

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_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 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_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_3 is more responsive (ranging from -9 to $+7$ ppbv) to the reported changes in anthropogenic NO_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_3 response to anthropogenic NO_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_3 concentrations, suggesting a possible role for decadal changes in meteorology, hemispheric background O_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_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_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.

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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_3) smog remains elusive, with over 100 million Americans living in counties exceeding the O_3 standard in 2002 [*United States Environmental Protection Agency (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 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_5H_8) plays a critical role in surface O_3 formation [*Trainer et al.*,

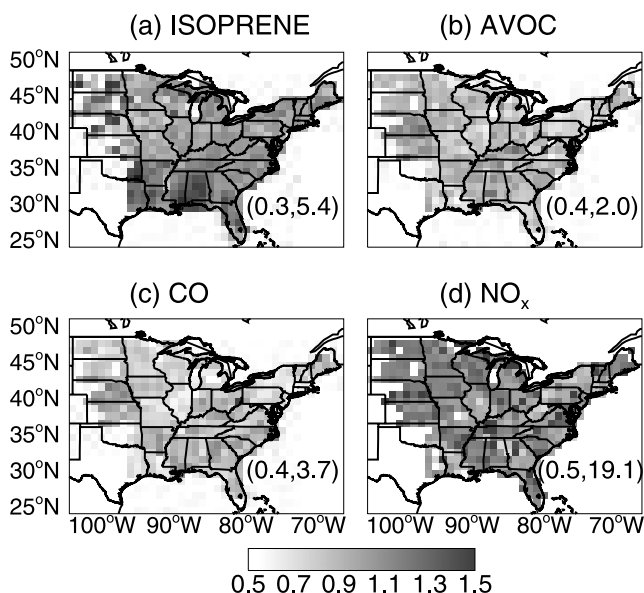


Figure 1. Ratio of emissions in 1995 to 1985 over the eastern United States for (a) isoprene (actually mid-1990s to mid-1980s) as estimated by *Purves et al.* [2004], and anthropogenic (b) VOC, (c) CO, and (d) NO_x from the U.S. EPA national emissions inventory (<http://www.epa.gov/air/data/geosel.html>). 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. See color version of this figure at back of this issue.

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].

[3] 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 mid-1980s to the mid-1990s in the eastern United States, possibly offsetting any improvements in O₃ air quality attained with legislated decreases in AVOC during this period [*Purves et al.*, 2004]. We examine here the implications of these estimated changes in isoprene emissions (Figure 1a) for surface O₃ trends over the eastern United States, in light of current uncertainties in isoprene emissions and chemistry.

[4] The relative magnitudes of NO_x emissions and isoprene emissions determine whether a given increase in isoprene emissions will enhance, deplete, or have little impact on surface O₃ [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 (HO₂) and organic peroxy (RO₂) radicals, which can react with NO_x (primarily from anthropogenic sources [*Logan*, 1983; *Levy et al.*, 1999]) to stimulate O₃ 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, O₃ production is typically NO_x-sensitive, and largely insensitive to VOC [e.g., *Sillman et al.*, 1990a]. (See also *Thornton et al.* [2002]

for an observation-based characterization of the nonlinear dependence of O₃ production on the supply of HO_x (OH + HO₂ + RO₂) and NO_x radicals.) Finally, high isoprene emissions (especially in regions of low NO_x emissions) can decrease O₃ by (1) sequestering NO_x as isoprene nitrates and thereby suppressing O₃ formation (as occurs in the southeastern United States [*Kang et al.*, 2003]), and (2) direct ozonolysis of isoprene, associated with depletion of OH concentrations in the boundary layer by high isoprene emissions (as occurs in the tropics [*von Kuhlmann et al.*, 2004]).

[5] The strongly nonlinear isoprene-NO_x-O₃ chemistry [e.g., *Paulson and Seinfeld*, 1992; *Carter and Atkinson*, 1996] 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 peroxides 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 peroxides in chemical transport models and show that different assumptions lead to substantial regional discrepancies in the surface O₃ concentrations simulated with chemical transport models.

[6] 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 decadal 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 monoterpene-emitting pine plantations, which inadvertently provide a suitable habitat for high isoprene-emitting sweetgum [*Purves et al.*, 2004].

[7] 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

[8] 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

| Model | Simulation Name | Base Year for Isoprene Inventory ^a | Year for Anthropogenic Inventories ^a |
|---|-------------------------------------|---|---|
| GEOS-CHEM (1° × 1°; GMAO 2001 meteorology) | (G/P) ^b STD ^c | mid-1980s | 1995 |
| | (G/P)A95B95 | mid-1990s | 1995 |
| | (G/P)A85B85 | mid-1980s | 1985 |
| | (G/P)A85B95 | mid-1990s | 1985 |
| | (G/P)ISOP25 | mid-1980s reduced by 25% | 1995 |
| | (G/P)NOx25 | mid-1980s | 1995 anthropogenic NO _x reduced by 25% early 1990s |
| MOZART-2 (1.9° × 1.9°; NCEP 2001 meteorology) | MOZSTD ^c | mid-1980s | MOZSTD with isoprene nitrates acting as a NO _x sink (section 2.2) |
| | MOZB95 | MOZNIT with mid-1990s | MOZNIT with early 1990s |
| | MOZNIT | MOZSTD with isoprene nitrates acting as a NO _x sink (section 2.2) | MOZSTD with isoprene nitrates acting as a NO _x sink (section 2.2) |
| | MOZPER | MOZSTD with isoprene peroxides acting as a HO _x sink (section 2.2) | MOZSTD with isoprene peroxides acting as a HO _x sink (section 2.2) |

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

^bTwo 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.

