

## 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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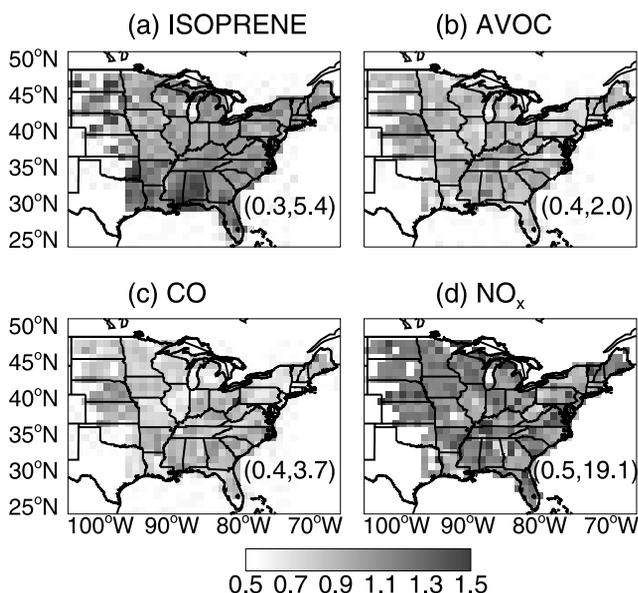
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### 1. Introduction

[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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> trends over the eastern United States, in light of current uncertainties in isoprene emissions and chemistry.

[4] The relative magnitudes of NO<sub>x</sub> emissions and isoprene emissions determine whether a given increase in isoprene emissions will enhance, deplete, or have little impact on surface O<sub>3</sub> [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<sub>2</sub>) and organic peroxy (RO<sub>2</sub>) radicals, which can react with NO<sub>x</sub> (primarily from anthropogenic sources [*Logan*, 1983; *Levy et al.*, 1999]) to stimulate O<sub>3</sub> 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<sub>x</sub> emissions, O<sub>3</sub> production is typically NO<sub>x</sub>-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 O<sub>3</sub> production on the supply of HO<sub>x</sub> (OH + HO<sub>2</sub> + RO<sub>2</sub>) and NO<sub>x</sub> radicals.) Finally, high isoprene emissions (especially in regions of low NO<sub>x</sub> emissions) can decrease O<sub>3</sub> by (1) sequestering NO<sub>x</sub> as isoprene nitrates and thereby suppressing O<sub>3</sub> 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<sub>x</sub>-O<sub>3</sub> chemistry [e.g., *Paulson and Seinfeld*, 1992; *Carter and Atkinson*, 1996] complicates efforts to quantify the isoprene-O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> from the reported isoprene (Figure 1a) and anthropogenic O<sub>3</sub> precursor (Figures 1b–1d) emission changes with the observed O<sub>3</sub> changes over the same period (section 3). We then examine the influence of precursor emissions changes on the occurrence of high-O<sub>3</sub> events, which are relevant for public health and for compliance with the national O<sub>3</sub> standard (section 4). Finally, we demonstrate the sensitivity of our surface O<sub>3</sub> 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 O<sub>3</sub> 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 <sup>a</sup>	Year for Anthropogenic Inventories <sup>a</sup>
GEOS-CHEM (1° × 1°; GMAO 2001 meteorology)	(G/P) <sup>b</sup> STD <sup>c</sup>	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 <sub>x</sub> reduced by 25% early 1990s
MOZART-2 (1.9° × 1.9°; NCEP 2001 meteorology)	MOZSTD <sup>c</sup>	mid-1980s	MOZSTD with isoprene nitrates acting as a NO <sub>x</sub> sink (section 2.2)
	MOZB95	MOZNIT with mid-1990s	MOZNIT with early 1990s
	MOZNIT	MOZSTD with isoprene nitrates acting as a NO <sub>x</sub> sink (section 2.2)	MOZSTD with isoprene nitrates acting as a NO <sub>x</sub> sink (section 2.2)
	MOZPER	MOZSTD with isoprene peroxides acting as a HO <sub>x</sub> sink (section 2.2)	MOZSTD with isoprene peroxides acting as a HO <sub>x</sub> sink (section 2.2)

<sup>a</sup>See Table 2 for emission totals. The standard GEIA isoprene inventory is considered to be representative of the mid-1980s.

<sup>b</sup>Two sets of simulations using different isoprene inventories are conducted with GEOS-CHEM: one with GEIA (“G”) and one with the Purves (“P”). The MOZART-2 simulations use only the GEIA isoprene inventory.

<sup>c</sup>Standard is labeled as such for consistency with prior work [e.g., *Bey et al.*, 2001; *Horowitz et al.*, 2003].

