in GEOS-Chem. The degradation of these secondary organic nitrates is assumed to return NO_x with a yield of 55% (Paulot et al., 2009a).

Nighttime isoprene oxidation is updated from Xie et al.(2012), 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 (R₄N₂), which has a global mean lifetime of 5 d
against OH oxidation and photolysis in GEOS-Chem.

Several additional updates are included in this new mechanism. First, we implemented
the isomerization of methacrolein peroxy radicals (MACRO₂) based on experiments by
Crounse et al. (2012). Second, we updated the reaction rate of HO₂ with > C₂ peroxy
radicals to the expression in Saunders et al. (2003), leading to an increase of factor 2 for
HO₂ + ISOPO₂ at 298 K. Third, we updated OH regeneration for the reactions of HO₂
with acetyl peroxy (CH₃C(O)O₂) and acetonyl peroxy (CH₃C(O)CH₂O₂) radicals based
on laboratory measurements (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley,
2008). 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

Here we use the ICARTT observations to evaluate our new isoprene oxidation
mechanism implemented in GEOS-Chem. 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 US,
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 (CH₃CN > 225 ppt or HCN > 425 ppt or NO₂ > 4 ppb or NOₓ/NOy > 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 ozone/CΟ > 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. Almost all of the data were collected between 08:00 and 18:00 local time.

Figure 4 (top panels) 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 (lower left panel). The model largely captures the spatial pattern of boundary layer ozone, but with a relatively low correlation, likely due to the inaccuracy in locating point emission sources. The model overestimates boundary layer ozone in the Southeast US 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).

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), HNO$_3$, NO$_x$, and MVK+MACR concentrations measured by the aircraft and simulated by the model. The spatial distributions of summertime HCHO, CO, and NO$_x$ over the eastern US during ICARTT have been examined in previous GEOS-Chem studies (Millet et al., 2006; Hudman et al., 2007; Hudman et al., 2008). 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.
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 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 et al., 2009; Peeters and Müller, 2010) we find mean MVK + MACR concentrations of 100 pptv in the boundary layer, much lower than observed.

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 US (Horowitz et al., 1998) as well as observed correlations with other peroxyacylnitrates (Williams et al., 1997).

The most recent previous evaluation of the GEOS-Chem ozone simulation over the US 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\textsubscript{x} (section 2.2), (2) inclusion of tropospheric bromine chemistry (Parrella et al., 2012), (3) heterogeneous loss of HO\textsubscript{x} radicals (Mao et al., 2013), and (4) correction of the diurnal cycle of NO\textsubscript{x} emissions. For the eastern US boundary layer and free troposphere in summer, (1) causes a 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. 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

Perring et al. (2009a) made measurements of total organic nitrates other than peroxyacylnitrates (RONO\textsubscript{2}, hereinafter \(\Sigma\text{ANs}\)) aboard the DC-8 during ICARTT. As \(\Sigma\text{ANs}\) 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 \(\Sigma\text{ANs}\) data has been presented previously in several studies. Perring et al. (2009a) found good correlation between observed HCHO and \(\Sigma\text{ANs}\) in the boundary layer. Horowitz et al. (2007) found that the vertical profile of \(\Sigma\text{ANs}\) and the ozone-\(\Sigma\text{ANs}\) correlation could be best reproduced by a 4% yield of isoprene nitrates with 40% recycling efficiency. Xie et al. (2012) applied the treatment of isoprene nitrates from Paulot et al. (2009a) to the CMAQ regional air quality.
model, but they find an overestimate of $\Sigma$ANs by 30% in their model. We here examine organic nitrates and their relationship with HCHO and ozone in GEOS-Chem.

Figure 6 shows the mean vertical profile of $\Sigma$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. (2012), we show very little overestimation of $\Sigma$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 $\Sigma$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 $\Sigma$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 $\Sigma$ANs, as ISOPND is mainly oxidized by OH. A sensitivity simulation using the fast isomerization of ISOPO$_2$ (Peeters et al., 2009; Peeters and Müller, 2010) produces less than 100 pptv $\Sigma$ANs in the boundary layer.