^cStandard 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

[9] We apply a 1° × 1° one-way nested version of the GEOS-CHEM three-dimensional tropospheric NO_x-O₃-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; *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 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/USclimdivs.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 HO_x 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 [*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 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 NO_x emissions, taken from the Global Emission Inventory Activity (GEIA), which include the 1985 National Acid Precipitation Assessment Program inventory for the United States [*Benkovitz et al.*, 1996]. The GEIA isoprene emissions in GEOS-CHEM are widely used in global tropospheric chemistry models [e.g., *Houweling 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 NO_x) 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

| | Year | | Isoprene, ^b Tg C | | Anthropogenic | | |
|-----------|-----------|---------------|-----------------------------|--------|-------------------------|------------------------|-----------|
| | Isoprene | Anthropogenic | GEIA | PURVES | NMHC, ^c Tg C | NO _x , Tg N | CO, Tg CO |
| GEOS-CHEM | mid-1980s | 1985 | 5.9 | 3.0 | 0.94 | 0.45 | 7.02 |
| | mid-1990s | 1995 | 6.5 | 3.2 | 0.80 | 0.47 | 5.71 |
| MOZART-2 | mid-1980s | early 1990s | 5.0 ^d | – | 0.20 | 0.49 | 4.8 |

^aSee section 2 for details.

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

^cThis comprises C₂H₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₁₀ in MOZART-2; C₂H₆, C₃H₈, lumped \geq C₃ alkenes and \geq C₄ alkanes in GEOS-CHEM.

^dThis 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).

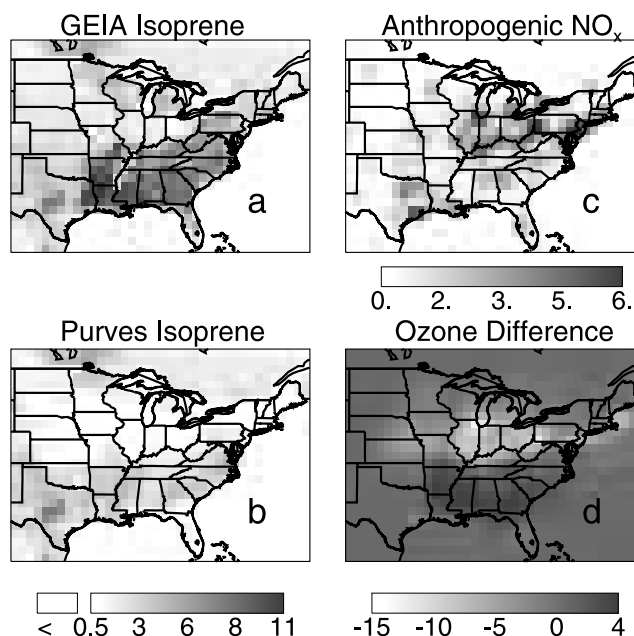


Figure 2. Emissions (10^{11} molecules cm^{-2}) of isoprene from the (a) GEIA (b) *Purves et al.* [2004], and (c) anthropogenic NO_x inventories in GEOS-CHEM, and (d) the difference in July mean afternoon (1300–1700 LT) surface O₃ (ppbv) resulting from application of the *Purves et al.* [2004] isoprene 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 NO_x 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° × 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, AVOC, and NO_x 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 NO_x emissions were much less regionally coherent. The reported overall increase in NO_x emissions mainly reflects changes in area sources (responsible for 70% of the total domain-wide changes in NO_x 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 NO_x emissions [Trainer *et al.*, 2000, and references therein], but substantial uncertainties exist in road-traffic (area) NO_x 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° × 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 ($r^2 = 0.40$; 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 NO_x and isoprene emissions (Figure 2). The model overestimate in the Ohio River valley (Figure 3) may be associated with controls on power plant NO_x emissions that were implemented in 1999 [Frost *et al.*, 2004] and are not reflected in the 1995 GEOS-CHEM anthropogenic NO_x 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 ($r^2 = 0.29$; 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 NO_x-sensitive O₃ production over the eastern United States in July, the only month considered in our study. 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 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-NO_x-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 NO_x via reaction with OH, based upon the assumption that OH reaction is a more important loss

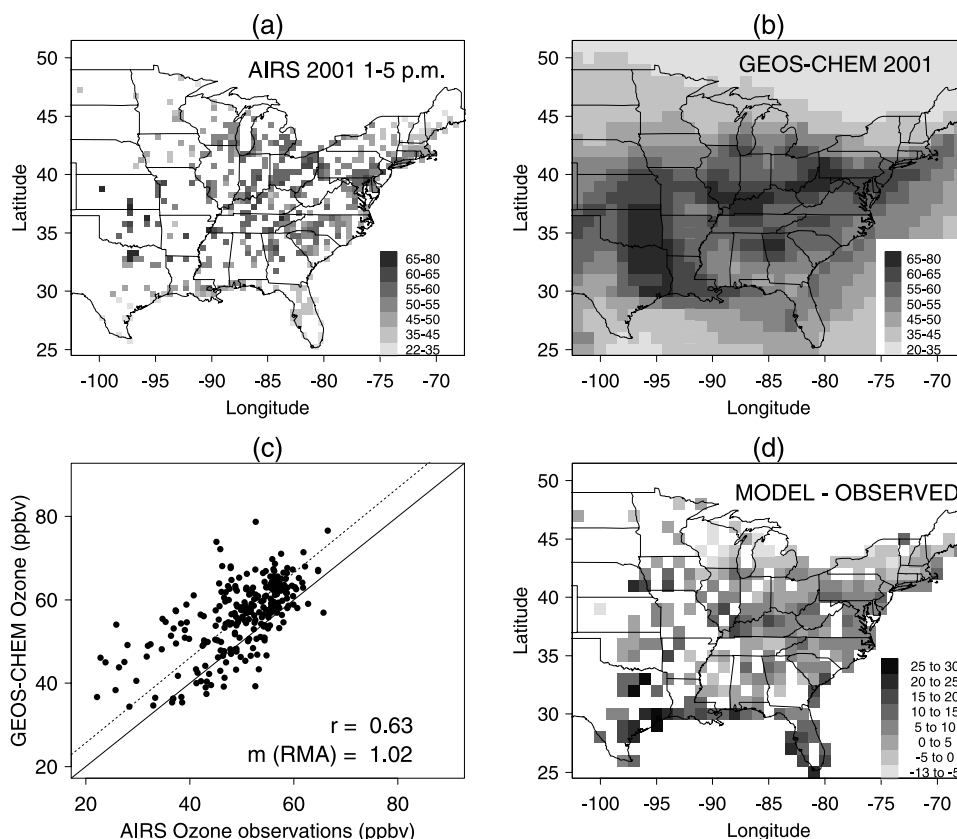


Figure 3. Mean afternoon (1300–1700 LT) O_3 concentrations (ppbv) in surface air over the eastern United States in July 2001: (a) U.S. EPA AIRS observations averaged over a 0.5° latitude by 0.5° longitude grid, (b) GEOS-CHEM model surface layer (GSTD in Table 1), (c) correlation, and (d) difference between GSTD and the AIRS observations averaged over the $1^\circ \times 1^\circ$ 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.