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

## 2.1. GEOS-CHEM

[9] We apply a 1° × 1° one-way nested version of the GEOS-CHEM three-dimensional tropospheric NO<sub>x</sub>-O<sub>3</sub>-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 O<sub>3</sub> 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 O<sub>3</sub> 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<sub>x</sub> 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](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<sub>x</sub> from the atmosphere. Organic peroxides react with OH or recycle HO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub>) 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)<sup>a</sup>

	Year		Isoprene, <sup>b</sup> Tg C		Anthropogenic		
	Isoprene	Anthropogenic	GEIA	PURVES	NMHC, <sup>c</sup> Tg C	NO <sub>x</sub> , 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 <sup>d</sup>	–	0.20	0.49	4.8

<sup>a</sup>See section 2 for details.

<sup>b</sup>GEIA inventory fills in where the Purves inventory lacks data (i.e., white regions in Figure 1).

<sup>c</sup>This comprises C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> in MOZART-2; C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, lumped  $\geq$ C<sub>3</sub> alkenes and  $\geq$ C<sub>4</sub> alkanes in GEOS-CHEM.

<sup>d</sup>This increases to 5.6 Tg C when the changes in Figure 1a are applied.

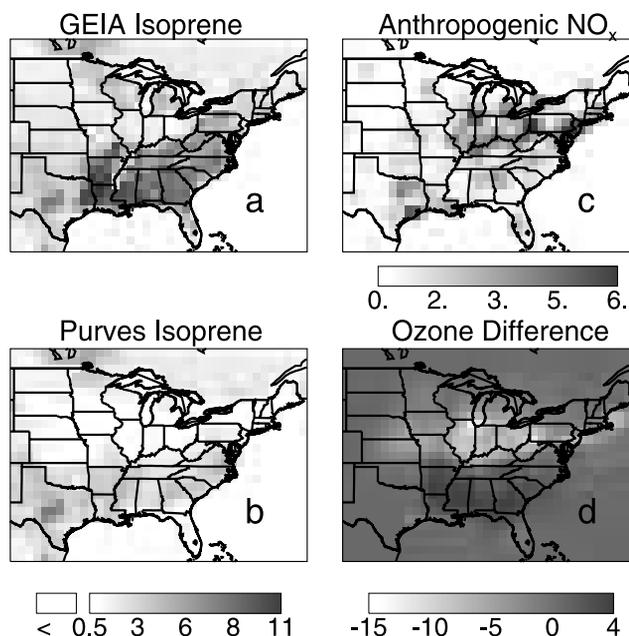
### 2.1.1. Modifications to Isoprene Emissions

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

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

columns (5.7 Tg C), whereas the GEIA isoprene emissions are 20% higher (7.1 Tg C) [*Palmer et al.*, 2003], although uncertainties remain in the satellite estimates. Thus the discrepancies between the isoprene inventories used in this study are a fair representation of the current level of uncertainty in isoprene emissions from the eastern United States.

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



**Figure 2.** Emissions ( $10^{11}$  molecules  $\text{cm}^{-2}$ ) of isoprene from the (a) GEIA (b) *Purves et al.* [2004], and (c) anthropogenic NO<sub>x</sub> inventories in GEOS-CHEM, and (d) the difference in July mean afternoon (1300–1700 LT) surface O<sub>3</sub> (ppbv) resulting from application of the *Purves et al.* [2004] isoprene inventory versus GEIA (PSTD–GSTD in Table 1). The color bar for NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> emissions were much less regionally coherent. The reported overall increase in NO<sub>x</sub> emissions mainly reflects changes in area sources (responsible for 70% of the total domain-wide changes in NO<sub>x</sub> 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<sub>x</sub> emissions [Trainer *et al.*, 2000, and references therein], but substantial uncertainties exist in road-traffic (area) NO<sub>x</sub> 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 O<sub>3</sub> Simulation

[18] GEOS-CHEM has been evaluated extensively with observations of O<sub>3</sub> 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, O<sub>3</sub>, and aerosols [Li *et al.*, 2005]. Prior evaluations of O<sub>3</sub> simulations over the United States show that GEOS-CHEM adequately captures much of the spatial and temporal variability in summer afternoon O<sub>3</sub> concentrations [Fiore *et al.*, 2002, 2003a, 2003b] as well as the observed distribution of CH<sub>2</sub>O, 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 O<sub>3</sub> 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) O<sub>3</sub> monitoring stations for July 2001. We focus on afternoon hours,

