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

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Abstract

Reducing surface ozone (O$_3$) to concentrations in compliance with the national air quality standard has proven to be challenging, despite tighter controls on O$_3$ precursor emissions over the past few decades. New evidence indicates that biogenic volatile organic compound (BVOC) emissions (in particular isoprene) changed considerably from the mid-1980s to the mid-1990s due to land-use changes in the eastern United States [Purves et al., 2004]. Over this period, anthropogenic U.S. VOC emissions decreased substantially but total U.S. NO$_x$ emissions changed little. 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$_3$ trends over much of the eastern United States may reflect a balance between increases in BVOC emissions and decreases in anthropogenic VOC (AVOC) emissions. We find little evidence for this hypothesis; over the most of the domain, surface O$_3$ is much more responsive (ranging from -15 to +13 ppbv) to the reported changes in anthropogenic NO$_x$ emissions than to either the concurrent BVOC (ranging from -5 to +8 ppbv) or AVOC (less than 2 ppbv) emission changes. The estimated magnitude of the O$_3$ response to anthropogenic NO$_x$ emission changes, however, depends on the choice of isoprene emission inventory 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$_3$ concentrations, suggesting a possible role for decadal changes in meteorological variability, hemispheric background O$_3$, or plume chemistry. We demonstrate that two major uncertainties, the base isoprene emission inventory and the fate of isoprene nitrates (both of which influence surface O$_3$ in the model by 4-15 ppbv) preclude an accurate quantification of the present-day contribution of biogenic or anthropogenic emissions to surface O$_3$ 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

Despite more than three decades of efforts to improve U.S. air quality, widespread attainment of the national ambient air quality standard for surface ozone (O$_3$) smog remains elusive, with over 100 million Americans living in counties exceeding the O$_3$ standard in 2002 [U.S. EPA, 2004]. High O$_3$ concentrations in surface air are produced by rapid photochemical oxidation of volatile organic compounds (VOC) in the presence of nitrogen oxides (NO$_x$=NO+NO$_2$). Over the past decades, legislation enacted to reduce surface O$_3$ has led to substantial decreases in anthropogenic VOC (AVOC) emissions (Figure 1). Over much of the eastern United States, however, isoprene (the most abundant and highly reactive biogenic VOC; C$_5$H$_8$) plays a critical role in surface O$_3$ formation [Trainer et al., 1987; National Research Council, 1991]. The availability of isoprene limits the efficacy of AVOC controls to major urban areas with large NO$_x$ sources and a total VOC budget dominated by AVOC sources [e.g., McKeen et al., 1991].

A recent study based upon Forest Inventory Analysis (FIA) data of over 250,000 surveyed forest plots indicates that isoprene emissions have increased from the 1980s to the 1990s in the eastern United States, possibly offsetting any improvements in O$_3$ air quality attained with legislated decreases in anthropogenic VOCs during this time period [Purves et al., 2004]. We examine here the implications of these estimated changes in isoprene emissions (Figure 1) for surface O$_3$ trends over the eastern United States, in light of current uncertainties in isoprene emissions and chemistry.

The relative magnitudes of NO$_x$ emissions and isoprene emissions determine whether a given increase in isoprene emissions will produce, deplete, or have little impact on surface O$_3$ [e.g., Roselle, 1994; Wiedinmyer et al., 2001; Kang et al., 2003; von Kuhlmann et al., 2004]. Isoprene oxidation is a large source of hydroperoxy (HO$_2$) and organic peroxy (RO$_2$) radicals, which can react with NO$_x$ (primarily from anthropogenic sources [Logan, 1983; Levy et al, 1999]) to stimulate O$_3$ production, as is generally thought to occur in polluted regions of the eastern United States [Trainer et al., 1987, National Research Council, 1991]. In rural areas with low NO$_x$ emissions, O$_3$ production is typically NO$_x$-sensitive, and largely independent of hydrocarbons [e.g. Sillman et al., 1990]. (See also Thornton et al. [2002] for an observation-based characterization of the non-linear dependence of O$_3$ production on the supply of HO$_x$.
(OH+HO₂+RO₂) and NOₓ radicals.) Finally, high isoprene emissions (especially in
general, regions of low NOₓ emissions) can decrease O₃ (1) by sequestering NOₓ as isoprene
nitrates and thereby suppressing O₃ formation (as occurs in the southeastern United States
[Kang et al., 2003]), and (2) by direct ozonolysis of isoprene, associated with titrated OH
(as occurs in the tropics [von Kuhlmann et al., 2004]). This second process may have
been important in maintaining low surface O₃ concentrations in the pre-industrial
northern mid-latitudes [Mickley et al., 2001].