We see from Figure 6 that $\Sigma$ANs in the model is mainly contributed by the second generation of isoprene nitrates, i.e., PROPNN, MVKN+MACRN and R$_4$N$_2$ (Figure 2). 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 $\Sigma$ANs is contributed by the longer-lived R$_4$N$_2$ and PROPNN species. Oxidation of isoprene by NO$_3$ accounts for 80% of R$_4$N$_2$ in the model, emphasizing the need for better understanding of this chemistry (Grossenbacher et al., 2001; Brown et al., 2009; Beaver et al., 2012; Kwan et al., 2012).
Perring et al. (2009a) pointed out that the observed HCHO - $\sum$ANs correlation provides an additional constraint on the bulk yield of isoprene nitrates, due to the co-production of HCHO and $\sum$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 ISOPO$_2$ (Peeters et al., 2009) underestimates the $\sum$ANs yield. Despite the large fraction of R$_4$N$_2$ in $\sum$ANs, we find that the variability of $\sum$ANs in boundary layer is largely determined by the daytime products of isoprene oxidation.

$\sum$ANs and ozone are co-produced 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 (Rosen et al., 2004; Perring et al., 2010; Farmer et al., 2011). We find that the observed correlation in ICARTT (Figure 7) is reproduced by GEOS-Chem. Similar to $\sum$ANs vs. HCHO, this correlation cannot be reproduced by the model using the fast isomerization of ISOPO$_2$.

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 dataset, they found that $\sum$ANs vs. ozone correlation can best match their model with 4% yield of isoprene nitrates. With 8% yield, they overestimated boundary layer $\sum$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 ETLHN and MACRN (Figure 3), can degrade in a matter of hours returning NO$_x$, with little contribution to $\sum$ANs.
Secondary organic nitrates from daytime and nighttime isoprene oxidation provide an important mechanism for exporting NOx from the US boundary layer. We show in Table 1 that nitrogen is more efficiently exported as \( \sum \) ANs than as PAN, partly due to their longer photochemical lifetimes. Long-range transport of \( \sum \) ANs is supported by measurements of \( \geq C_3 \) alkyl nitrates in rural and remote atmospheres (Atlas, 1988; Russo et al., 2010).

5. Ozone – CO correlation

Observations in polluted regions show positive ozone-CO correlations in summer, and these correlations can be related to the ozone production efficiency per unit NOx emitted (OPE) through the NOx/CO emission ratio (Horowitz et al., 1998; Hudman et al., 2009). Chin et al. (1994) reported a regression slope \( \frac{dO_3}{dCO} \) of 0.28-0.32 mol mol\(^{-1}\) at three eastern U.S. sites in 1988-1992. Parrish et al. (1998) reported \( \frac{dO_3}{dCO} \) of 0.28-0.40 for 1991-1994 at four sites in Atlantic Canada. Hudman et al. (2009) found higher observed \( \frac{dO_3}{dCO} \) of 0.41-0.46 in the continental boundary layer during ICARTT, reflecting decadal changes in U.S. CO and NOx emissions as well as an apparent increase in the OPE. Their GEOS-Chem simulation indicated a smaller \( \frac{dO_3}{dCO} \) (0.34 – 0.36), likely due to an excessive yield of isoprene nitrates as discussed above.

The bottom right panel of Figure 4 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 \( \frac{dO_3}{dCO} \) value is determined by the slope of the reduced-major-axis regression line, with errors determined by nonparametric bootstrap resampling. The observations indicate \( \frac{dO_3}{dCO} = 0.43 \pm 0.03 \), 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 NOₓ). 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 NOₓ through higher OH.

6. Sensitivity of surface ozone to isoprene emissions

Isoprene emissions may change rapidly on decadal time scales due to ecosystem evolution and changes in forestry practices (Purves et al., 2004; Guenther et al., 2006; Heald et al., 2009; 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 US to isoprene emissions, varying from a decrease (Fiore et al., 2005; Wu et al., 2008; Wu et al., 2012) 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), NOₓ recycling efficiency from isoprene nitrates (Ito et al., 2009) and the relative magnitude of isoprene and NOₓ emissions (Fiore et al., 2005).