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 RO_2 with NO [Sprengnether *et al.*, 2002] and treat them as a NO_x sink by converting them directly to nitric acid (MOZKIT) as in GEOS-CHEM. The MOZART-2 mechanism also recycles HO_x radicals via photolysis of isoprene peroxides (similar to GEOS-CHEM); we examine the impact of this recycling on surface O_3 by turning off this photolysis and instead permitting isoprene peroxides to be a sink for HO_x (MOZPER).

3. Surface O_3 Response to Recent Precursor Emissions Trends

3.1. Biogenic Isoprene

[23] The simulated changes in mean July afternoon (1300–1700 local time (LT)) surface O_3 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 O_3 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 O_3

by 1–2 ppbv in the GEIA-based simulation (Figure 4a). In this region, isoprene emissions are already high (Figure 2a) and NO_x emissions are low (Figure 2c). Under these conditions, isoprene ozonolysis is an important sink for O_3 (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 O_3 decreases (<0.5 ppbv) in the southern states when the BVOC changes are applied. Increases in O_3 concentrations of up to 2 ppbv occur in northeastern Texas where NO_x emissions are high (Figure 2c) and the rise in isoprene emissions (Figure 1a) leads to enhanced O_3 formation. With the GEIA inventory, O_3 concentrations show no response in northeastern Texas, presumably because the higher base-case GEIA isoprene emissions have pushed the chemistry of O_3 formation to a NO_x -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 O_3 by 1–2 ppbv

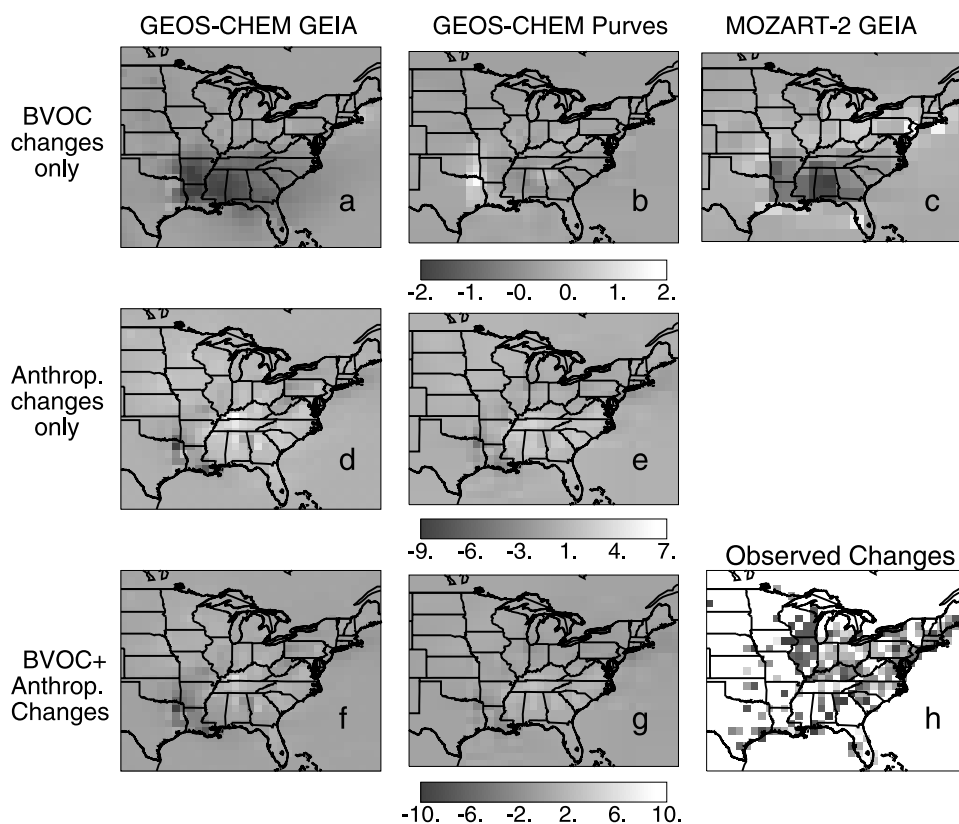


Figure 4. Change in mean July afternoon (1300–1700 LT) surface O_3 concentrations (ppbv) from the mid-1980s to the mid-1990s over the eastern United States, resulting from (top row) changes in biogenic isoprene: (a) GA85B95-GA85B85, (b) PA85B95-PA85B85, (c) MOZB95-MOZNIT; (middle row) changes in anthropogenic NO_x , 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 O_3 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. See color version of this figure at back of this issue.

in MOZART-2, similar to the O_3 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 NO_x , VOC, and CO

[26] The changes in anthropogenic emissions from 1985 to 1995 increase O_3 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 O_3 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

Table 3. Near-Surface O_3 Lifetime (days) Against Selected Photochemical Loss Pathways in the Southeastern United States^a

| Simulation (Table 1) | Reaction with OH, HO_2 , or CH_3O_2 | Photolysis (OH production) | Reaction with Biogenics ^b |
|----------------------|---|----------------------------|--------------------------------------|
| GSTD | 16 | 11 | 10 |
| GISOP25 | 17 | 11 | 16 |
| GNOx25 | 17 | 11 | 9 |
| PSTD | 18 | 11 | 58 |
| PISOP25 | 18 | 11 | 87 |
| PNOx25 | 19 | 11 | 49 |

^aLifetime is the spatial average for $30.5^\circ N$ – $37.5^\circ N$ and $81.5^\circ W$ – $91.5^\circ W$ (encompassing Georgia, Alabama, Mississippi, Tennessee, Arkansas, and northern Louisiana), calculated from the column sum of the simulated 24-hour mean July O_3 concentration and chemical loss rates in the bottom seven model boxes (~ 1.3 km altitude).