The strongly non-linear isoprene-NOₓ-O₃ chemistry [e.g., Paulson and Seinfeld,
1992; Carter and Atkinson, 1996] complicates modeling efforts to quantify the isoprene-
O₃ relationship, particularly in light of large uncertainties in isoprene emission
inventories [e.g., Roselle, 1994; Stillman, 1999; and 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 peroxides produced during isoprene oxidation,
and whether they serve as sinks for NOₓ and HOₓ [e.g., Horowitz et al., 1998; Liang et
al., 1998]. Von Kuhlmann et al. [2004] summarize the various representations of
isoprene nitrates and peroxides in chemical transport models (their sections 4.3, 4.4, 7
and 8) 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 [e.g. Guenther et al., 1995; Pierce et al.,
1998]. Purves et al. [2004], however, found that decadal changes in forest structure and
species composition over the eastern U.S. had a substantial impact on isoprene emissions,
which is not presently accounted for in isoprene inventories. For example, the dramatic
increases in isoprene and monoterpenes in Alabama from the mid-1980s to the mid-1990s
(Figure 1) are associated with the growth of high monoterpane-emitting pine plantations,
which inadvertently provide a suitable habitat for high isoprene-emitting sweetgum
[Purves et al., 2004]. In this study, we investigate the effect of isoprene emission
changes resulting from such shifts in the base vegetation (Figure 1) [Purves et al., 2004]
on surface O₃, using two chemical-transport models. We compare these changes, as well
as those resulting from the reported trends in anthropogenic O_3 precursor emissions to observed O_3 changes over the same period (Section 3). We also examine the impact of these emissions changes on high-O_3 events, which are relevant for public health and compliance with the national O_3 standard (Section 4). Finally, we address how robust our surface O_3 simulations are to the uncertainties in isoprene emissions and chemistry (Section 5).

2. Model Description and Evaluation

We employ several model simulations to quantify the sensitivity of O_3 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°x1° regionally nested version of the GEOS-CHEM tropospheric chemistry model for North America, described in Section 2.1. We also use the global MOZART-2 model (Section 2.2) to test the robustness of our results 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 in the GEOS-CHEM isoprene-NO_x-O_3 chemical mechanism, on our results.

2.1 GEOS-CHEM

We apply a 1°x1° one-way nested version of the GEOS-CHEM three-dimensional tropospheric NO_x-O_3-CO-hydrocarbon chemical transport model coupled to aerosol chemistry (v. 5-07-08; http://www-as.harvard.edu/chemistry/trop/geos/index.html) [Bey et al., 2001, Evans et al., 2004, Park et al., 2004] for the North American domain (10-60 °N, 40-140 °W) [Wang et al., 2004, Li et al., 2004]. 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°x1° 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 1999-2003. The meteorological year 2001 is chosen for our study since we have previously shown that the 2001 O_3 simulation captures much of the day-to-day variability observed at rural monitoring stations in the United States [Fiore et al., 2003a].
We degrade the 1°x1° fields to a horizontal resolution of 4°x5° 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°x1° domain. We further spin up the 1°x1° domain for June of 2001 and present results for July. A one-month initialization is sufficient to identify the sensitivity of regional O$_3$ to changes in local emissions given the regional domain and rapid summertime photochemistry.

The GEOS-CHEM chemical mechanism provides a relatively detailed treatment of isoprene oxidation [Horowitz et al., 1998, Bey et al., 2001, Evans et al., 2004] (for the most recent version, 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 [Sprengnether 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 NO$_x$ from the atmosphere. Organic peroxides react with OH or recycle HO$_x$ radicals via photolysis as in Horowitz et al. [1998].

Emissions in GEOS-CHEM are taken from Bey et al. [2001], with updates described by Martin et al. [2002] and Park et al. [2004]. For our study, we modify biogenic and anthropogenic emissions to be representative of the mid-1980s and mid-1990s as discussed below. Table 1 provides total July emissions over the eastern U.S. domain for our simulations.

**Biogenic Isoprene Emissions.** Standard isoprene emissions in GEOS-CHEM are taken from the Global Emissions Inventory Activity (GEIA) inventory [Guenther et al., 1995], which is widely used in global tropospheric chemistry models [e.g. Houweling et al., 1998; Horowitz et al., 2003; von Kuhlmann et al., 2004]. Isoprene emissions are calculated from a static base distribution and fluctuations associated with temperature, light, and leaf area according to Guenther et al. [1995], with modifications described by Wang et al. [1998] and Bey et al. [2001]. Global 2001 GEOS-CHEM isoprene emissions are 490 Tg C; July 2001 eastern U.S. emissions in the standard 1°x1° model are 5.6 Tg C (Table 1) and are shown in the upper left panel of Figure 2.
For this study, we implement a second isoprene emission inventory ("Purves case") for July in the eastern United States, in order to test the sensitivity of our results to uncertainties in current isoprene emissions inventories. The Purves inventory, also shown in Figure 2, is estimated as described 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°x1° grid. The Purves isoprene emission inventory can be calculated using forest data from either the mid-1980s or the mid-1990s. In our Purves-base simulations, we scale the standard GEOS-CHEM July mean isoprene emissions (from the GEIA inventory) in each grid-cell to match the magnitude of the mid-1980s 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 2001 meteorology, as is done 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 the high emissions that can be seen in western Texas in Figure 2.

To apply the changes in biogenic emissions, we calculate the ratio of the mid-1990s to the mid-1980s July mean Purves isoprene emissions for each 1°x1° grid-cell (Figure 1). We then use these ratios (one for each grid-cell) to scale the mid-1980s emissions to obtain the mid-1990s emissions for both the Purves and the GEIA inventories. Thus, the percentage difference in the mid-1980s and mid-1990s emissions are the same for the GEIA and Purves inventories but the absolute change is larger in the GEIA inventory since the GEIA mid-1980s emissions are higher (Figure 2 and Table 1).

