Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States

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[1] Reducing surface ozone (O\textsubscript{3}) to concentrations in compliance with the national air quality standard has proven to be challenging, despite tighter controls on O\textsubscript{3} precursor emissions over the past few decades. New evidence indicates that isoprene emissions changed considerably from the mid-1980s to the mid-1990s owing to land-use changes in the eastern United States (Purves et al., 2004). Over this period, U.S. anthropogenic VOC (AVOC) emissions decreased substantially. Here we apply two chemical transport models (GEOS-CHEM and MOZART-2) to test the hypothesis, put forth by Purves et al. (2004), that the absence of decreasing O\textsubscript{3} trends over much of the eastern United States may reflect a balance between increases in isoprene emissions and decreases in AVOC emissions. We find little evidence for this hypothesis; over most of the domain, mean July afternoon (1300–1700 local time) surface O\textsubscript{3} is more sensitive (ranging from −9 to +7 ppbv) to the reported changes in anthropogenic NO\textsubscript{x} emissions than to the concurrent isoprene (−2 to +2 ppbv) or AVOC (−2 to 0 ppbv) emission changes. The estimated magnitude of the O\textsubscript{3} response to anthropogenic NO\textsubscript{x} emission changes, however, depends on the base isoprene emission inventory used in the model. The combined effect of the reported changes in eastern U.S. anthropogenic plus biogenic emissions is insufficient to explain observed changes in mean July afternoon surface O\textsubscript{3} concentrations, suggesting a possible role for decadal changes in meteorology, hemispheric background O\textsubscript{3}, or subgrid-scale chemistry. We demonstrate that two major uncertainties, the base isoprene emission inventory and the fate of isoprene nitrates (which influence surface O\textsubscript{3} in the model by −15 to +4 and +4 to +12 ppbv, respectively), preclude a well-constrained quantification of the present-day contribution of biogenic or anthropogenic emissions to surface O\textsubscript{3} concentrations, particularly in the high-isoprene-emitting southeastern United States. Better constraints on isoprene emissions and chemistry are needed to quantitatively address the role of isoprene in eastern U.S. air quality.


1. Introduction

[2] Despite more than 3 decades of efforts to improve U.S. air quality, widespread attainment of the national ambient air quality standard for surface ozone (O\textsubscript{3}) smog remains elusive, with over 100 million Americans living in counties exceeding the O\textsubscript{3} standard in 2002 [United States Environmental Protection Agency (U.S. EPA), 2004]. High O\textsubscript{3} concentrations in surface air are produced by rapid photochemical oxidation of volatile organic compounds (VOC) in the presence of nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}). Over the past decades, legislation enacted to reduce surface O\textsubscript{3} has led to substantial decreases in anthropogenic non-methane VOC (AVOC) emissions (Figure 1). Over much of the eastern United States, however, isoprene (the most abundant and highly reactive biogenic VOC; C\textsubscript{5}H\textsubscript{8}) plays a critical role in surface O\textsubscript{3} formation [Trainer et al.,

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Levy et al. [1991]. In rural areas with low NOx emissions, O3 production is typically NOx-sensitive, and largely insensitive to VOC emissions (as occurs in the tropics [von Kuhlmann et al., 2004]).

The strongly nonlinear isoprene-NOx-O3 chemistry complicates efforts to quantify the isoprene-O3 relationship, particularly in light of large uncertainties in isoprene emission inventories [Roselle, 1994; Sillman, 1999] (see also reviews by Fehsenfeld et al. [1992] and Fuentes et al. [2000]). Another major source of uncertainty is the chemistry and ultimate fate of the organic nitrates and peroxy radicals produced during isoprene oxidation [e.g., Horowitz et al., 1998; Liang et al., 1998]. Von Kuhlmann et al. [2004] summarize the various representations of isoprene nitrates and peroxydes in chemical transport models and show that different assumptions lead to substantial regional discrepancies in the surface O3 concentrations simulated with chemical transport models.

The current generation of isoprene emission schemes in chemical transport models assumes a static vegetation distribution and corresponding base isoprene emission. Temporal grid-scale variability is driven by fluctuations in temperature, photosynthetically active radiation, and leaf area [Guenther et al., 1995; Pierce et al., 1998]. Purves et al. [2004], however, found that deciduous changes in forest structure and species composition over the eastern United States had a substantial impact on isoprene (and monoterpene) emissions, which is not accounted for in current inventories. For example, the dramatic increases in isoprene in Alabama from the mid-1980s to the mid-1990s (Figure 1a) are associated with the growth of high monoterpenic-emitting pine plantations, which inadvertently provide a suitable habitat for high isoprene-emitting sweetgum [Purves et al., 2004].

In this study, we use two chemical-transport models to compare the impact on surface O3 from the reported isoprene (Figure 1a) and anthropogenic O3 precursor (Figures 1b–1d) emission changes with the observed O3 changes over the same period (section 3). We then examine the influence of precursor emissions changes on the occurrence of high-O3 events, which are relevant for public health and for compliance with the national O3 standard (section 4). Finally, we demonstrate the sensitivity of our surface O3 simulations to uncertainties in isoprene emissions and chemistry (section 5).

2. Model Description and Evaluation

We employ several model simulations (Table 1) to quantify the sensitivity of O3 to reported changes in precursor emissions, as well as to uncertainties in isoprene emissions and chemistry. Most of these simulations are conducted with a 1° × 1° regionally nested version of the GEOS-CHEM tropospheric chemistry model for North
Table 1. Simulations Used in This Work