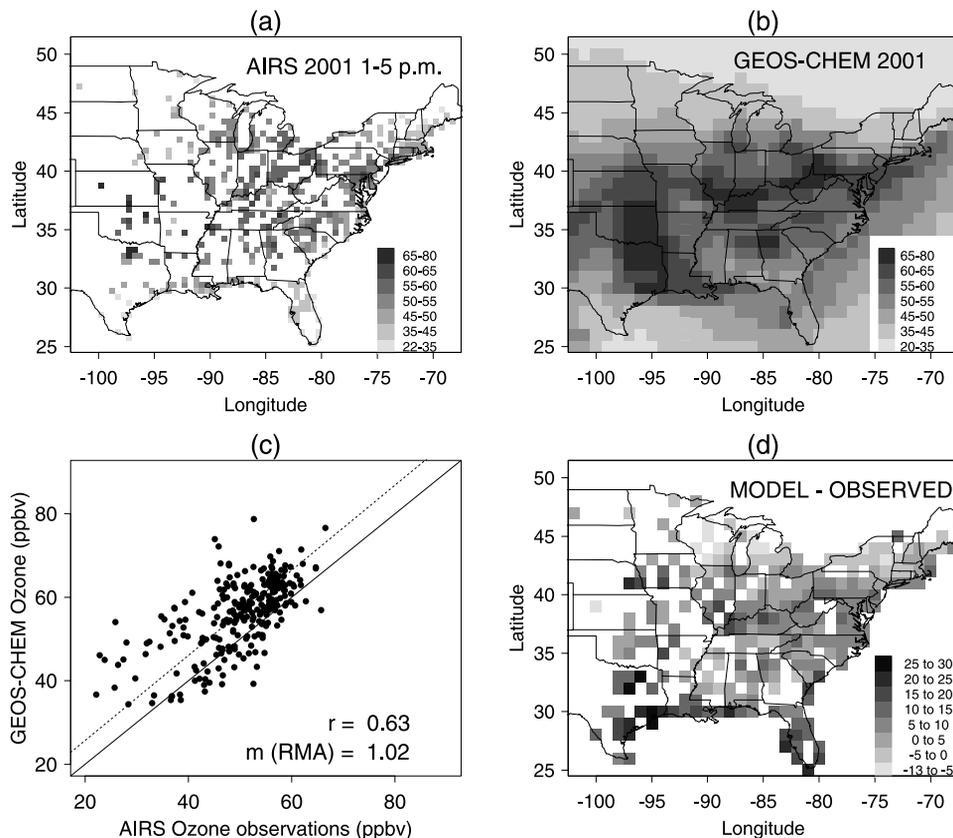
when O<sub>3</sub> concentrations tend to peak, and when the observations should represent a relatively deep mixed layer which is most suitable for model evaluation [Fiore *et al.*, 2002]. The model captures nearly half of the spatial variance of the mean July afternoon observations ( $r^2 = 0.40$ ; 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  $6 \pm 7$  ppbv. Consistent with earlier GEOS-CHEM evaluations [Fiore *et al.*, 2002, 2003b], the model severely overestimates O<sub>3</sub> concentrations in Florida and along the Gulf of Mexico. The high-O<sub>3</sub> 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<sub>x</sub> and isoprene emissions (Figure 2). The model overestimate in the Ohio River valley (Figure 3) may be associated with controls on power plant NO<sub>x</sub> emissions that were implemented in 1999 [Frost *et al.*, 2004] and are not reflected in the 1995 GEOS-CHEM anthropogenic NO<sub>x</sub> emissions inventory used here. The PSTD simulation (not shown) gives a lower mean July afternoon O<sub>3</sub> bias ( $4 \pm 8$  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 O<sub>3</sub> 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<sub>x</sub>-sensitive O<sub>3</sub> 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<sub>x</sub>-O<sub>3</sub> 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<sub>x</sub> 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  $0.5^\circ$  latitude by  $0.5^\circ$  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