Both the GEIA and Purves isoprene inventories predict maximum isoprene emissions in the southeastern United States. The Purves emissions are generally a factor of 2 lower than the GEIA inventory, 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 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]. 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.

**Anthropogenic emissions.** Global anthropogenic emissions for 1995 are used in our simulations as described by Bey et al. [2001]. We obtain county-specific emissions for CO, VOCs, and NO\textsubscript{x} for 1985 and 1995 from the U.S. Environmental Protection Agency (EPA) national emissions inventory database (http://www.epa.gov/air/data/neidb.html) and grid these data to the 1°x1° GEOS-CHEM grid, following Purves et al. [2004]. Figure 1 shows the 1995 to 1985 emissions ratios from the EPA inventories, which we use to scale the standard 1995 GEOS-CHEM anthropogenic emissions to obtain emissions for 1985; eastern U.S. July emissions totals are provided in Table 1. Anthropogenic CO and VOC emissions mainly decreased (by an average of 16% each for the domain in Figure 1) from 1985 to 1995 while changes in NO\textsubscript{x} emissions were much less regionally coherent, with some local increases. Although this study focuses on uncertainties in isoprene emissions, there are substantial uncertainties in anthropogenic emissions, especially for road-traffic NO\textsubscript{x} emissions [Parrish et al., 2002].

**Evaluation of the Surface O\textsubscript{3} Simulation.** GEOS-CHEM has been evaluated extensively with observations of O\textsubscript{3} and related species, both globally [Bey et al., 2001], and in various world regions [e.g. Li et al., 2004; Wang et al., 2004]. The nested 1°x1° model over North America was recently applied to identify North American outflow
pathways for CO, O₃ and aerosols [Li et al., 2004]. 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; Fiore et al., 2003ab] as well as the observed distribution of CH₂O, an intermediate product of isoprene oxidation [Palmer et al., 2003; Martin et al., 2004].

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 GEOS-CHEM 1°x1° July afternoon (1-5 p.m.) O₃ simulation for the meteorological year 2001 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 because afternoon observations are representative of 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 ($r^2 = 0.40$; reduced major axis (RMA) slope = 1.0 [Hirsch and Gilroy, 1984]) with a mean model bias of 6±7 ppbv. Consistent with earlier GEOS-CHEM evaluations [Fiore et al. 2002, 2003a], 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 simulation with the Purves inventory (not shown) gives a lower mean July afternoon O₃ bias (4±8 ppbv) but captures less of the spatial variance ($r^2 = 0.29$; RMA slope=1.0).

2.2 MOZART-2

We use a second global tropospheric chemistry model, MOZART-2 [Horowitz et al., 2003] to test the robustness of our results. We also 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).

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 1. Isoprene emissions are based upon 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 2001 meteorology as they do in GEOS-CHEM. This different treatment of isoprene emissions is likely responsible for the somewhat lower July isoprene emissions from the GEIA inventory in MOZART-2 than in GEOS-CHEM (Table 1).

MOZART-2 also employs a detailed isoprene-NO$_x$-O$_3$ chemical mechanism, which includes an 8% yield of isoprene nitrates from the isoprene-OH reaction [Carter and Atkinson, 1996]. In contrast to GEOS-CHEM, the standard MOZART-2 model transports isoprene nitrates and recycles NO$_x$ via their 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 convert the isoprene nitrates directly to nitric acid (with a 12% yield from reaction of isoprene-derived RO$_2$ with NO [Sprengnether et al., 2002] as in GEOS-CHEM), treating them as a NO$_x$ sink. Similar to the GEOS-CHEM mechanism, the MOZART-2 mechanism also recycles HO$_x$ radicals via photolysis of isoprene peroxides; we examine the impact of this recycling on surface O$_3$ by turning off their photolysis (and reaction with OH) and instead permitting isoprene peroxides to be a sink for HO$_x$.

3. Surface O$_3$ Response to Recent Precursor Emissions Trends

3.1 Biogenic Isoprene

The changes in mean July afternoon (1-5 p.m.) surface O$_3$ concentrations due to the changes in isoprene emissions (for both the GEIA and the Purves cases) from the mid-1980s to mid-1990s (Figure 1) are shown in Figure 4 (upper panels). There is little change in O$_3$ concentrations in the northern half of the domain despite the reduction in anthropogenic O$_3$ precursors. Surprisingly, the large increases in isoprene emissions in the southern states of Arkansas, northern Louisiana, Mississippi and Alabama cause O$_3$ decreases of 1-2 ppbv in the GEIA-based simulation. In this region, isoprene emissions
are already high (Figure 2) and isoprene ozonolysis is an important sink for O₃ (Table 2), so the higher isoprene emissions in the mid-1990s increase the size of this sink.

In contrast, the Purves-based simulation in Figure 4 shows only slight O₃ decreases (< 1 ppbv) in the southern states when the BVOC changes are applied. Increases in O₃ concentrations of 2-4 ppbv occur in northeastern Texas where NOₓ emissions are high (Figure 2) and the rise in isoprene emissions (Figure 1) 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., 1990; Kang et al., 2003].