<table>
<thead>
<tr>
<th>Model</th>
<th>Simulation Name</th>
<th>Base Year for Isoprene Inventory*</th>
<th>Year for Anthropogenic Inventories*</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEOS-CHEM (1° × 1°; GMAO 2001 meteorology)</td>
<td>(G/P) STD</td>
<td>mid-1980s</td>
<td>1995</td>
</tr>
<tr>
<td></td>
<td>(G/P)A5B95</td>
<td>mid-1990s</td>
<td>1995</td>
</tr>
<tr>
<td></td>
<td>(G/P)A85B95</td>
<td>mid-1990s</td>
<td>1995</td>
</tr>
<tr>
<td></td>
<td>(G/P)ISOP25</td>
<td>mid-1980s reduced by 25%</td>
<td>1995</td>
</tr>
<tr>
<td></td>
<td>(G/P)NOx25</td>
<td>mid-1980s</td>
<td>1995 NOx reduced by 25%</td>
</tr>
<tr>
<td>MOZART-2 (1.9° × 1.9°; NCEP 2001 meteorology)</td>
<td>MOZSTD</td>
<td>mid-1980s</td>
<td>1995</td>
</tr>
<tr>
<td></td>
<td>MOZB95</td>
<td>MOZSTD with mid-1990s</td>
<td>moznit with early 1990s</td>
</tr>
<tr>
<td></td>
<td>MOZNIT</td>
<td>MOZSTD with isoprene nitrates</td>
<td>MOZSTD with isoprene peroxides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acting as a NOx sink</td>
<td>acting as a HOx sink</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(section 2.2)</td>
<td>(section 2.2)</td>
</tr>
<tr>
<td></td>
<td>MOZPER</td>
<td>MOZSTD with isoprene peroxides</td>
<td>MOZSTD with isoprene peroxides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acting as a HOx sink</td>
<td>acting as a HOx sink</td>
</tr>
<tr>
<td></td>
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<td>(section 2.2)</td>
<td>(section 2.2)</td>
</tr>
</tbody>
</table>

*See Table 2 for emission totals. The standard GEIA isoprene inventory is considered to be representative of the mid-1980s.

†Two sets of simulations using different isoprene inventories are conducted with GEOS-CHEM: one with GEIA ("G") and one with the Purves ("P"). The MOZART-2 simulations use only the GEIA isoprene inventory.

‡Standard is labeled as such for consistency with prior work [e.g., Bey et al., 2001; Horowitz et al., 2003].

America (section 2.1). We then use the global MOZART-2 model (section 2.2) to test the robustness of our conclusions to the assumptions inherent in any one chemical-transport model. We further use MOZART-2 to assess the impact of uncertainties concerning the fate of isoprene nitrates and peroxides on our results.

2.1. GEOS-CHEM

[6] We apply a 1° × 1° one-way nested version of the GEOS-CHEM three-dimensional tropospheric NOx-O3-CO-hydrocarbon chemical transport model coupled to aerosol chemistry (v. 5-07-08; http://www-as.harvard.edu/chemistry/trop/geos/geos_mech.html) [Bey et al., 2001; Park et al., 2004] for the North American domain (10°N–60°N, 40°W–140°W) [Wang et al., 2004; Li et al., 2005]. GEOS-CHEM is driven by assimilated meteorological fields from the NASA Global Modeling Assimilation Office (GMAO), provided every 6 hours (3 hours for surface fields) at 1° × 1° horizontal resolution on 48 vertical levels (9 levels below 2 km and an average vertical grid spacing of 1.1 km in the free troposphere). These fields are available from 1999 to 2003. The meteorological year 2001 is chosen for our study since we have previously shown that the 2001 O3 simulation captures much of the day-to-day variability observed at rural monitoring stations in the United States [Fiore et al., 2003a].

[10] We degrade the 1° × 1° fields to a horizontal resolution of 4° × 5° for the global model, which we spin up for a full year. The resulting concentrations provide initial and 3-hour boundary conditions to the 1° × 1° domain. We further spin up the 1° × 1° domain for June of 2001 and present results for July. A 1-month initialization is sufficient to identify the sensitivity of regional O3 changes to changes in local emissions given the regional domain and rapid summertime photochemistry. Surface temperature anomalies for July 2001 versus the 1971–2000 mean obtained from the NOAA-CIRES Climate Diagnostics Center (http://www.cdc.noaa.gov/USclimate/USeclimdivs.html) indicate that temperatures for July 2001 were: a few degrees cooler than the climatology in the eastern United States; typical in the southern and midwestern states (along the Mississippi and Ohio River valleys); and a few degrees warmer than the mean in western Texas, Oklahoma, and Kansas (not shown).

[11] The GEOS-CHEM chemical mechanism provides a relatively detailed treatment of isoprene oxidation [Horowitz et al., 1998; Bey et al., 2001; Palmer et al., 2003], including HOx radical recycling from alkene ozonolysis [Paulson and Seinfeld, 1992; Aschmann and Atkinson, 1994] (for the current GEOS-CHEM mechanism, see http://www-as.harvard.edu/chemistry/trop/geos/geos_mech.html). Most relevant to our study is the treatment of the organic nitrates and peroxides produced during isoprene oxidation (see section 1). The GEOS-CHEM chemical mechanism produces isoprene nitrates with an approximate yield of 12% following the reaction of isoprene with OH [Sprenger et al., 2002]. The isoprene nitrates are converted directly to nitric acid [Bey et al., 2001] based upon the conclusion of Chen et al. [1998] that isoprene nitrate production permanently removes NOx from the atmosphere. Organic peroxides react with OH or recycle HOX radicals via photolysis as noted by Horowitz et al. [1998].

[12] Global emissions in the standard GEOS-CHEM simulation (GSTD) are described by Bey et al. [2001], with recent updates by Martin et al. [2002], Park et al. [2004], and Xiao et al. [2004]. Anthropogenic emissions are based upon work by Wang et al. [1998] and scaled, typically on a national basis, to the simulation year (1995 in our case) [Bey et al., 2001]. Most relevant for our study are the anthropogenic NOx emissions, taken from the Global Emission Inventory Activity (GEIA), which include the 1985 National Acid Precipitation Assessment Program inventory for the United States [Kahl et al., 1996]. The GEIA isoprene emissions in GEOS-CHEM are widely used in global tropospheric chemistry models [e.g., Horowitz et al., 1998; Horowitz et al., 2003; von Kuhlmann et al., 2004] and are generally calculated from a static base distribution upon which temporal fluctuations associated with temperature, light, and leaf area are imposed according to Guenther et al. [1995]. Wang et al. [1998] and Bey et al. [2001] provide details on the implementation of this temporal variability in GEOS-CHEM. Annual isoprene emissions in GSTD are 490 Tg C; eastern U.S. emissions for July are 5.9 Tg C (Table 2, Figure 2a). For our study, we implement a second isoprene emission inventory ("Purves") and modify biogenic (both GEIA and Purves inventories) and anthropogenic emissions (AVOC, CO, and NOx) to represent emissions in the mid-1980s and mid-1990s.
Table 2. July Emissions in the Eastern United States (24.5°N–51.5°N; 66.5°W–104.5°W)\(^a\)