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 NOₓ emissions (for the year of 2004), we find an ozone increase of 2 – 4 ppbv with the new implemented isoprene mechanism (top left panel). When anthropogenic NOₓ 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 panel). Reduction of NOx 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 NOx, we find similar negative sensitivity of ozone to isoprene emissions (bottom panels in Figure 8), consistent with previous model studies as described above. This reflects in part the importance of isoprene ozonolysis as a sink for ozone under low-NOx conditions because of OH titration (Mickley et al., 2001; Fiore et al., 2005). As pointed out above, such OH titration by isoprene in models appears inconsistent with observations. Nevertheless, our work indicates that reducing anthropogenic NOx emissions to improve ozone air quality significantly reduces the sensitivity of ozone to isoprene emissions.

7. Conclusions

We implemented a state-of-science isoprene chemistry mechanism in GEOS-Chem, based on Paulot et al. (2009a) and Paulot et al. (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 US in the summer of 2004. Models have a general tendency to overestimate surface ozone in the eastern US (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 NOx. Our improved representation of isoprene chemistry increases ozone over the eastern US 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 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.

ICARTT observations of total organic nitrates other than PANs ($\sum$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 ISOPO$_2$ radical. $\sum$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 US 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.

Our improved representation of isoprene chemistry yields a positive dependence of ozone on isoprene emissions throughout the US, in contrast to previous model studies that found a negative dependence particularly in the southeastern US. 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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Figures and Tables

Table 1 NO\textsubscript{x} budget in eastern U.S. Boundary Layer for July 2004

<table>
<thead>
<tr>
<th>Species</th>
<th>Emission</th>
<th>Chemical (P-L)</th>
<th>Dry Deposition</th>
<th>Wet Deposition</th>
<th>Net Export</th>
</tr>
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<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>386</td>
<td>-337</td>
<td>44</td>
<td>-----</td>
<td>5</td>
</tr>
<tr>
<td>PANs\textsuperscript{a}</td>
<td>24</td>
<td>13</td>
<td>-----</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>ΣANs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANs \textsuperscript{b}</td>
<td>18</td>
<td>7.4</td>
<td>3.6</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{4}N\textsubscript{2} \textsuperscript{c}</td>
<td>10</td>
<td>0.5</td>
<td>-----</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>277</td>
<td>180</td>
<td>110</td>
<td>-3</td>
<td></td>
</tr>
</tbody>
</table>

We 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 GgN.

\textsuperscript{a} PANs include peroxyacetyl nitrate (PAN), peroxymethacryloyl nitrate (PMN) and peroxypropionyl nitrate (PPN).

\textsuperscript{b} ANs include δ-hydroxyl isoprene nitrates (ISOPND), β-hydroxyl isoprene nitrates (ISOPNB), methacrolein nitrates (MACRN), methylvinylketone nitrates (MVKN), propanone nitrate (PROPNN) and ethanal nitrate (ETHLN).

\textsuperscript{c} Nighttime isoprene oxidation contributes to 80% of R\textsubscript{4}N\textsubscript{2} production.
Figure 1 Schematic of the first stage of the isoprene oxidation mechanism initiated by OH.
Figure 2 Schematic of the oxidation of isoprene nitrates by OH following Paulot et al. (2009a).
Figure 3 Partial schematic of isoprene oxidation by NO$_3$ following Rollins et al. (2009) and Xie et al. (2012).
Figure 4 Ozone concentrations and ozone-CO correlations in the boundary layer (0 – 1.5 km) during ICARTT (July 1 – August 15, 2004). The top panels show observed and simulated values averaged over the 2° × 2.5° GEOS-Chem grid. The bottom left panel is a model vs. observed scatterplot of these values. The bottom right panel shows 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 (July 1st-Aug 15th 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).
Figure 6 Left panel: mean vertical profiles of total organic nitrates excluding peroxycylnitrates ($\sum$ANs) during ICARTT (July 1st-Aug 15th 2004) over land (Figure 4). Observations (black) are compared to GEOS-Chem (red). Right panel: contributions of individual species to mean $\sum$ANs in GEOS-Chem including $\beta$-hydroxyl isoprene nitrates (ISOPNB), $\delta$-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.
Figure 7 (left) ∑ANs vs. HCHO and ozone vs. ∑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).
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 NOx emissions. The top panels use the isoprene oxidation mechanism in this work, and the bottom panels use the isoprene chemistry applied in Zhang et al. (2011) that assumed a high yield of isoprene nitrates (18%) without recycling of NOx.
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