We also test the sensitivity of our results to the chemistry of isoprene nitrates, using MOZART-2 (which uses GEIA for isoprene emissions – see Section 2.2). The isoprene increases in the southeastern states lead to decreased surface O₃ by 1-2 ppbv in MOZART-2 (Figure 4) only when isoprene nitrates are converted directly to nitric acid (as is done in GEOS-CHEM). In the standard MOZART-2 simulation, which recycles the isoprene nitrates to NOₓ, we find that the increased isoprene actually increases O₃ by 1-2 ppbv in eastern Texas and Oklahoma and through the industrial Midwest, with little change over the southeastern U.S. We conclude that isoprene ozonolysis is an important photochemical O₃ loss pathway in the southeastern United States only if isoprene nitrates are a sink for NOₓ. We further explore this chemical uncertainty in section 5.2.

3.2 Anthropogenic NOₓ, VOC, and CO

Trends in anthropogenic emissions over this time period increase O₃ concentrations over much of Tennessee, North Carolina, South Carolina, southern Virginia, western Kentucky, and northern Georgia and Alabama, by 2-4 and 3-7 ppbv for the Purves- and GEIA-based GEOS-CHEM simulations, respectively (middle panels of Figure 4). We conduct additional simulations where we change only NOₓ or only the CO and VOC emissions to determine that the O₃ response is largely driven by the changes in NOₓ emissions, as expected for the highly NOₓ-sensitive eastern United States [Sillman, 1999 and references therein]. However, consistent with earlier modeling studies [Roselle, 1994], the simulated response to anthropogenic NOₓ changes depends upon the
distribution and magnitude of isoprene emissions, with more pronounced changes (in magnitude and spatial extent) when the GEIA inventory is used (Figure 4). For the Purves case, the extremely low isoprene emissions in the high-NO\textsubscript{x} region around Chicago, Illinois (Figure 2; an order of magnitude lower than those predicted by GEIA), lead to an O\textsubscript{3} production regime that is sensitive to anthropogenic VOCs. Reductions in anthropogenic VOC emissions thus decrease O\textsubscript{3} by a few ppbv in the Chicago area. Decreases of up to 9 and 6 ppbv, which occur in eastern Texas for the GEIA- and Purves-based simulations, respectively, are associated with the decreases in NO\textsubscript{x} emissions (Figure 1). We caution that these results reflect the reported NO\textsubscript{x} changes and their variable local changes, which are uncertain (Section 2.1).

The simulated O\textsubscript{3} changes resulting from the combination of anthropogenic and biogenic emissions changes are shown in the bottom panels of Figure 4. For the GEIA case, the simulated O\textsubscript{3} response from the combined emissions changes is roughly equal to the sum of the O\textsubscript{3} responses when the biogenic and anthropogenic emissions are changed separately. For the Purves-based simulations, however, the combined change compared to the individual emission changes yield O\textsubscript{3} differences of up to 3 ppbv over eastern Texas, due to non-linear interactions between the changes in isoprene and anthropogenic NO\textsubscript{x}.

3.3 Comparison with Observed O\textsubscript{3} Changes

We assess whether the reported emissions changes explain the observed trends in O\textsubscript{3} from the 1980s to the 1990s. We use hourly observations from the U.S. EPA Aerometric Information Retrieval System (EPA AIRS) to calculate the change in mean July afternoon O\textsubscript{3} concentrations from the mid-1980s (1983-1987 mean) to the mid-1990s (1993-1997 mean), shown in the bottom right panel of Figure 4. Averaging over five years reduces the influence of meteorology-driven interannual variability. The resulting changes in surface O\textsubscript{3} are consistent with observed trends for O\textsubscript{3} concentrations from 1985-1996 [Wolff et al., 2001]. Decreases in O\textsubscript{3} are observed in the Chicago area and throughout Illinois, along the Northeast Corridor, and in several of the southern states. Increases in surface O\textsubscript{3} occur in the Midwest (Ohio, Indiana, and western Pennsylvania), Tennessee, and Florida.
The observations could represent VOC-limited urban plumes not resolved in a 1°x1° model. While the EPA provides an “urban”, “rural”, or “suburban” designation that could be used to remove urban sites, earlier work has shown that sites labeled urban are actually associated with a wide range of local NO\textsubscript{x} emissions [Fiore et al., 1998]. As an alternative approach, we used ratios of night (1-5 a.m. local time) to day (1-5 p.m. local time) O\textsubscript{3} concentrations below 0.3 to screen out urban sites (screened out 154 sites out of 602 total). Our results, however, were largely unaffected by removing these sites, so we retain all EPA AIRS sites in our observational analysis.

Consistent with the observed changes, the GEIA-based simulations show the increases in the Midwest, but they miss the decreases near Chicago and along the Northeast corridor. While the GEIA-based simulations show substantial O\textsubscript{3} decreases in the southern states, they do not extend eastward across Alabama and into Georgia where the largest observed decreases occur. The Purves-based simulated changes capture the decreases in the Chicago area, but do not reproduce the spread of these decreases into Wisconsin and western Illinois. They also fail to capture the observed decreases in the southeastern states. The range of the observed changes is at least twice that of the simulated changes, leading to the poor correlations between the observed and simulated changes in the bottom row of Figure 4 ($r^2$~0.01 for both GEIA- and Purves-based simulations). Overall, we conclude that the anthropogenic and biogenic emission changes considered here are insufficient to explain the O\textsubscript{3} observations.