<table>
<thead>
<tr>
<th>Isoprene,(^b) Tg C</th>
<th>Anthropogenic</th>
<th>Isoprene,(^b) Tg C</th>
<th>Anthropogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Year</strong></td>
<td>GEIA</td>
<td>PURVES</td>
<td>NMHC,(^c) Tg C</td>
</tr>
<tr>
<td>GEOS-CHEM mid-1980s</td>
<td>5.9</td>
<td>3.0</td>
<td>0.94</td>
</tr>
<tr>
<td>mid-1990s</td>
<td>6.5</td>
<td>3.2</td>
<td>0.80</td>
</tr>
<tr>
<td>MOZART-2 mid-1980s</td>
<td>5.0(^d)</td>
<td>–</td>
<td>0.20</td>
</tr>
<tr>
<td>early 1990s</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)See section 2 for details.

\(^b\)GEIA inventory fills in where the Purves inventory lacks data (i.e., white regions in Figure 1).

\(^c\)This comprises C\(_2\)H\(_4\), C\(_3\)H\(_6\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), and C\(_4\)H\(_10\) in MOZART-2; C\(_2\)H\(_6\), C\(_3\)H\(_8\), lumped \(\geq C\(_3\)\) alkenes and \(\geq C\(_4\)\) alkanes in GEOS-CHEM.

\(^d\)This increases to 5.6 Tg C when the changes in Figure 1a are applied.

2.1.1. Modifications to Isoprene Emissions

[13] We use the “Purves” isoprene emission inventory for July in the eastern United States (Figure 2b) to test the sensitivity of our results to uncertainties in current isoprene emissions inventories. This inventory is described in detail by Purves et al. [2004] and summarized here. First, a base rate for isoprene emission per unit leaf area is assigned to each tree species in the eastern U.S. Forest Inventory Analysis (FIA). A leaf area is calculated for each tree in the FIA database (over 2.7 million trees). This information is used, in conjunction with the light and temperature algorithms from Guenther et al. [1993] and a simple model of the within-canopy distribution of light and temperature driven by 6-hour 1990 ECMWF meteorological fields interpolated to an hourly resolution, to estimate mean July isoprene emissions for each tree. Results are then aggregated to a 1° × 1° grid. The Purves isoprene emission inventory can be calculated for either the mid-1980s or the mid-1990s, using the appropriate FIA data. In our Purves inventory simulations (denoted “P” in Table 1), we scale the GSTD July mean isoprene emissions in each grid cell to match the magnitude of the mid-1980s or mid-1990s July mean isoprene emissions from the Purves et al. [2004] inventory for that grid cell. With this approach, the July mean and spatial distribution of isoprene emissions is that of Purves et al. [2004], but the simulated hourly variability reflects the model meteorology, as is the case for the GEIA inventory. Outside of the region covered by the Purves inventory (the colored domain in Figure 1) we continue to use the GEIA inventory, which yields high emissions in western Texas (Figures 2a and 2b).

[14] We assume that the standard GEIA isoprene emission inventory is representative of the mid-1980s and compare with the mid-1980s Purves inventory in Figure 2. Both isoprene inventories predict maximum emissions in the southeastern United States. The Purves emissions are generally a factor of 2 lower than the GEIA emissions, pointing to a major uncertainty in the magnitude of isoprene emissions, particularly when compared to the 30% interannual variability in isoprene emissions estimated by Abbot et al. [2003]. The Purves inventory is similar both in spatial pattern and in magnitude to the Biogenic Emissions Inventory System (BEIS2) [Pierce et al., 1998], a biogenic emissions inventory commonly used in regional models, which also incorporates FIA data [Kinnee et al., 1997]. Previous comparisons with in situ observations suggest that BEIS2 isoprene emissions are too low [Pierce et al., 1998; Kang et al., 2003, Palmer et al., 2003]. The BEIS2 emissions over North America in July 1996 (2.6 Tg C) are about half of those derived from space-based measurements of formaldehyde columns (5.7 Tg C), whereas the GEIA isoprene emissions are 20% higher (7.1 Tg C) [Palmer et al., 2003], although uncertainties remain in the satellite estimates. Thus the discrepancies between the isoprene inventories used in this study are a fair representation of the current level of uncertainty in isoprene emissions from the eastern United States.

[15] To apply the changes in biogenic emissions reported by Purves et al. [2004], we calculate the ratio of the mid-1990s to the mid-1980s July mean Purves isoprene emissions for each 1° × 1° grid cell (Figure 1a). We then use these ratios to scale the mid-1980s GEIA emissions to obtain mid-1990s GEIA isoprene emissions. Thus the same percentage difference between the mid-1980s and mid-1990s isoprene emissions is applied to each grid cell in the GEIA and Purves inventories, but the absolute change is larger in the GEIA inventory since the GEIA emissions are higher (Figure 2 and Table 2).

Figure 2. Emissions (10\(^{11}\) molecules cm\(^{-2}\)) of isoprene from the (a) GEIA (b) Purves et al. [2004], and (c) anthropogenic NO\(_x\) inventories in GEOS-CHEM, and (d) the difference in July mean afternoon (1300–1700 LT) surface O\(_3\) (ppbv) resulting from application of the Purves et al. [2004] isoprene inventory versus GEIA (PSTD–GSTD in Table 1). The color bar for NO\(_x\) emissions saturates (maximum is 8). See color version of this figure at back of this issue.
2.1.2. Modifications to Anthropogenic Emissions