^bThis includes isoprene, other biogenic alkenes, methylvinylketone, methacrolein, peroxyacetyl nitrates, and isoprene aldehydes.

shown), however, indicate that our results in Figures 4d and 4e are largely driven by the changes in NO_x emissions (Figure 1d), as expected for the highly NO_x -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 NO_x emissions (Figure 1). Consistent with earlier modeling studies [Roselle, 1994], the simulated response to anthropogenic NO_x 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.

[27] The simulated O_3 changes resulting from the combination of anthropogenic and biogenic emissions changes range from -10 to $+6$ and -5 to $+3$ ppbv in Figures 4f (GEIA case) and 4g (Purves case), respectively. The simulated O_3 responses from the combined emissions changes in Figures 4f and 4g are roughly equal (within 1 ppbv) to the sum of the O_3 responses when the biogenic and anthropogenic emissions are changed separately (Figures 4a plus 4d; 4b plus 4e), indicating that the chemical responses are fairly linear.

3.3. Comparison With Observed O_3 Changes

[28] In this section, we assess whether the reported emissions changes explain the observed trends in O_3 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 O_3 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 O_3 are consistent with previously reported trends for observed O_3 concentrations from 1985–1996 [Wolff *et al.*, 2001]. Widespread decreases in O_3 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.

[29] Consistent with the observed changes, Figures 4f (GEIA case) and 4g (Purves case) show O_3 decreases along the northeast corridor, and over eastern Illinois (especially the Purves case), eastern Texas, Arkansas, and Louisiana, and O_3 increases over Tennessee. Overall, however, the spatial pattern of the simulated changes (Figures 4f and 4g) differs substantially from those observed (Figure 4h; $r^2 \sim 0.0$ for both GEIA- and Purves-based simulations). We conclude that the anthropogenic and biogenic emission changes considered here are insufficient to explain the observed O_3 trends.

[30] The disagreement between simulated and observed O_3 changes suggests that other factors, not considered in this study, may have contributed to the O_3 changes from the mid-1980s to the mid-1990s. One possibility is that the $1^\circ \times 1^\circ$ horizontal resolution of the GEOS-CHEM model is too coarse to resolve power plant or urban plume chemistry. In particular, the dispersal of NO_x emissions over a coarse Eulerian grid cell could result in higher O_3 production efficiency (per molecule of NO_x emitted). Indeed, Sillman *et al.* [1990b] showed that degrading horizontal resolution

from 20 to 80 km yielded 7–10 ppbv increases in rural O_3 concentrations. Results from regional models incorporating subgrid-scale plume models, however, indicate little net change in surface O_3 over the northeastern United States despite substantial changes in local O_3 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- NO_x power plant plumes matters little for our comparison with observations, as Karamchandani *et al.* [2002] found that power plant plumes are not detected by the EPA AIRS O_3 stations. Nevertheless, the observations could reflect NO_x -saturated urban plumes not resolved in the model. While the EPA designates AIRS sites as “urban,” “rural,” or “suburban,” earlier work has shown that sites labeled urban are actually associated with a wide range of local NO_x emissions [Fiore *et al.*, 1998], suggesting that urban plumes cannot be easily excluded from the data.

[31] Additional factors that may contribute to the discrepancies between our simulations and the observations include decadal shifts in meteorology (and their effect on isoprene emissions), changes in global background O_3 associated with foreign emission trends, or problems with the reported domestic emission changes. These factors could be addressed in a future study with a model that resolves both global emission changes and urban plume chemistry. An alternative explanation for the discrepancy between observed and simulated O_3 changes during this period is that the current understanding of isoprene emissions and chemistry may not support a quantitative attribution of observed O_3 trends to precursor emission changes. We examine this possibility further with sensitivity studies designed to show the impact on surface O_3 from (1) the choice of isoprene emission inventory and (2) uncertainties in isoprene chemistry.

4. Ozone Sensitivity to Anthropogenic NO_x and Biogenic Isoprene Emissions

4.1. Diagnosing the O_3 Chemical Regime

[32] The chemical O_3 formation regime is typically determined with modeling studies where anthropogenic NO_x and anthropogenic VOC are reduced separately by a uniform percentage. Whichever precursor control strategy yields the larger decrease in O_3 concentrations is deemed to be the “limiting” or “sensitive” precursor for O_3 production. Here we extend this approach to examine whether O_3 formation is more sensitive to NO_x or to biogenic isoprene emissions. 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. Figures 5a and 5b show the changes in surface O_3 resulting from 25% decreases in isoprene emissions for the GEIA- and Purves-based simulations, respectively. Larger O_3 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 O_3 concentrations. In GSTD, the high isoprene concentrations react directly with O_3 (Table 3) and remove NO_x from the atmosphere (as isoprene nitrates), suppressing O_3 production. The region of largest

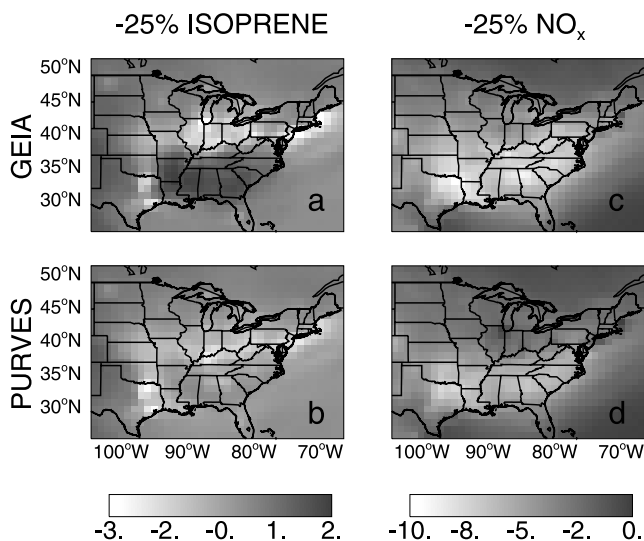


Figure 5. Change in mean July afternoon (1300–1700 LT) surface O_3 concentrations (ppbv) when isoprene and anthropogenic NO_x emissions are decreased by 25% in GEOS-CHEM: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNO $_x$ 25-GSTD, and (d) PNO $_x$ 25-PSTD. Simulations are described in Table 1. See color version of this figure at back of this issue.