We have shown that the response of surface O\textsubscript{3} to biogenic emission changes is small (Section 3.1), and that the O\textsubscript{3} response to the combined biogenic and anthropogenic emission changes is dependent on the isoprene emission inventory (Purves vs. GEIA in Figure 4). While applying the reported trends in biogenic plus anthropogenic emissions in the GEOS-CHEM model with two different isoprene inventories captures some of the features in observed eastern U.S. O\textsubscript{3} changes from the mid-1980s to the mid-1990s, neither offers a satisfactory attribution of the observed O\textsubscript{3} trends to emission changes. This disagreement suggests that other factors, not considered in this study, may have contributed to the observed changes, including: decadal shifts in inter-annual meteorological variability (and their effect on isoprene emissions), plume chemistry, changes in global background O\textsubscript{3} associated with foreign emission trends, or problems
with the reported domestic emission changes. Another possibility is that the current understanding of isoprene emissions and chemistry may not support a quantitative attribution of observed \( \text{O}_3 \) trends to precursor emission changes. We examine this possibility further with sensitivity studies designed to show the influence of (1) the choice of isoprene emission inventory and (2) uncertainties in isoprene chemistry, on surface \( \text{O}_3 \) simulations.

4. Characterizing the \( \text{O}_3 \) Response to Uniform Emissions Perturbations

We conduct four sensitivity simulations in which we reduce biogenic isoprene and anthropogenic NO\(_x\) emissions by 25%, separately, for both the GEIA and Purves isoprene inventories. Figure 5 shows the changes in surface \( \text{O}_3 \) resulting from 25% decreases in isoprene (left) and anthropogenic NO\(_x\) emissions (right) for both the GEIA- and Purves-based simulations. Larger \( \text{O}_3 \) responses are seen for the GEIA-based simulation and its correspondingly larger isoprene emission perturbation. In the southeastern states, decreases in the GEIA isoprene emissions lead to higher \( \text{O}_3 \) concentrations because the high base-case GEIA-generated isoprene concentrations remove NO\(_x\) from the atmosphere (as isoprene nitrates) and react directly with \( \text{O}_3 \) (Table 2). The region of largest \( \text{O}_3 \) decreases is further south in the Purves-based simulation as compared to the GEIA-based simulation, reflecting the smaller Purves isoprene emissions in the Midwest (Figure 2). In the Purves-based case, the reduced isoprene emissions translate into lower \( \text{O}_3 \) concentrations in the vicinity of NO\(_x\) sources. Little change in \( \text{O}_3 \) concentrations occurs over the high-isoprene-emitting southeastern region, where the chemical regime is transitioning from one in which additional isoprene (or any VOC) will increase \( \text{O}_3 \) to one in which additional isoprene will decrease \( \text{O}_3 \) [Kang et al., 2003].

The \( \text{O}_3 \) response to 25% reductions in anthropogenic NO\(_x\) emissions shown in Figure 5 is highly dependent on the base isoprene emission inventory. The larger \( \text{O}_3 \) decreases in the GEIA-based simulation reflect the stronger NO\(_x\)-sensitivity associated with the higher isoprene concentrations; decreases in NO\(_x\) further decrease OH, which competes with \( \text{O}_3 \) for reaction with isoprene. These results indicate that quantifying the uncertainties in isoprene emissions is critical, as the non-linear chemical interactions of
isoprene, NO\textsubscript{x}, and O\textsubscript{3} will affect conclusions drawn about O\textsubscript{3} sensitivity to anthropogenic emission controls [Roselle, 1994].

Table 2 compares the importance of selected photochemical O\textsubscript{3} loss mechanisms in the southeastern region. Loss of O\textsubscript{3} via reaction with biogenic compounds is equivalent to the typical major photochemical O\textsubscript{3} loss pathways (photolysis and reaction with HO\textsubscript{x} radicals) in the GEIA-based simulations. For the Purves-based simulations, the much lower isoprene emissions prevent this pathway from being an important O\textsubscript{3} loss mechanism. Thus, given our present understanding, the contribution of various pathways to the regional photochemical O\textsubscript{3} sink over the southern United States will depend strongly upon the assumed isoprene and NO\textsubscript{x} emissions.

4.1 High-O\textsubscript{3} Events

Figure 7 shows the impact of the emissions perturbations discussed above on high-O\textsubscript{3} events (defined here as O\textsubscript{3} > 70 ppbv) from selected simulations, plotted as a function of the surface O\textsubscript{3} in the corresponding base-case simulation. Consistent with our July mean analysis (Section 3), we find that the high-O\textsubscript{3} events respond strongly to NO\textsubscript{x} controls, but that 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 O\textsubscript{3} decrease produced by a given NO\textsubscript{x} reduction.