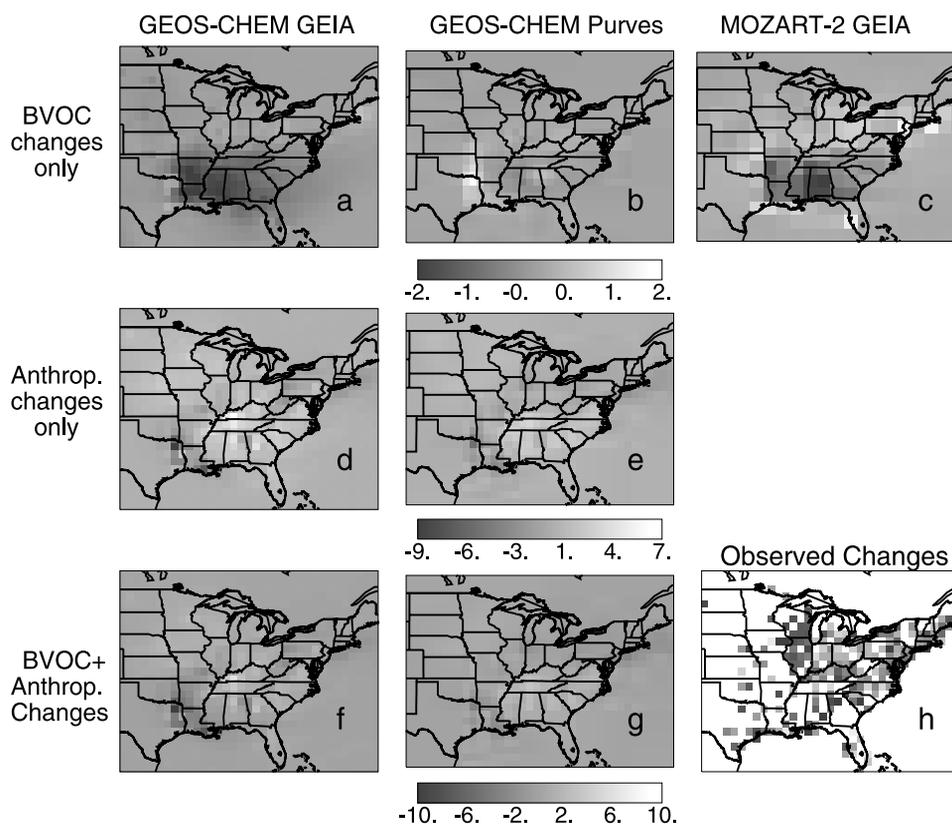
#### 3.1. Biogenic Isoprene

[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<sup>a</sup>

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

<sup>a</sup>Lifetime 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 ( $\sim 1.3$  km altitude).

<sup>b</sup>This 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  $\text{NO}_x$  emissions (Figure 1d), as expected for the highly  $\text{NO}_x$ -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  $\text{NO}_x$  emissions (Figure 1). Consistent with earlier modeling studies [Roselle, 1994], the simulated response to anthropogenic  $\text{NO}_x$  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  $\text{O}_3$  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  $\text{O}_3$  responses from the combined emissions changes in Figures 4f and 4g are roughly equal (within 1 ppbv) to the sum of the  $\text{O}_3$  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 $\text{O}_3$ Changes

[28] In this section, we assess whether the reported emissions changes explain the observed trends in  $\text{O}_3$  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  $\text{O}_3$  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  $\text{O}_3$  are consistent with previously reported trends for observed  $\text{O}_3$  concentrations from 1985–1996 [Wolff *et al.*, 2001]. Widespread decreases in  $\text{O}_3$  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  $\text{O}_3$  decreases along the northeast corridor, and over eastern Illinois (especially the Purves case), eastern Texas, Arkansas, and Louisiana, and  $\text{O}_3$  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  $\text{O}_3$  trends.

[30] The disagreement between simulated and observed  $\text{O}_3$  changes suggests that other factors, not considered in this study, may have contributed to the  $\text{O}_3$  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  $\text{NO}_x$  emissions over a coarse Eulerian grid cell could result in higher  $\text{O}_3$  production efficiency (per molecule of  $\text{NO}_x$  emitted). Indeed, Sillman *et al.* [1990b] showed that degrading horizontal resolution

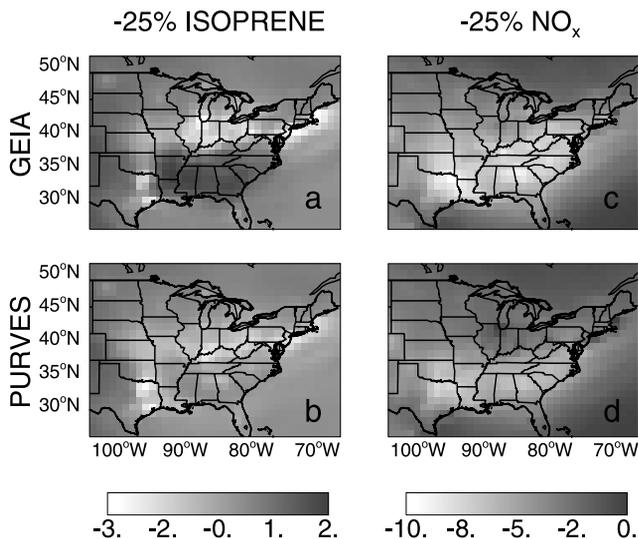
from 20 to 80 km yielded 7–10 ppbv increases in rural  $\text{O}_3$  concentrations. Results from regional models incorporating subgrid-scale plume models, however, indicate little net change in surface  $\text{O}_3$  over the northeastern United States despite substantial changes in local  $\text{O}_3$  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- $\text{NO}_x$  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  $\text{O}_3$  stations. Nevertheless, the observations could reflect  $\text{NO}_x$ -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  $\text{NO}_x$  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  $\text{O}_3$  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  $\text{O}_3$  changes during this period 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 impact on surface  $\text{O}_3$  from (1) the choice of isoprene emission inventory and (2) uncertainties in isoprene chemistry.