[16] For consistency with previous GEOS-CHEM simulations, we retain the standard 1995 GEOS-CHEM anthropogenic emissions for our “A95” simulations in Table 1. In order to simulate the regional changes in U.S. anthropogenic emissions from 1985 to 1995, we take county-specific CO, VOC, and NOx emissions for 1985 and 1995 from the U.S. Environmental Protection Agency (EPA) national emissions inventory (NEI) (http://www.epa.gov/air/data/geosel.html), grid them to 1° x 1° resolution (following Purves et al. [2004]), and apply the ratio of 1995 to 1985 emissions (Figures 1b – 1d) to produce anthropogenic emissions for 1985. For consistency with the reported isoprene trends, we only change anthropogenic emissions for the region examined by Purves et al. [2004] (Figure 1). [17] Eastern U.S. anthropogenic emissions totals for July are provided in Table 2. Total anthropogenic CO, A VOC, and NOx emission changes from 1985 to 1995 in the EPA NEI were –19%, –16%, and +10%, respectively, for the FIA domain (colored regions in Figure 1), as compared to –23%, –17%, and +5% when we apply the ratios in Figure 1 to the GEOS-CHEM anthropogenic emissions. Discrepancies reflect differences between the U.S. emissions distributions for 1995 in the standard GEOS-CHEM anthropogenic emissions inventory and the EPA NEI. While anthropogenic CO and VOC emissions decreased over most of the eastern United States during this time, changes in NOx emissions were much less regionally coherent. The reported overall increase in NOx emissions mainly reflects changes in area sources (responsible for 70% of the total domain-wide changes in NOx emissions). The patchy effect in Figure 1d to the west of 85°W is almost entirely driven by changes in point source emissions but includes some combination from changes in both area and point sources to the east of 85°W. Aircraft campaigns have shown good agreement with reported power plant NOx emissions [Trainer et al., 2000, and references therein], but substantial uncertainties exist in road-traffic (area) NOx emissions as reported in the EPA inventories [Parrish et al., 2002]. Our study, however, will focus on the uncertainties in biogenic isoprene emissions.

2.1.3. Evaluation of the Surface O3 Simulation

[18] GEOS-CHEM has been evaluated extensively with observations of O3 and related species, both globally [Bey et al., 2001], and in various world regions [e.g., Li et al., 2005; Wang et al., 2004]. The nested 1° x 1° model over North America was recently applied to identify North American outflow pathways for CO, O3, and aerosols [Li et al., 2005]. Prior evaluations of O3 simulations over the United States show that GEOS-CHEM adequately captures much of the spatial and temporal variability in summer afternoon O3 concentrations [Fiore et al., 2002, 2003a, 2003b] as well as the observed distribution of CH2O, an intermediate product of isoprene oxidation [Palmer et al., 2003; Martin et al., 2004].

[19] Synoptic meteorology is responsible for much of the observed variability in surface O3 concentrations [Logan, 1989; Eder et al., 1993; Oltmans and Levy, 1994; Vukovich, 1995, 1997]. In Figure 3, we compare our GSTD simulation (Table 1) with observations from the EPA Aerometric Information Retrieval System (AIRS) O3 monitoring stations for July 2001. We focus on afternoon hours, when O3 concentrations tend to peak, and when the observations should represent a relatively deep mixed layer which is most suitable for model evaluation [Fiore et al., 2002]. The model captures nearly half of the spatial variance of the mean July afternoon observations (r2 = 0.40; reduced major axis (RMA) slope = 1.0 [Hirsch and Gilroy, 1984] (see also Davis [1986] for a detailed description of RMA regression method, which allows for uncertainty in both variables) with a mean model bias of 6 ± 7 ppbv. Consistent with earlier GEOS-CHEM evaluations [Fiore et al., 2002, 2003b], the model severely overestimates O3 concentrations in Florida and along the Gulf of Mexico. The high-O3 feature over eastern Texas and southern Oklahoma in the model, and to some extent in the observations, is associated with warm July mean temperatures (27°–29°C) and high NOx and isoprene emissions (Figure 2). The model overestimate in the Ohio River valley (Figure 3) may be associated with controls on power plant NOx emissions that were implemented in 1999 [Frost et al., 2004] and are not reflected in the 1995 GEOS-CHEM anthropogenic NOx emissions inventory used here. The PSTD simulation (not shown) gives a lower mean July afternoon O3 bias (4 ± 8 ppbv) but captures less of the spatial variance (r2 = 0.29; RMA slope = 1.0).

2.2. MOZART-2

[20] We use a second global tropospheric chemistry model, MOZART-2 [Horowitz et al., 2003] to test the robustness of our results to different meteorological drivers and chemical mechanisms. In particular, we take advantage of the easily modified MOZART-2 chemical mechanism to examine the sensitivity of surface O3 to the uncertain fate of isoprene nitrates and peroxides (see section 5.2).

[21] The version of MOZART-2 applied here is driven with NCEP reanalysis meteorological fields for 2001 at T62 horizontal resolution (~1.9°) and 28 vertical levels. Emissions are intended to represent the early 1990s and are described in detail by Horowitz et al. [2003]. July emissions totals for the eastern United States are given in Table 2. Although total CO and NMHC emissions are lower in MOZART-2 than in GEOS-CHEM, this discrepancy should not affect our conclusions since isoprene is the dominant hydrocarbon contributing to the largely NOx-sensitive O3 production over the eastern United States in July, the only month considered in our study. Isoprene emissions are based on the GEIA inventory, as in GEOS-CHEM, but are applied in MOZART-2 as a monthly mean emission rate upon which a diurnal cycle is imposed. Thus the MOZART-2 isoprene emissions do not respond to day-to-day fluctuations in the model meteorology. The lower isoprene emissions from the GEIA inventory in MOZART-2 than in GEOS-CHEM (Table 2) presumably reflect differences in the implementation of the GEIA inventory in the two models [Wang et al., 1998; Horowitz et al., 2003].

[22] MOZART-2 also employs a detailed isoprene-NOx-O3 chemical mechanism, which includes an 8% yield of isoprene nitrates from the isoprene-OH reaction [Carter and Atkinson, 1996]. In contrast to GEOS-CHEM, isoprene nitrates in the standard MOZART-2 model (MOZSTD in Table 1) recycle NOx via reaction with OH, based upon the assumption that OH reaction is a more important loss
mechanism than deposition [e.g., Shepson et al., 1996]. We modify the mechanism to produce isoprene nitrates with a 12% yield from reaction of isoprene-derived RO2 with NO [Sprengnether et al., 2002] and treat them as a NOx sink by converting them directly to nitric acid (MOZNIT) as in GEOS-CHEM. The MOZART-2 mechanism also recycles HOx radicals via photolysis of isoprene peroxides (similar to GEOS-CHEM); we examine the impact of this recycling on surface O3 by turning off this photolysis and instead permitting isoprene peroxides to be a sink for HOx (MOZPER).