For the most extreme events (O\textsubscript{3} > 90 ppbv), the anthropogenic and biogenic emission changes from the mid-1980s to the mid-1990s (Figure 1), yield opposite responses, particularly in the simulation with the Purves isoprene inventory. These events occur over eastern Texas where increased isoprene emissions in the mid-1990s tend to increase O\textsubscript{3} but lower anthropogenic VOC, CO, and NO\textsubscript{x} emissions tend to decrease O\textsubscript{3}. For most of the eastern United States, the changes in BVOC emissions between the mid-1980s and mid-1990s have a smaller impact on surface O\textsubscript{3} concentrations (< 5 ppbv) than the changes in anthropogenic emissions over the same period (up to 13 ppbv). While the magnitude of the O\textsubscript{3} response to the decadal changes in the biogenic isoprene emissions is small for both the GEIA and Purves inventories, they differ in the sign of the response: reducing O\textsubscript{3} concentrations over the eastern United States.
States when the GEIA emissions are used, while increasing O$_3$ 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 tended to mitigate or exacerbate O$_3$ pollution over the eastern United States. The uncertainty in the fate of isoprene nitrates is of particular relevance here, as discussed in Section 3.1.

5. Uncertainty Analysis: Implications for Quantifying Surface O$_3$

5.1 Isoprene Emissions

The GEIA inventory yields higher O$_3$ concentrations than the Purves inventory in the Midwest-northeast region where NO$_x$ emissions are high (Figure 2) and the Purves inventory predicts little isoprene. In the southern states, the GEIA inventory leads to lower O$_3$ concentrations than the Purves inventory. The high GEIA isoprene emissions deplete OH concentrations in this region, enabling isoprene to react directly with O$_3$ (see Table 2 and section 4) and remove NO$_x$ (through isoprene nitrates). Overall, the simulated surface O$_3$ concentrations differ by between -15 and +4 ppbv when the Purves inventory is used instead of GEIA (Figure 2). The difference in O$_3$ associated with choosing a different base isoprene inventory is thus larger than the O$_3$ response to the reported emissions changes (Figure 4), and points to a substantial source of uncertainty in our current generation of surface O$_3$ simulations.

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 NOx to the atmosphere and (2) isoprene nitrates are considered a permanent sink for NOx and converted directly to nitric acid with a 12% yield, as is done in the GEOS-CHEM mechanism. The results in Figure 6 show that O$_3$ concentrations over the eastern U.S. decrease by 5 ppbv on average over the domain, and up to as much as 12 ppbv for a given model grid box when isoprene nitrates are considered to be a NO$_x$ sink, consistent with the findings of Horowitz et al. [1998], Liang et al. [1998] and von Kuhlmann et al. [2004].
A second uncertainty in isoprene-O$_3$-NO$_x$ chemistry concerns the fate of the organic peroxides produced during isoprene oxidation and whether they recycle HO$_x$ via photolysis and reaction with OH or serve as a net HO$_x$ sink [von Kuhlmann et al., 2004]. The sensitivity of O$_3$ to this uncertainty is smaller, a 1-2 ppbv decrease in July mean afternoon surface O$_3$ (Figure 6), although it is similar in magnitude to the response due to the decadal changes in isoprene emissions (section 3). A recent analysis of field measurements is consistent with the recycling of HO$_x$ 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 about a factor of 3-12 or they are rapidly photolyzed and serve only as a temporary reservoir of HO$_x$.

We thus find in our model that the largest uncertainties in determining the contribution of isoprene to surface O$_3$ over the eastern United States are the choice of isoprene inventory and the fate of isoprene nitrates. Resolving these uncertainties is critical as they influence simulated base-case O$_3$ concentrations, as well as the magnitude, and in some cases the sign, of the simulated O$_3$ response to changes in precursor emissions.

6. Conclusions

We have investigated the hypothesis that substantial increases in eastern U.S. biogenic isoprene emissions may have offset improvements in surface O$_3$ air quality associated with decreases in anthropogenic VOCs from the mid-1980s to the mid-1990s [Purves et al., 2004]. With MOZART-2 and a 1°x1° North American nested version of the GEOS-CHEM tropospheric chemistry models, we examined the impact of these isoprene emission changes and concurrent anthropogenic emission changes on surface O$_3$. We then compared the O$_3$ response due to the emission changes with observed O$_3$ trends from the EPA AIRS network. A suite of sensitivity simulations enabled us to determine the sensitivity of surface O$_3$ in the eastern United States to uncertainties in isoprene emissions and chemistry.

The simulated O$_3$ response to natural versus anthropogenic emissions offset each other to some extent during the most extreme events (O$_3$ > 90 ppbv) over eastern Texas,
with isoprene emission changes increasing O\textsubscript{3} but anthropogenic NO\textsubscript{x} emission changes decreasing O\textsubscript{3}. Even in this case, as over most of the eastern United States, we find that the influence of reported anthropogenic NO\textsubscript{x} emissions changes on surface O\textsubscript{3} outweighs that from the increases in isoprene emissions from the mid-1980s to the mid-1990s. Our results show that the estimated efficacy of anthropogenic NO\textsubscript{x} emission controls on simulated O\textsubscript{3} depends strongly upon the chosen isoprene emission inventory, consistent with prior studies \textit{e.g.} Roselle, 1994. A satisfactory explanation for observed changes in mean July afternoon surface O\textsubscript{3} concentrations remains elusive, suggesting a possible role for decadal meteorological variability (and its influence on isoprene emissions), global precursor emission trends or sub-grid plume chemistry, processes not considered in this study. Inaccuracies in the reported emission trends (particularly NO\textsubscript{x} emissions from road traffic \textit{Parrish et al., 2002}) and uncertainties in isoprene emissions and chemistry may also preclude an accurate attribution of observed O\textsubscript{3} trends to precursor emission changes.