O_3 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 O_3 concentrations in the vicinity of NO_x sources. In contrast to the GEIA case, little change in O_3 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 O_3 to one in which additional isoprene will decrease O_3 [Kang *et al.*, 2003].

[33] The O_3 response to 25% reductions in anthropogenic NO_x emissions (Figures 5c and 5d) is highly dependent on the base isoprene emission inventory. The larger 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 O_3 for reaction with isoprene. These results indicate that quantifying the uncertainties in isoprene emissions is critical, as the nonlinear chemical interactions of isoprene, NO_x , and O_3 will affect conclusions drawn about O_3 sensitivity to anthropogenic emission controls [Roselle, 1994].

[34] Table 3 compares the importance of selected photochemical O_3 loss mechanisms in the southeastern region. Loss of O_3 via reaction with biogenic compounds is as large as the typical major photochemical O_3 loss pathways (photolysis and reaction with HO_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_3 loss mechanism. Thus, given our present understanding, estimates of the contribution of various pathways to the regional photochemical O_3 sink

over the southern United States will depend strongly upon the assumed isoprene and NO_x emissions.

4.2. Sensitivity of High- O_3 Events

[35] Figure 6 shows the impact of the emissions perturbations discussed above on high- O_3 events (defined here as $O_3 > 70$ ppbv) from selected simulations, plotted as a function of the surface O_3 in the corresponding base-case simulation. Decreases in isoprene emissions reduce nearly all high- O_3 events for the Purves case while decreases in GEIA isoprene emissions lead to some increases in high- O_3 events, particularly in the southeastern United States, for the reasons discussed in sections 3.1 and 4.1. All high- O_3 events respond strongly to NO_x 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 O_3 decrease achieved with a given NO_x reduction.

[36] For the most extreme events ($O_3 > 90$ 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 O_3 but lower anthropogenic VOC, CO, and NO_x emissions tend to decrease O_3 . 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 O_3 concentrations (<5 ppbv) than the changes in anthropogenic emissions over the same period (up to 15 ppbv). While the magnitude of the O_3 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 O_3 concentrations over the eastern United 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 mitigated or exacerbated O_3 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 O_3

5.1. Isoprene Emissions

[37] July mean afternoon O_3 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 O_3 associated with the choice of isoprene inventory is thus larger than the O_3 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 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

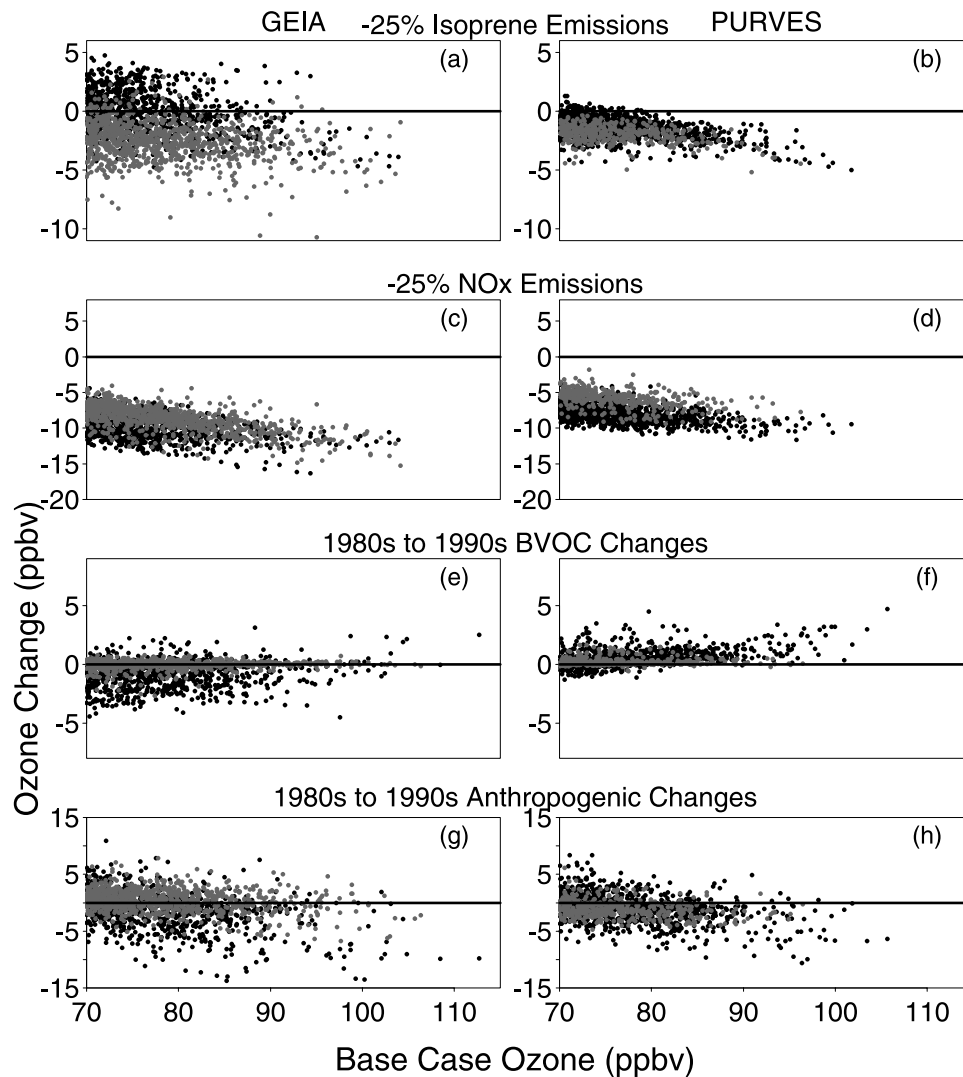


Figure 6. Change in July daily mean afternoon (1300–1700 LT) high- O_3 events ($O_3 > 70$ ppbv) for selected GEOS-CHEM simulations with the (left) GEIA and (right) Purves isoprene emissions, plotted as a function of the corresponding base-case simulation: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNOX25-GSTD, (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 O_3 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 . See color version of this figure at back of this issue.