## 4. Ozone Sensitivity to Anthropogenic $\text{NO}_x$ and Biogenic Isoprene Emissions

### 4.1. Diagnosing the $\text{O}_3$ Chemical Regime

[32] The chemical  $\text{O}_3$  formation regime is typically determined with modeling studies where anthropogenic  $\text{NO}_x$  and anthropogenic VOC are reduced separately by a uniform percentage. Whichever precursor control strategy yields the larger decrease in  $\text{O}_3$  concentrations is deemed to be the “limiting” or “sensitive” precursor for  $\text{O}_3$  production. Here we extend this approach to examine whether  $\text{O}_3$  formation is more sensitive to  $\text{NO}_x$  or to biogenic isoprene emissions. We conduct four sensitivity simulations in which we reduce biogenic isoprene and anthropogenic  $\text{NO}_x$  emissions by 25%, separately, for both the GEIA and Purves isoprene inventories. Figures 5a and 5b show the changes in surface  $\text{O}_3$  resulting from 25% decreases in isoprene emissions for the GEIA- and Purves-based simulations, respectively. Larger  $\text{O}_3$  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  $\text{O}_3$  concentrations. In GSTD, the high isoprene concentrations react directly with  $\text{O}_3$  (Table 3) and remove  $\text{NO}_x$  from the atmosphere (as isoprene nitrates), suppressing  $\text{O}_3$  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

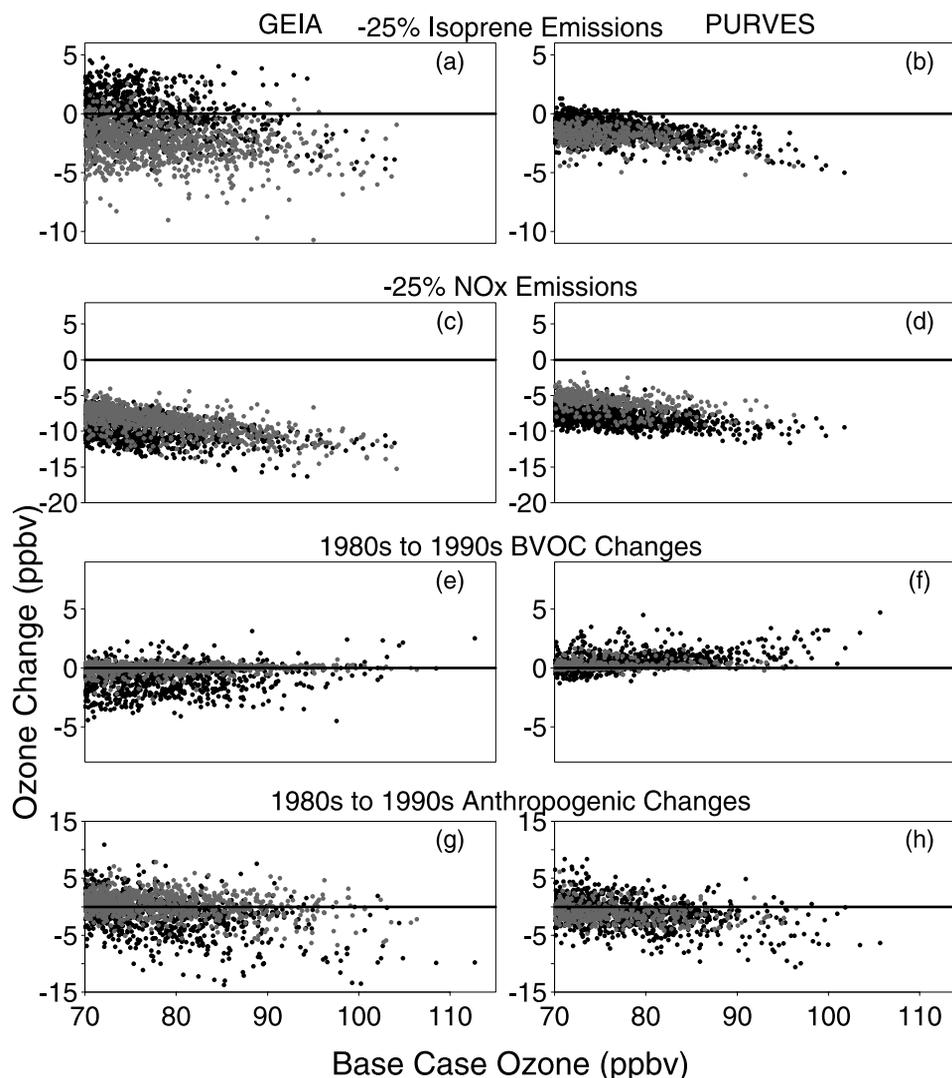
[35] Figure 6 shows the impact of the emissions perturbations discussed above on high- $O_3$  events (defined here as  $O_3 > 70$  ppbv) from selected simulations, plotted as a function of the surface  $O_3$  in the corresponding base-case simulation. Decreases in isoprene emissions reduce nearly all 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  $36^\circ\text{N}$ ) and southeastern (black; 253 total grid cells) United States, spanning  $66.5^\circ\text{W}$ – $104.5^\circ\text{W}$  and  $24.5^\circ\text{W}$ – $51.5^\circ\text{N}$ . See color version of this figure at back of this issue.