The magnitude of the O\textsubscript{3} sensitivity to uncertainties in isoprene emissions and chemistry is similar or greater than the O\textsubscript{3} response to reported emissions changes, natural or anthropogenic. Surface O\textsubscript{3} 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 peroxy chemistry have a smaller impact on surface O\textsubscript{3} (< 2 ppbv). These uncertainties translate into a major uncertainty in the magnitude, and in some cases the direction, of the O\textsubscript{3} response to changes in precursor emissions. Coordinated \textit{in-situ} measurements of a suite of relevant compounds (\textit{e.g.}, O\textsubscript{3}, 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 O\textsubscript{3} concentrations. Our results indicate such work is particularly warranted 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 O\textsubscript{3} loss pathway and increases in isoprene emissions decrease O\textsubscript{3}
concentrations. The existence of this regime, however, depends strongly upon the magnitude of the isoprene emissions and the assumption that isoprene nitrates are a true sink for NO\textsubscript{x}. 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 O\textsubscript{3} concentrations as much as might be anticipated from the strong correlation of high-O\textsubscript{3} events with temperature [e.g. Lin et al., 2001], particularly if more stringent controls on anthropogenic NO\textsubscript{x} emissions are implemented.

We conclude that our current understanding of the impact of isoprene emissions on regional air quality is insufficient to conclusively determine whether changes in isoprene emissions from the mid-1980s to the mid-1990s have tended to mitigate or exacerbate O\textsubscript{3} pollution over the eastern United States. Better constraints on isoprene emissions and isoprene-NO\textsubscript{x}-O\textsubscript{3} chemistry are essential for such a quantitative understanding, and for predicting how surface O\textsubscript{3} will respond to future changes in both biogenic and anthropogenic emissions perturbations.

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**Figure Captions**

**Figure 1.** Ratio of emissions in the mid-1990s to the mid-1980s over the eastern United States. The upper panels show changes for biogenic isoprene and monoterpenes estimated by Purves et al. [2004]. The bottom panels show the ratio of 1995 to 1985 CO, VOC, and NO\textsubscript{x} anthropogenic emissions from the U.S. EPA national emissions inventory (http://www.epa.gov/air/data/neidb.html). The color bar is designed to emphasize regional features and saturates. The range of values is 0.3-3.3 (isoprene) 0.3-1.9 (monoterpenes), 0.4-3.7 (CO), 0.3-2.6 (VOC), and 0.4-3.1 (NO\textsubscript{x}).

**Figure 2.** Isoprene from the GEIA (top left) and Purves et al. [2004] (bottom left) emissions inventory and anthropogenic NO\textsubscript{x} (top right) emissions (molec cm\textsuperscript{-2} s\textsuperscript{-1}), in GEOS-CHEM, and the difference in surface O\textsubscript{3} (ppbv; bottom right) resulting from application of the Purves et al. [2004] isoprene inventory vs. GEIA (Purves – GEIA). The color bars for isoprene and NO\textsubscript{x} emissions saturate to emphasize regional patterns.

**Figure 3.** Average afternoon (1300-1700 local time) O\textsubscript{3} concentrations (ppbv) in surface air over the eastern United States in July 2001. (top left) U.S. EPA AIRS observations averaged over a 0.5° latitude by 0.5° longitude grid, (top right) results from the GEOS-CHEM model surface layer at 1°x1° horizontal resolution, (bottom left) the correlation and (bottom right) the difference between the model results and the AIRS observations averaged over the 1°x1° model grid. The correlation coefficient (r) and the reduced-major-axis (RMA) slope (m) are given, along with the 1:1 line (solid) and the RMA-best-fit line (dotted).

**Figure 4.** Change in mean July afternoon (1300-1700 LT) surface O\textsubscript{3} concentrations (ppbv) from the 1980s to the 1990s over the eastern United States resulting from changes...
in biogenic isoprene (top row), anthropogenic NO$_x$, CO, and VOC (middle row) emissions, in GEOS-CHEM for the GEIA (left) and Purves (middle) isoprene inventories, and in MOZART-2 for the GEIA inventory when isoprene nitrates are converted directly to nitric acid (upper right). The bottom panels show the surface O$_3$ response to the combined anthropogenic plus biogenic emissions changes in GEOS-CHEM, as well as the observed change in surface O$_3$ as recorded by the EPA AIRS network. Observed changes may also reflect changes in meteorological variability, global emissions and plume chemistry, not considered in these simulations. See Section 3 for further discussion. The color bar saturates to emphasize regional patterns rather than extreme values. Ranges are –2 to +1 (GEIA), -1 to +4 (Purves), -2 to +2 (MOZART-2 GEIA) for the BVOC changes; -9 to +7 (GEIA), -6 to +4 (Purves) for the anthropogenic changes; –10 to +6 (GEIA), -5 to +4 (Purves) for the combined changes; and –21 to +21 in the EPA AIRS observations.