3. Surface O3 Response to Recent Precursor Emissions Trends

3.1. Biogenic Isoprene

[23] The simulated changes in mean July afternoon (1300–1700 local time (LT)) surface O3 concentrations due to the changes in isoprene emissions (Figure 1a), for both the GEIA and the Purves cases, are shown in Figures 4a and 4b. There is little change in O3 concentrations in the northern half of the domain. Surprisingly, the large increases in isoprene emissions in the southern states of Arkansas, northern Louisiana, Mississippi, and Alabama decrease O3 by 1–2 ppbv in the GEIA-based simulation (Figure 4a). In this region, isoprene emissions are already high (Figure 2a) and NOx emissions are low (Figure 2c). Under these conditions, isoprene ozonolysis is an important sink for O3 (Table 3), and the higher isoprene emissions in the mid-1990s increase the size of this sink.

[24] In contrast, the Purves-based simulation in Figure 4b shows only slight O3 decreases (<0.5 ppbv) in the southern states when the BVOC changes are applied. Increases in O3 concentrations of up to 2 ppbv occur in northeastern Texas where NOx emissions are high (Figure 2c) and the rise in isoprene emissions (Figure 1a) leads to enhanced O3 formation. With the GEIA inventory, O3 concentrations show no response in northeastern Texas, presumably because the higher base-case GEIA isoprene emissions have pushed the chemistry of O3 formation to a NOx-sensitive chemical regime where additional VOCs have little influence [e.g., Sillman et al., 1990a; Kang et al., 2003].

[25] We also apply the changes in isoprene emissions in Figure 1a to a version of MOZART-2 in which isoprene nitrates are converted directly to nitric acid (as is done in GEOS-CHEM). Figure 4c shows that the isoprene increases (applied to the GEIA inventory; see section 2.2) in the southeastern United States decrease surface O3 by 1–2 ppbv.

Figure 3. Mean afternoon (1300–1700 LT) O3 concentrations (ppbv) in surface air over the eastern United States in July 2001: (a) U.S. EPA AIRS observations averaged over a 0.5° latitude by 0.5° longitude grid, (b) GEOS-CHEM model surface layer (GSTD in Table 1), (c) correlation, and (d) difference between GSTD and the AIRS observations averaged over the 1° × 1° model grid. The correlation coefficient (r) and the reduced-major-axis (RMA) slope (m) are given, along with the 1:1 line (solid line) and the RMA best fit line (dotted line). See color version of this figure at back of this issue.
in MOZART-2, similar to the O₃ response obtained in GEOS-CHEM with GEIA emissions. This result is sensitive to the fate of isoprene nitrates as discussed further in section 5.2.

3.2. Anthropogenic NOₓ, VOC, and CO

The changes in anthropogenic emissions from 1985 to 1995 increase O₃ concentrations over much of the southeastern United States by up to 3 and 7 ppbv for the Purves- and GEIA-based GEOS-CHEM simulations, respectively (Figures 4d and 4e). The simulated O₃ responses to changes in biogenic versus anthropogenic emissions offset each other to some extent in eastern Texas with the Purves isoprene inventory (Figures 4b and 4e) and in the southeastern United States with the GEIA isoprene inventory (Figures 4a and 4d). Sensitivity simulations (not shown) with increased anthropogenic NOₓ, CO, and VOC emissions relative to the baseline simulations show increased O₃ responses, particularly in eastern Texas and the southeastern United States. The color bar saturates for the observed changes, which range from −21 to +21. Simulations are given in Table 1. See color version of this figure at back of this issue.

Table 3. Near-Surface O₃ Lifetime (days) Against Selected Photochemical Loss Pathways in the Southeastern United States

| Simulation (Table 1) | Reaction with OH, HO₂, or CH₃O₂ | Photolysis (OH production) | Reaction with Biogenics
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>GSTD</td>
<td>16</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>GISOP25</td>
<td>17</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>GNOx25</td>
<td>17</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>PSTD</td>
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<td>11</td>
<td>58</td>
</tr>
<tr>
<td>PISOP25</td>
<td>18</td>
<td>11</td>
<td>87</td>
</tr>
<tr>
<td>PN Ox25</td>
<td>19</td>
<td>11</td>
<td>49</td>
</tr>
</tbody>
</table>

*Lifetime is the spatial average for 30.5°N–37.5°N and 81.5°W–91.5°W (encompassing Georgia, Alabama, Mississippi, Tennessee, Arkansas, and northern Louisiana), calculated from the column sum of the simulated 24-hour mean July O₃ concentration and chemical loss rates in the bottom seven model boxes (~1.3 km altitude).

*This includes isoprene, other biogenic alkenes, methylvinylketone, methacrolein, peroxyacetyl nitrate, and isoprene aldehydes.
shown), however, indicate that our results in Figures 4d and 4e are largely driven by the changes in NOx emissions (Figure 1d), as expected for the highly NOx-sensitive eastern United States [Sillman, 1999, and references therein]. For example, decreases of up to 9 and 6 ppbv, which occur in eastern Texas for the GEIA- and Purves-based simulations (Figures 4d and 4e), respectively, are associated with decreases in NOx emissions (Figure 1). Consistent with earlier modeling studies [Roselle, 1994], the simulated response to anthropogenic NOx changes depends upon the distribution and magnitude of isoprene emissions, with O3 are observed throughout Illinois and Wisconsin, along 1985–1996 [Karamchandani et al., 1999, and references there-

3.3. Comparison With Observed O3 Changes

In this section, we assess whether the reported emissions changes explain the observed trends in O3 from the mid-1980s to the mid-1990s. We use hourly observations from the U.S. EPA Aerometric Information Retrieval System (EPA AIRS) to calculate the change in mean July afternoon O3 concentrations from the mid-1980s (1983–1987 mean) to the mid-1990s (1993–1997 mean), shown in Figure 4h. Averaging over 5 years reduces the influence of meteorology-driven inter-annual variability. The resulting changes in surface O3 are consistent with previously reported trends for observed O3 concentrations from 1985–1996 [Wolff et al., 2001]. Widespread decreases in O3 are observed throughout Illinois and Wisconsin, along the northeast corridor, and in several of the southern states. Smaller regions of increases occur in the midwest, Tennessee, and Florida.