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

[38] 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].

[39] 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).

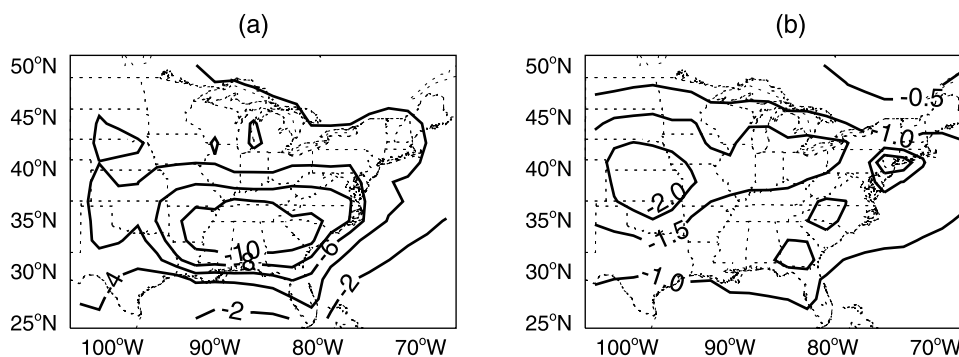


Figure 7. Change in mean July afternoon (1300–1700 LT) surface O_3 concentrations in MOZART-2 associated with uncertainties in the fate of (a) isoprene nitrates (MOZNIT-MOZSTD) and (b) organic peroxides formed during isoprene oxidation (MOZPER-MOZSTD). Simulations are described in Table 1.

We conclude that our earlier finding that isoprene ozonolysis may be an important photochemical O_3 loss pathway in the southeastern United States (section 4.1) is only true if isoprene nitrates are a sink for NO_x (as is the case for GSTD in Table 3).

[40] 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 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 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 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 a factor of 3–12 or they are rapidly photolyzed and serve only as a temporary reservoir of HO_x .

[41] 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 stem from 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

[42] 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 O_3 associated with concurrent reductions in anthropogenic VOC [Purves *et al.*, 2004]. With MOZART-2 and a $1^\circ \times 1^\circ$ 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 NO_x) emission changes on surface O_3 over this period. We then compared the simulated 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 characterize the sensitivity of surface O_3 in the

eastern United States to uncertainties in isoprene emissions and chemistry.

[43] The simulated O_3 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 NO_x emissions changes on surface O_3 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 O_3 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 NO_x emissions from road traffic [Parrish *et al.*, 2002]) and uncertainties in isoprene emissions and chemistry may also preclude an accurate attribution of observed O_3 trends to precursor emission changes. Furthermore, we find that the estimated efficacy of anthropogenic NO_x emission controls on simulated O_3 depends strongly upon the chosen isoprene emission inventory, consistent with prior studies [e.g., Roselle, 1994].

[44] The magnitude of the O_3 sensitivity to uncertainties in isoprene emissions and chemistry is similar to or greater than the simulated O_3 response to the reported emissions changes, biogenic or anthropogenic. Surface O_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 peroxide chemistry have a smaller impact on surface O_3 (<3 ppbv). These uncertainties translate into a major uncertainty in the magnitude, and in some cases the sign, of the O_3 response to changes in precursor emissions. Coordinated in situ measurements of a suite of relevant compounds (such as O_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_3 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 NO_x 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 NO_x emissions are implemented.

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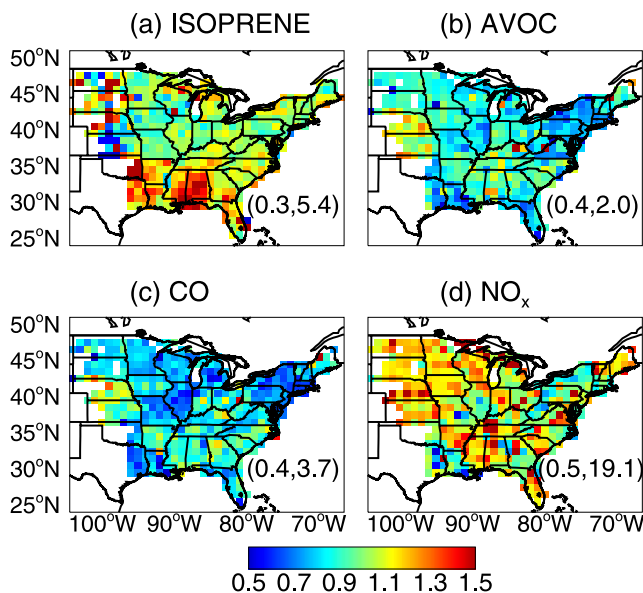


Figure 1. Ratio of emissions in 1995 to 1985 over the eastern United States for (a) isoprene (actually mid-1990s to mid-1980s) as estimated by *Purves et al.* [2004], and anthropogenic (b) VOC, (c) CO, and (d) NO_x from the U.S. EPA national emissions inventory (<http://www.epa.gov/air/data/geosel.html>). 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.

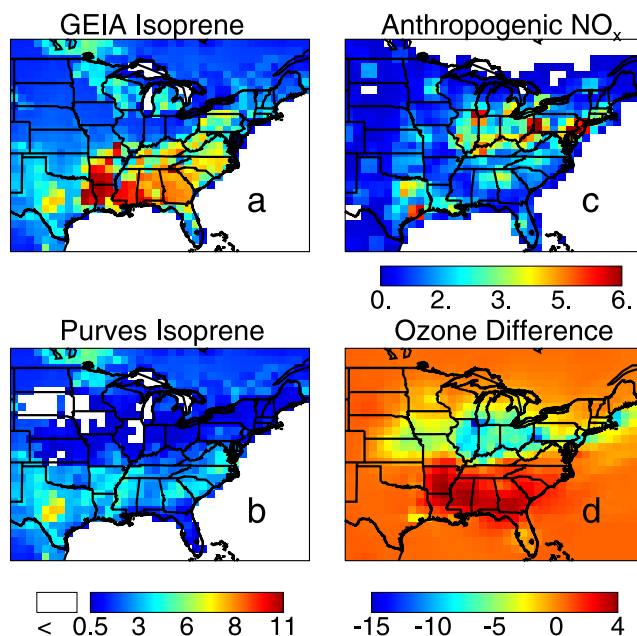


Figure 2. Emissions (10^{11} molecules cm^{-2}) of isoprene from the (a) GEIA (b) *Purves et al.* [2004], and (c) anthropogenic NO_x inventories in GEOS-CHEM, and (d) the difference in July mean afternoon (1300–1700 LT) surface O₃ (ppbv) resulting from application of the *Purves et al.* [2004] isoprene inventory versus GEIA (PSTD–GSTD in Table 1). The color bar for NO_x emissions saturates (maximum is 8).