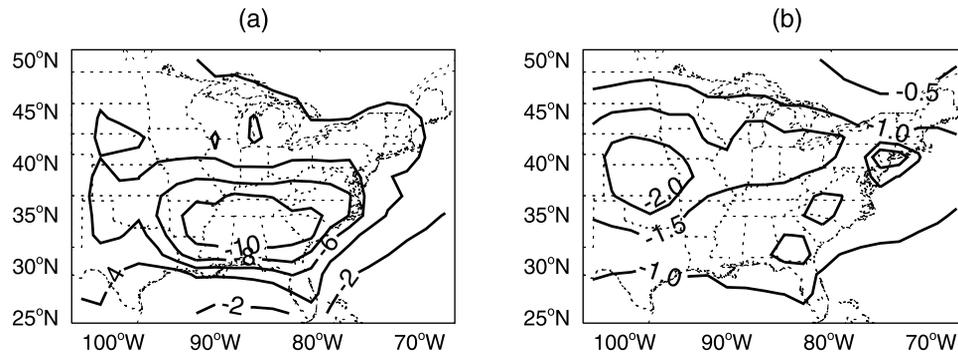
concentrations than the Purves inventory because the high GEIA-generated isoprene concentrations remove  $\text{NO}_x$  (through isoprene nitrates) and deplete OH concentrations, enabling isoprene to react directly with  $O_3$  (see Table 3 and section 4.1).

## 5.2. Isoprene- $\text{NO}_x$ - $O_3$ 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  $\text{NO}_x$  to the atmosphere (MOZSTD) and (2) isoprene nitrates are considered a permanent sink for  $\text{NO}_x$  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  $\text{NO}_x$  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  $\text{NO}_x$  (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

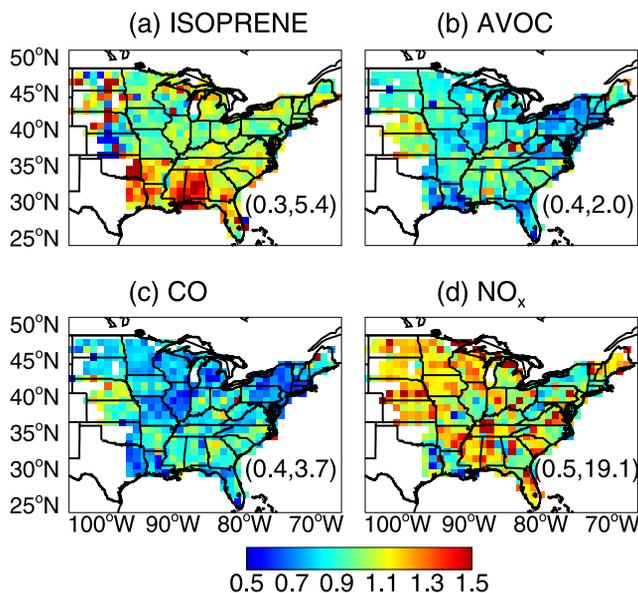
results indicate that such work is particularly needed in the southeastern United States where the high GEIA-inventory isoprene emissions promote an “isoprene-saturated” chemical regime. Under this regime, isoprene ozonolysis is an important O<sub>3</sub> loss pathway and increases in isoprene emissions decrease O<sub>3</sub> 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<sub>x</sub> 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 O<sub>3</sub> concentrations as much as might be anticipated from the strong correlation of high-O<sub>3</sub> events with temperature [e.g., Lin *et al.*, 2001], particularly if more stringent controls on anthropogenic NO<sub>x</sub> emissions are implemented.