Consistent with the observed changes, Figures 4f (GEIA case) and 4g (Purves case) show O3 decreases along the northeast corridor, and over eastern Illinois (especially the Purves case), eastern Texas, Arkansas, and Louisiana, and O3 increases over Tennessee. Overall, however, the spatial pattern of the simulated changes (Figures 4f and 4g) differs substantially from those observed (Figure 4h; r2 ~ 0.0 for both GEIA- and Purves-based simulations). We conclude that the anthropogenic and biogenic emission changes considered here are insufficient to explain the observed O3 trends.

The disagreement between simulated and observed O3 changes suggests that other factors, not considered in this study, may have contributed to the O3 changes from the mid-1980s to the mid-1990s. One possibility is that the 1° x 1° horizontal resolution of the GEOS-CHEM model is too coarse to resolve power plant or urban plume chemistry. In particular, the dispersal of NOx emissions over a coarse Eulerian grid cell could result in higher O3 production efficiency (per molecule of NOx emitted). Indeed, Sillman et al. [1990b] showed that degrading horizontal resolution from 20 to 80 km yielded 7–10 ppbv increases in rural O3 concentrations. Results from regional models incorporating subgrid-scale plume models, however, indicate little net change in surface O3 over the northeastern United States despite substantial changes in local O3 concentrations (within 50–200 km radii of the point source), since local increases offset local decreases [Kumar and Russell, 1996; Karamchandani et al., 2002]. The inability to resolve high-

4. Ozone Sensitivity to Anthropogenic NOx and
   Biogenic Isoprene Emissions

4.1. Diagnosing the O3 Chemical Regime

The chemical O3 formation regime is typically determined with modeling studies where anthropogenic NOx and anthropogenic VOC are reduced separately by a uniform percentage. Whichever precursor control strategy yields the larger decrease in O3 concentrations is deemed to be the “limiting” or “sensitive” precursor for O3 production. Here we extend this approach to examine whether O3 formation is more sensitive to NOx or to biogenic isoprene emissions. We conduct four sensitivity simulations in which we reduce biogenic isoprene and anthropogenic NOx emissions by 25%, separately, for both the GEIA and Purves isoprene inventories. Figures 5a and 5b show the changes in surface O3 resulting from 25% decreases in isoprene emissions for the GEIA- and Purves-based simulations, respectively. Larger O3 responses are seen for the GEIA-based simulation and its correspondingly larger isoprene emission perturbation. Figure 5a shows that in the southeastern states, decreases in the GEIA isoprene emissions lead to higher O3 concentrations. In GSTD, the high isoprene concentrations react directly with O3 (Table 3) and remove NOx from the atmosphere (as isoprene nitrates), suppressing O3 production. The region of largest
O₃ decreases is farther south along the Ohio River valley in the Purves-based simulation (Figure 5b) as compared to the GEIA-based simulation (Figure 5a), reflecting the smaller Purves isoprene emissions in the midwest (Figure 2). In the Purves case, the reduced isoprene emissions translate into lower O₃ concentrations in the vicinity of NOₓ sources. In contrast to the GEIA case, little change in O₃ concentrations occurs over the high-isoprene-emitting southeastern region (Figure 5b), where the chemical regime is transitioning from one in which additional isoprene (or any VOC) will increase O₃ to one in which additional isoprene will decrease O₃ [Kang et al., 2003].

The O₃ response to 25% reductions in anthropogenic NOₓ emissions (Figures 5c and 5d) is highly dependent on the base isoprene emission inventory. The larger O₃ decreases in the GEIA-based simulation reflect the stronger NOₓ-sensitivity associated with the higher isoprene concentrations; decreases in NOₓ further decrease OH, which competes with O₃ for reaction with isoprene. These results indicate that quantifying the uncertainties in isoprene emissions is critical, as the nonlinear chemical interactions of isoprene, NOₓ, and O₃ will affect conclusions drawn about O₃ sensitivity to anthropogenic emission controls [Roselle, 1994].

Table 3 compares the importance of selected photochemical O₃ loss mechanisms in the southeastern region. Loss of O₃ via reaction with biogenic compounds is as large as the typical major photochemical O₃ loss pathways (photolysis and reaction with HOₓ radicals) in the GEIA-based simulations. For the Purves-based simulations, the much lower isoprene emissions prevent this pathway from being an important O₃ loss mechanism. Thus, given our present understanding, estimates of the contribution of various pathways to the regional photochemical O₃ sink over the southern United States will depend strongly upon the assumed isoprene and NOₓ emissions.

4.2. Sensitivity of High-O₃ Events

Figure 6 shows the impact of the emissions perturbations discussed above on high-O₃ events (defined here as O₃ > 70 ppbv) from selected simulations, plotted as a function of the surface O₃ in the corresponding base-case simulation. Decreases in isoprene emissions reduce nearly all high-O₃ events for the Purves case while decreases in GEIA isoprene emissions lead to some increases in high-O₃ events, particularly in the southeastern United States, for the reasons discussed in sections 3.1 and 4.1. All high-O₃ events respond strongly to NOₓ controls, but the magnitude of this response depends critically upon the isoprene emission inventory. In regions such as the southeastern United States, where isoprene concentrations are sufficiently high in the GEIA-based simulation, isoprene ozonolysis amplifies the O₃ decrease achieved with a given NOₓ reduction.