**Figure 5.** Change in mean July surface O$_3$ concentrations (ppbv) due to 25% reductions in isoprene (left) and anthropogenic NO$_x$ (right) emissions, for the GEIA (top) and Purves (bottom) isoprene emissions in GEOS-CHEM.

**Figure 6.** Change in mean July afternoon (1300-1700 LT) surface O$_3$ concentrations in MOZART-2 associated with uncertainties in isoprene-O$_3$-NO$_x$ chemistry: conversion of isoprene nitrates directly to nitric acid rather than allowing them to recycle NO$_x$ (left) turning off recycling of HO$_x$ via OH reaction and photolysis of organic peroxides formed during isoprene oxidation (right).

**Figure 7.** Change in July high-O$_3$ events for selected GEOS-CHEM simulations with the GEIA (left) and Purves (right) isoprene emissions. Each point represents one model grid-cell where the afternoon average surface O$_3$ exceeded 70 ppbv, for all July days, in the northeastern (red; sampled from 386 total grid-cells north of 36°N) and southeastern (black; 234 total grid-cells) United States. The change in O$_3$ is plotted as a function of the surface O$_3$ concentrations in the corresponding base-case simulations (1995 and 1985 anthropogenic emissions for the top four and bottom four panels, respectively). All simulations use 2001 meteorology.
Table 1: July Emissions in the Eastern United States (24.5-51.5 °N; 67.5-102.5 °W)

<table>
<thead>
<tr>
<th></th>
<th>Year</th>
<th>GEIA</th>
<th>PURVES</th>
<th>NMHC$^e$ (Tg C)</th>
<th>NO$_x$ (Tg N)</th>
<th>CO (Tg CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEOS-CHEM</td>
<td>1980s</td>
<td>5.6</td>
<td>2.8</td>
<td>1.00</td>
<td>0.43</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>1990s</td>
<td>6.2</td>
<td>3.0</td>
<td>0.81</td>
<td>0.46</td>
<td>5.6</td>
</tr>
<tr>
<td>MOZART-2</td>
<td>Early 1990s</td>
<td>4.8$^d$</td>
<td>--</td>
<td>0.20</td>
<td>0.48</td>
<td>4.8</td>
</tr>
</tbody>
</table>

$^a$The GEIA inventory fills in where the Purves inventory lacks data (i.e., white regions in Figure 1) in GEOS-CHEM.
$^b$Anthropogenic emissions in GEOS-CHEM are for 1985 and 1995, based upon reported trends in the U.S. EPA national emissions inventory database (http://www.epa.gov/air/data/neidb.html) as described in the text.
$^c$C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_3$H$_8$, and C$_4$H$_{10}$ in MOZART-2; C$_2$H$_6$, C$_3$H$_8$, lumped ≥C$_3$ alkenes and ≥C$_4$ alkanes in GEOS-CHEM
$^d$Increases to 5.4 Tg C when the changes in Figure 1 are applied.

Table 2: Near-surface O$_3$ Lifetime (days) against selected photochemical loss pathways in the southeastern U.S.$^a$

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Reaction with OH, HO$_2$ or CH$_3$O$_2$</th>
<th>Photolysis (OH production)</th>
<th>Direct reaction with Biogenics$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard GEIA Isoprene</td>
<td>16</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>-25% GEIA Isoprene</td>
<td>17</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>GEIA -25% anthrop. NO$_x$</td>
<td>17</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Standard Purves Isoprene</td>
<td>18</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>-25% Purves Isoprene</td>
<td>18</td>
<td></td>
<td>87</td>
</tr>
<tr>
<td>Purves -25% anthrop. NO$_x$</td>
<td>19</td>
<td></td>
<td>49</td>
</tr>
</tbody>
</table>

$^a$Lifetime is the spatial average for 30.5-37.5°N and 81.5-91.5°W (encompassing Georgia, Alabama, Mississippi, Tennessee, Arkansas, northern Louisiana), calculated from the column sum of the simulated 24-hour mean July O$_3$ concentration and chemical loss rates in the bottom 7 model boxes (~1.3 km altitude)
$^b$Includes isoprene, other biogenic alkenes, methylvinylketone, methacrolein, peroxymethacryloyl nitrates, isoprene aldehydes
Figure 1. Ratio of emissions in the mid-1990s to the mid-1980s over the eastern United States. The upper panels show changes for biogenic isoprene and monoterpane estimated by Purves et al. [2004]. The bottom panels show the ratio of 1995 to 1985 CO, VOC, and NO\textsubscript{x} anthropogenic emissions from the U.S. EPA national emissions inventory (http://www.epa.gov/air/data/neidb.html). The color bar is designed to emphasize regional features and saturates. The range of values is 0.3-3.3 (isoprene), 0.3-1.9 (monoterpene), 0.4-3.7 (CO), 0.3-2.6 (VOC), and 0.4-3.1 (NO\textsubscript{x}).
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