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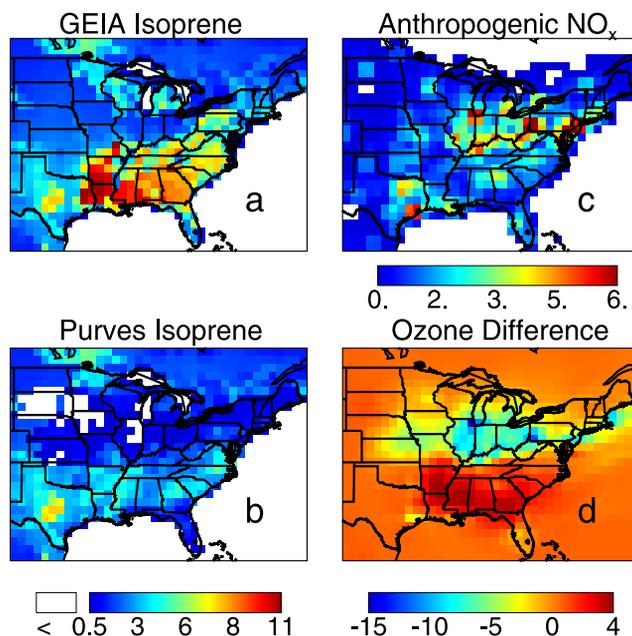
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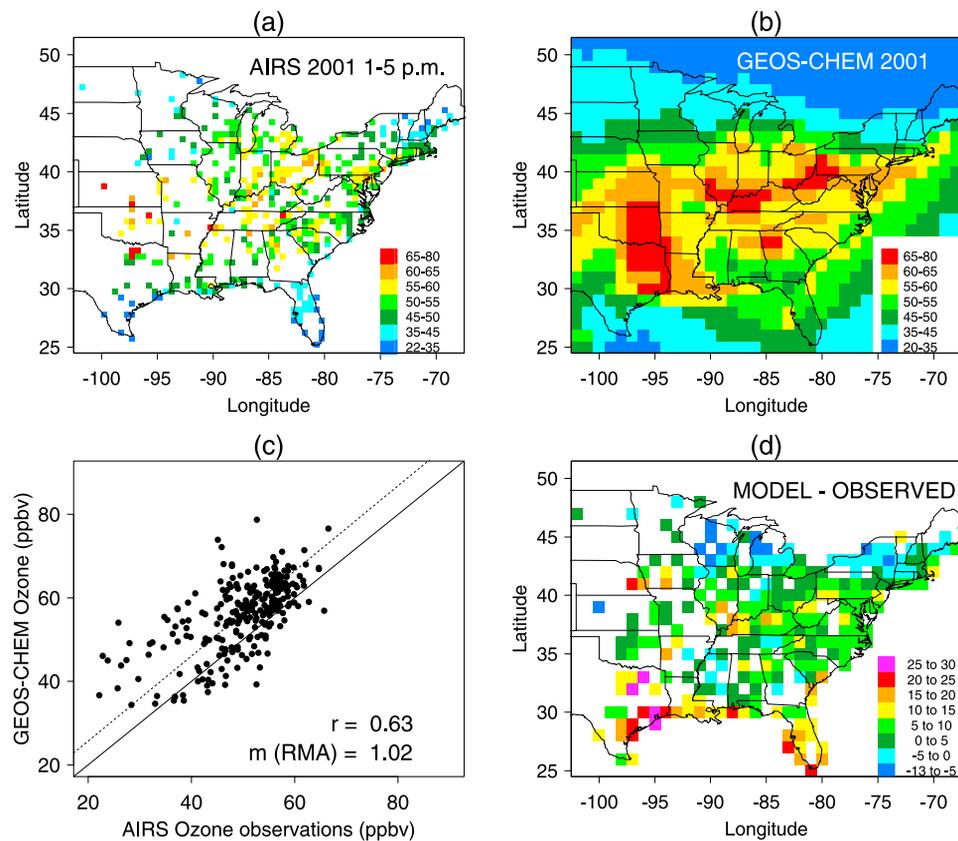
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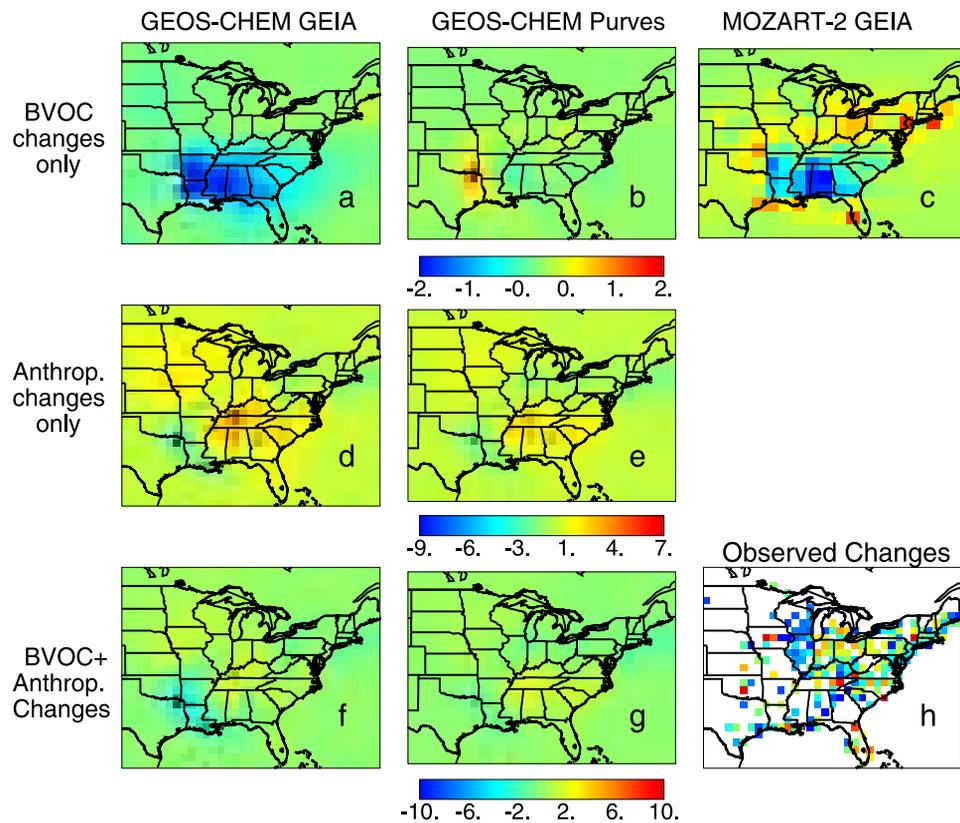
**Figure 1.** Ratio of emissions in 1995 to 1985 over the eastern United States for (a) isoprene (actually mid-1990s to mid-1980s) as estimated by *Purves et al.* [2004], and anthropogenic (b) VOC, (c) CO, and (d) NO<sub>x</sub> from the U.S. EPA national emissions inventory (<http://www.epa.gov/air/data/geosel.html>). See section 2 for details. Maximum and minimum values are shown in parentheses. The extreme increase in NO<sub>x</sub> emissions is driven by the reported changes for Cook County, Minnesota; the maximum value is 3.2 over the rest of the domain.