For the most extreme events (O₃ > 90 ppbv) in Figures 6f and 6h (Purves-based simulations), the anthropogenic and biogenic emission changes from the mid-1980s to the mid-1990s (Figure 1) yield responses that are opposite in sign. These events occur over eastern Texas (see Figures 4b and 4e) where increased isoprene emissions in the mid-1990s tend to increase O₃ but lower anthropogenic VOC, CO, and NOₓ emissions tend to decrease O₃. For most of the points in Figures 6e–6h, the changes in BVOC emissions between the mid-1980s and mid-1990s have a smaller impact on surface O₃ concentrations (<5 ppbv) than the changes in anthropogenic emissions over the same period (up to 15 ppbv). While the magnitude of the O₃ response to the decadal changes in the biogenic isoprene emissions is small for both the GEIA and Purves inventories, the response often differs in sign: reducing O₃ concentrations over the eastern United States when the GEIA emissions are used, while increasing O₃ concentrations when the Purves emissions are used. Our current understanding of the impact of isoprene emissions on regional air quality is thus insufficient to conclusively determine whether changes in isoprene emissions from the mid-1980s to the mid-1990s have mitigated or exacerbated O₃ pollution over the eastern United States. The uncertainty in the fate of isoprene nitrates is of particular relevance here, as discussed further in section 5.

5. Uncertainty Analysis: Implications for Quantifying Surface O₃

5.1. Isoprene Emissions

July mean afternoon O₃ concentrations change by −15 to +4 ppbv when the Purves isoprene inventory is substituted for the GEIA inventory in GEOS-CHEM (Figure 2d). The difference in O₃ associated with the choice of isoprene inventory is thus larger than the O₃ response to the reported emissions changes over much of the domain (Figure 4), pointing to a substantial source of uncertainty in our current generation of models. As discussed previously (section 4.1), the differences in the midwest and northeast regions occur because NOₓ emissions are high (Figure 2) and the Purves inventory predicts little isoprene. In the southern states, the GEIA inventory leads to lower O₃.
concentrations than the Purves inventory because the high GEIA-generated isoprene concentrations remove NO$_x$ (through isoprene nitrates) and deplete OH concentrations, enabling isoprene to react directly with O$_3$ (see Table 3 and section 4.1).

5.2. Isoprene-NO$_x$-O$_3$ Chemistry: Fate of Isoprene Nitrates and Peroxides

We test here the impact of uncertainties in the fate of isoprene nitrates on surface O$_3$ in the MOZART-2 model by conducting two simulations where (1) isoprene nitrates are produced with an 8% yield and permitted to recycle NO$_x$ to the atmosphere (MOZSTD) and (2) isoprene nitrates are considered a permanent sink for NO$_x$ and converted directly to nitric acid with a 12% yield (MOZNIT; as in section 3.1 and in the GEOS-CHEM mechanism). The results in Figure 7a show that O$_3$ concentrations over the eastern United States decrease by 4–12 ppbv when isoprene nitrates are considered to be a NO$_x$ sink. This result is consistent with previous findings by Horowitz et al. [1998], Liang et al. [1998], and von Kuhlmann et al. [2004].

We further use MOZART-2 to test the sensitivity of the results in Figure 4c (MOZB95-MOZNIT) to the chemistry of isoprene nitrates. In contrast to those results, we find that the increases in isoprene emissions (Figure 1a) have little influence on surface O$_3$ over the southeastern United States when isoprene nitrates recycle to NO$_x$ (not shown).
due to the emission changes with observed O₃ trends from surface O₃ (Figure 7b), although it is similar in magnitude smaller, a 1–2 ppbv decrease in July mean afternoon isoprene oxidation and whether they recycle HOₓ via organic peroxides formed during isoprene oxidation (MOZPER-MOZSTD). Simulations are described in Table 1.

Conclusions

We conclude that our earlier finding that isoprene ozonolysis may be an important photochemical O₃ loss pathway in the southeastern United States (section 4.1) is only true if isoprene nitrates are a sink for NOₓ (as is the case for GSTD in Table 3).

A second uncertainty in isoprene-O₃-NOₓ chemistry concerns the fate of the organic peroxides produced during isoprene oxidation and whether they recycle HOₓ via photolysis or serve as a net HOₓ sink [von Kuhlmann et al., 2004]. The sensitivity of O₃ to this uncertainty is smaller, a 1–2 ppbv decrease in July mean afternoon surface O₃ (Figure 7b), although it is similar in magnitude to the response due to the decadal changes in isoprene emissions (section 3). Results from a recent analysis of field measurements are consistent with the recycling of HOₓ through organic peroxides as included in the current GEOS-CHEM and MOZART-2 mechanisms; Thornton et al. [2002] conclude that either the formation rate of these organic peroxides is presently too high by a factor of 3–12 or they are rapidly photolyzed and serve only as a temporary reservoir of HOₓ.

We thus find in our model that the largest uncertainties in determining the contribution of isoprene to surface O₃ over the eastern United States stem from the choice of isoprene inventory and the fate of isoprene nitrates. Resolving these uncertainties is critical as they influence simulated base-case O₃ concentrations, as well as the magnitude, and in some cases the sign, of the simulated O₃ response to changes in precursor emissions.

6. Conclusions

We have investigated the hypothesis that substantial increases in eastern U.S. isoprene emissions from the mid-1980s to the mid-1990s may have offset decreases in surface O₃ associated with concurrent reductions in anthropogenic VOC [Purves et al., 2004]. With MOZART-2 and a 1° × 1° North American nested version of the global GEOS-CHEM tropospheric chemistry model, we examined the impact of the reported biogenic and anthropogenic (AVOC, CO, and NOₓ) emission changes on surface O₃ over this period. We then compared the simulated O₃ response due to the emission changes with observed O₃ trends from the EPA AIRS network. A suite of sensitivity simulations enabled us to characterize the sensitivity of surface O₃ to changes in precursor emissions.

The simulated O₃ responses to biogenic versus anthropogenic emissions offset each other to some extent in eastern Texas with the Purves isoprene inventory (Figures 4b and 4e) and in the southeastern United States with the GEIA isoprene inventory (Figures 4a and 4d). Over most of the eastern United States, however, we find that the influence of the reported anthropogenic NOₓ emissions changes on surface O₃ outweighs that from the increases in isoprene emissions from the mid-1980s to the mid-1990s. Our lack of success in simulating the observed changes in mean July afternoon surface O₃ concentrations suggests a possible role for decadal meteorology changes (and its influence on isoprene emissions), global precursor emission trends or sub-grid plume chemistry, none of which were considered in this study. Inaccuracies in the reported emission trends (particularly NOₓ emissions from road traffic [Parrish et al., 2002]) and uncertainties in isoprene emissions and chemistry may also preclude an accurate attribution of observed O₃ trends to precursor emission changes. Furthermore, we find that the estimated efficacy of anthropogenic NOₓ emission controls on simulated O₃ depends strongly upon the chosen isoprene emission inventory, consistent with prior studies [e.g., Roselle, 1994].