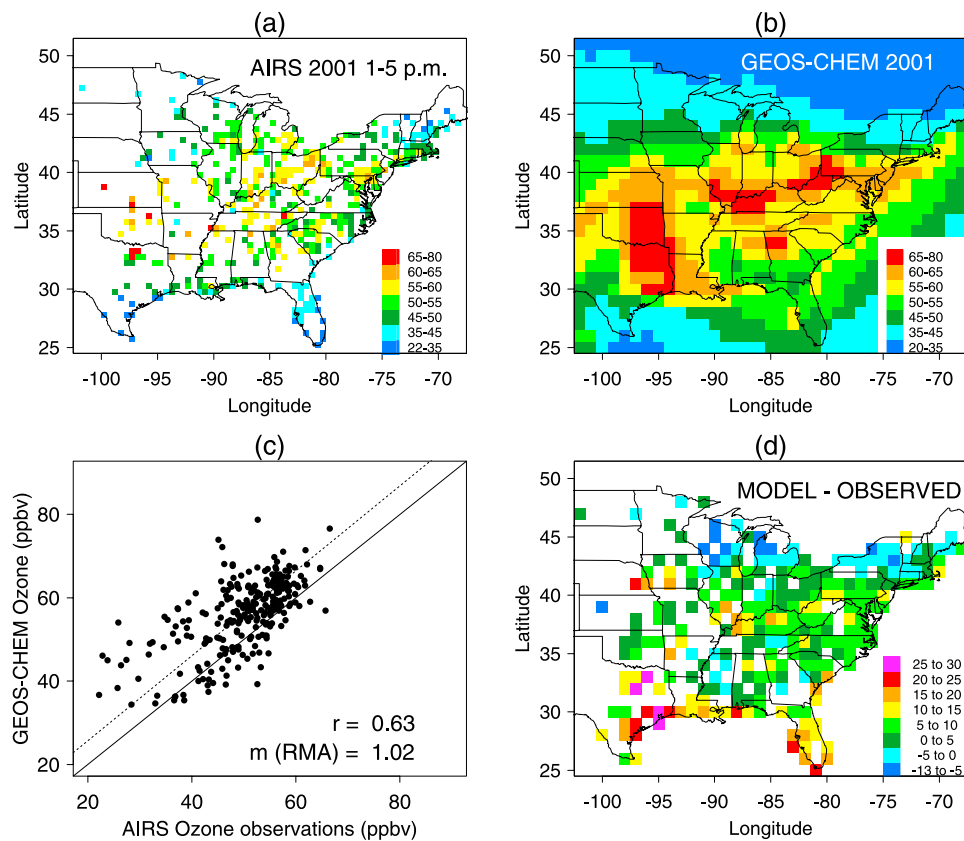


Figure 3. Mean afternoon (1300–1700 LT) O_3 concentrations (ppbv) in surface air over the eastern United States in July 2001: (a) U.S. EPA AIRS observations averaged over a 0.5° latitude by 0.5° longitude grid, (b) GEOS-CHEM model surface layer (GSTD in Table 1), (c) correlation, and (d) difference between GSTD and the AIRS observations averaged over the $1^\circ \times 1^\circ$ 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).

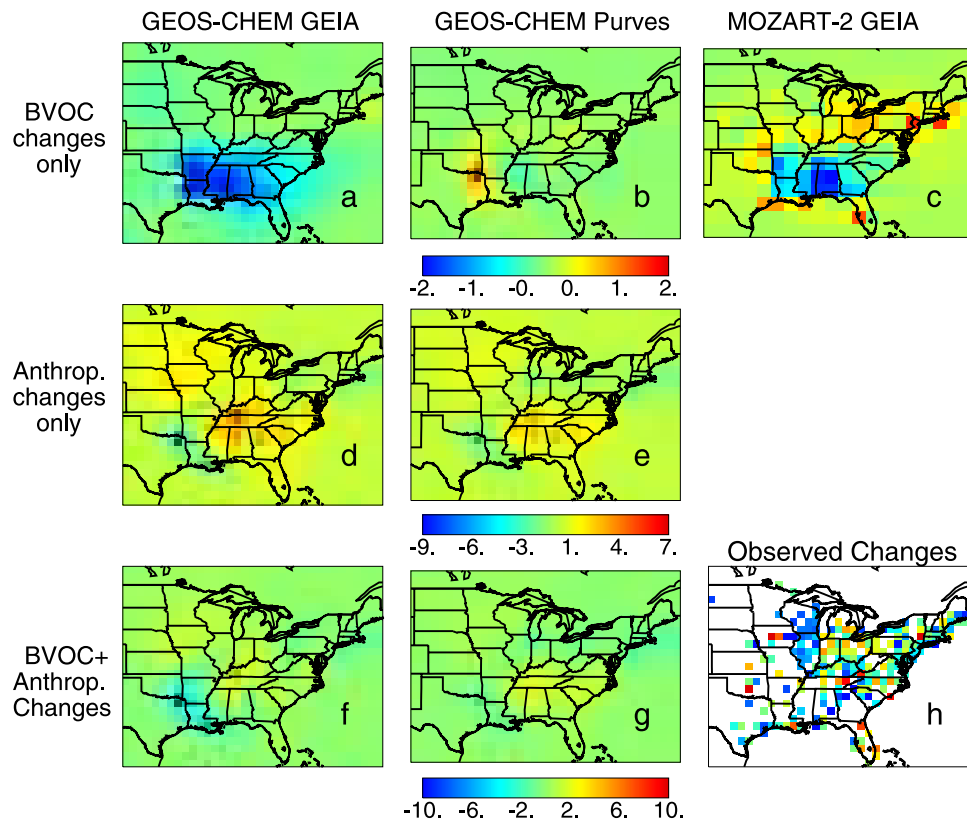


Figure 4. Change in mean July afternoon (1300–1700 LT) surface O_3 concentrations (ppbv) from the mid-1980s to the mid-1990s over the eastern United States, resulting from (top row) changes in biogenic isoprene: (a) GA85B95-GA85B85, (b) PA85B95-PA85B85, (c) MOZB95-MOZNIT; (middle row) changes in anthropogenic NO_x , 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 O_3 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.