The magnitude of the O₃ sensitivity to uncertainties in isoprene emissions and chemistry is similar to or greater than the simulated O₃ response to the reported emissions changes, biogenic or anthropogenic. Surface O₃ concentrations differ by −15 to +4 ppbv over the eastern United States when the Purves et al. [2004] isoprene emissions inventory (similar to BEIS-2) is substituted for the GEIA inventory. An additional 4–12 ppbv uncertainty stems from assumptions regarding the fate of isoprene nitrates. Uncertainties in organic peroxide chemistry have a smaller impact on surface O₃ (<3 ppbv). These uncertainties translate into a major uncertainty in the magnitude, and in some cases the sign, of the O₃ response to changes in precursor emissions. Coordinated in situ measurements of a suite of relevant compounds (such as O₃, isoprene, isoprene nitrates and peroxides, formaldehyde, peroxyacetyl nitrate, and other isoprene oxidation products) and future studies on the fate of isoprene nitrates should help to reduce these uncertainties and to better characterize the relationship between isoprene emissions and surface O₃ concentrations. Our
results indicate that such work is particularly needed in the southeastern United States where the high GEIA-inventory isoprene emissions promote an “isoprene-saturated” chemical regime. Under this regime, isoprene ozonolysis is an important O3 loss pathway and increases in isoprene emissions decrease O3 concentrations. The existence of this regime, however, depends strongly upon the magnitude of the isoprene emissions and the assumption that isoprene nitrates are a NOx sink, and possibly on other factors not examined here, such as vertical mixing in the boundary layer. Nevertheless, our results imply that the expected isoprene emission increases in a warmer future climate [e.g., Constable et al., 1999] may not raise surface O3 concentrations as much as might be anticipated from the strong correlation of high-O3 events with temperature [e.g., Lin et al., 2001], particularly if more stringent controls on anthropogenic NOx emissions are implemented.

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Wang, Y. X., D. J. Jacob, and F. M. Vukovich (1995), Regional-scale boundary layer ozone variations in the eastern United States and their association with meteorological variations, Atmos. Environ., 29, 2259–2273.
Figure 1. Ratio of emissions in 1995 to 1985 over the eastern United States for (a) isoprene (actually mid-1990s to mid-1980s) as estimated by Purves et al. [2004], and anthropogenic (b) VOC, (c) CO, and (d) NO$_x$ from the U.S. EPA national emissions inventory (http://www.epa.gov/air/data/geosel.html). See section 2 for details. Maximum and minimum values are shown in parentheses. The extreme increase in NO$_x$ emissions is driven by the reported changes for Cook County, Minnesota; the maximum value is 3.2 over the rest of the domain.

Figure 2. Emissions ($10^{11}$ molecules cm$^{-2}$) of isoprene from the (a) GEIA (b) Purves et al. [2004], and (c) anthropogenic NO$_x$ inventories in GEOS-CHEM, and (d) the difference in July mean afternoon (1300–1700 LT) surface O$_3$ (ppbv) resulting from application of the Purves et al. [2004] isoprene inventory versus GEIA (PSTD–GSTD in Table 1). The color bar for NO$_x$ emissions saturates (maximum is 8).
Figure 3. Mean afternoon (1300–1700 LT) O₃ concentrations (ppbv) in surface air over the eastern United States in July 2001: (a) U.S. EPA AIRS observations averaged over a 0.5° latitude by 0.5° longitude grid, (b) GEOS-CHEM model surface layer (GSTD in Table 1), (c) correlation, and (d) difference between GSTD and the AIRS observations averaged over the 1° x 1° model grid. The correlation coefficient (r) and the reduced-major-axis (RMA) slope (m) are given, along with the 1:1 line (solid line) and the RMA best fit line (dotted line).
Figure 4. Change in mean July afternoon (1300–1700 LT) surface O3 concentrations (ppbv) from the mid-1980s to the mid-1990s over the eastern United States, resulting from (top row) changes in biogenic isoprene: (a) GA85B95-GA85B85, (b) PA85B95-PA85B85, (c) MOZB95-MOZNIT; (middle row) changes in anthropogenic NOx, CO, and VOC emissions: (d) GSTD-GA85B85 (e) PSTD-PA85B85; and (bottom row) the combined anthropogenic plus biogenic emissions changes: (f) GA95B95-GA85B85 and (g) PA95B95-PA85B85; and (h) the observed change in surface O3 as recorded by the EPA AIRS network (1993–1997 mean)–(1983–1987 mean). The color bar saturates for the observed changes, which range from −21 to +21. Simulations are given in Table 1.
Figure 5. Change in mean July afternoon (1300–1700 LT) surface O₃ concentrations (ppbv) when isoprene and anthropogenic NOₓ emissions are decreased by 25% in GEOS-CHEM: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNOx25-GSTD, and (d) PNOx25-PSTD. Simulations are described in Table 1.
Figure 6. Change in July daily mean afternoon (1300–1700 LT) high-O₃ events (O₃ > 70 ppbv) for selected GEOS-CHEM simulations with the (left) GEIA and (right) Purves isoprene emissions, plotted as a function of the corresponding base-case simulation: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNOX25-GSTD, (d) PNOx25-PSTD, (e) GA85B95-GA85B85, (f) PA85B95-PA85B85, (g) GSTD-GA85B85, and (h) PSTD-PA85B85. Simulations are described in Table 1. Each point represents one model grid cell where the afternoon average surface O₃ exceeded 70 ppbv, sampled from all July days in the northeastern (shaded; 479 total grid cells north of 36°N) and southeastern (black; 253 total grid cells) United States, spanning 66.5°W–104.5°W and 24.5°W–51.5°N.