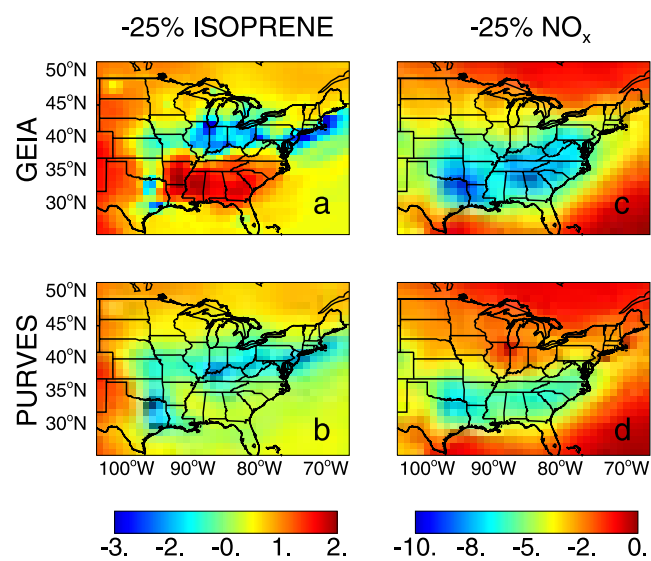


Figure 5. Change in mean July afternoon (1300–1700 LT) surface O₃ concentrations (ppbv) when isoprene and anthropogenic NO_x emissions are decreased by 25% in GEOS-CHEM: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNO_x25-GSTD, and (d) PNO_x25-PSTD. Simulations are described in Table 1.

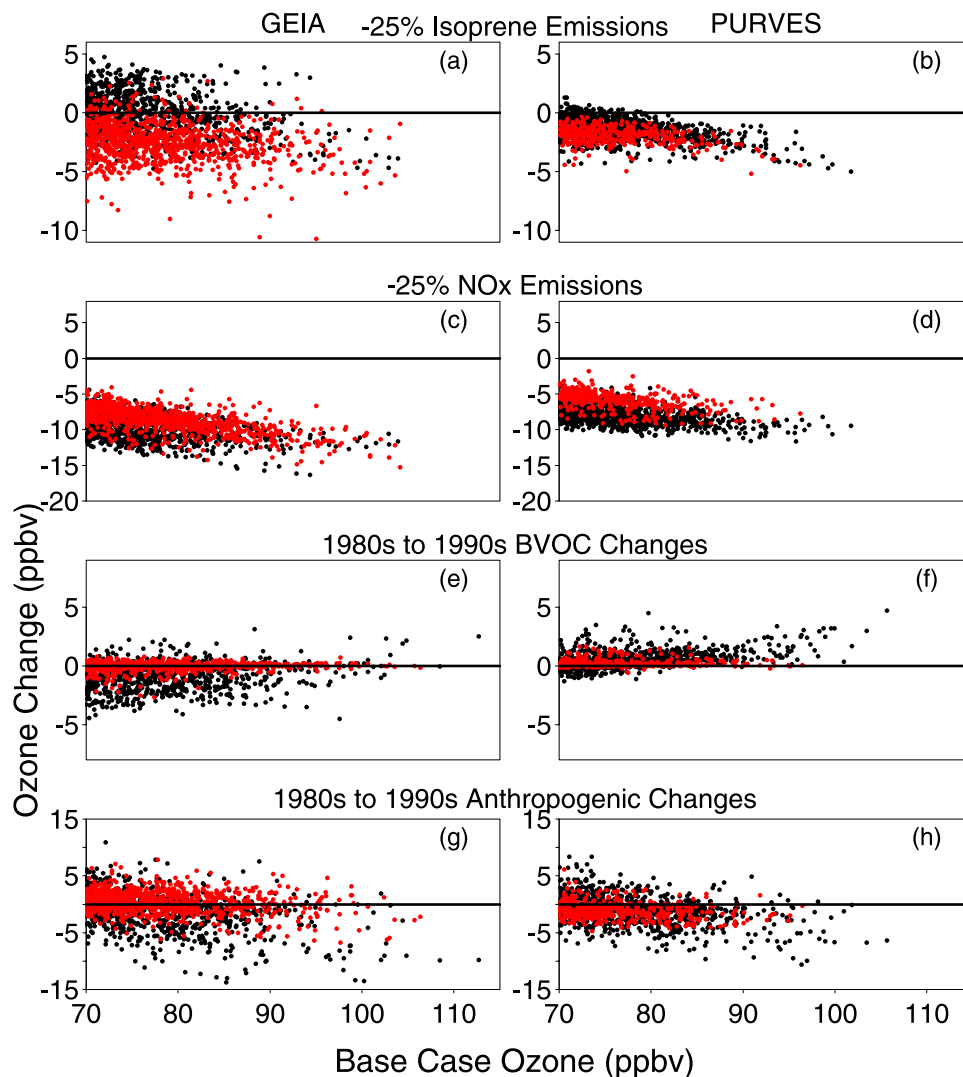


Figure 6. Change in July daily mean afternoon (1300–1700 LT) high- O_3 events ($O_3 > 70$ ppbv) for selected GEOS-CHEM simulations with the (left) GEIA and (right) Purves isoprene emissions, plotted as a function of the corresponding base-case simulation: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNOX25-GSTD, (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 O_3 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 .