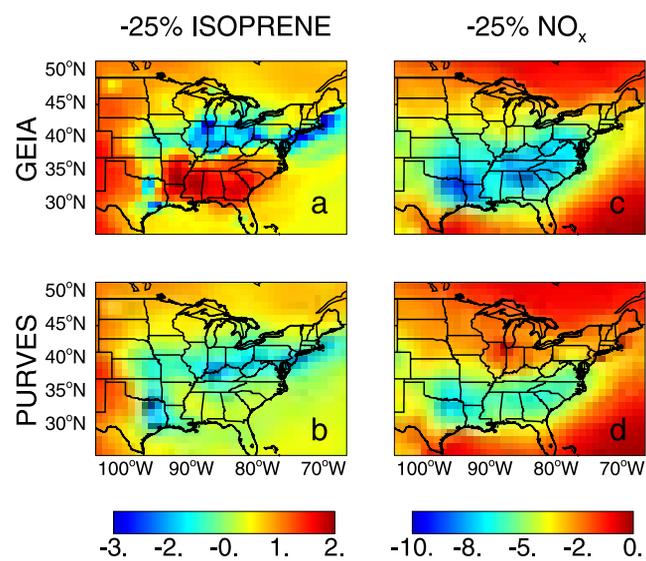
**Figure 2.** Emissions ( $10^{11}$  molecules  $\text{cm}^{-2}$ ) of isoprene from the (a) GEIA (b) *Purves et al.* [2004], and (c) anthropogenic NO<sub>x</sub> inventories in GEOS-CHEM, and (d) the difference in July mean afternoon (1300–1700 LT) surface O<sub>3</sub> (ppbv) resulting from application of the *Purves et al.* [2004] isoprene inventory versus GEIA (PSTD–GSTD in Table 1). The color bar for NO<sub>x</sub> emissions saturates (maximum is 8).



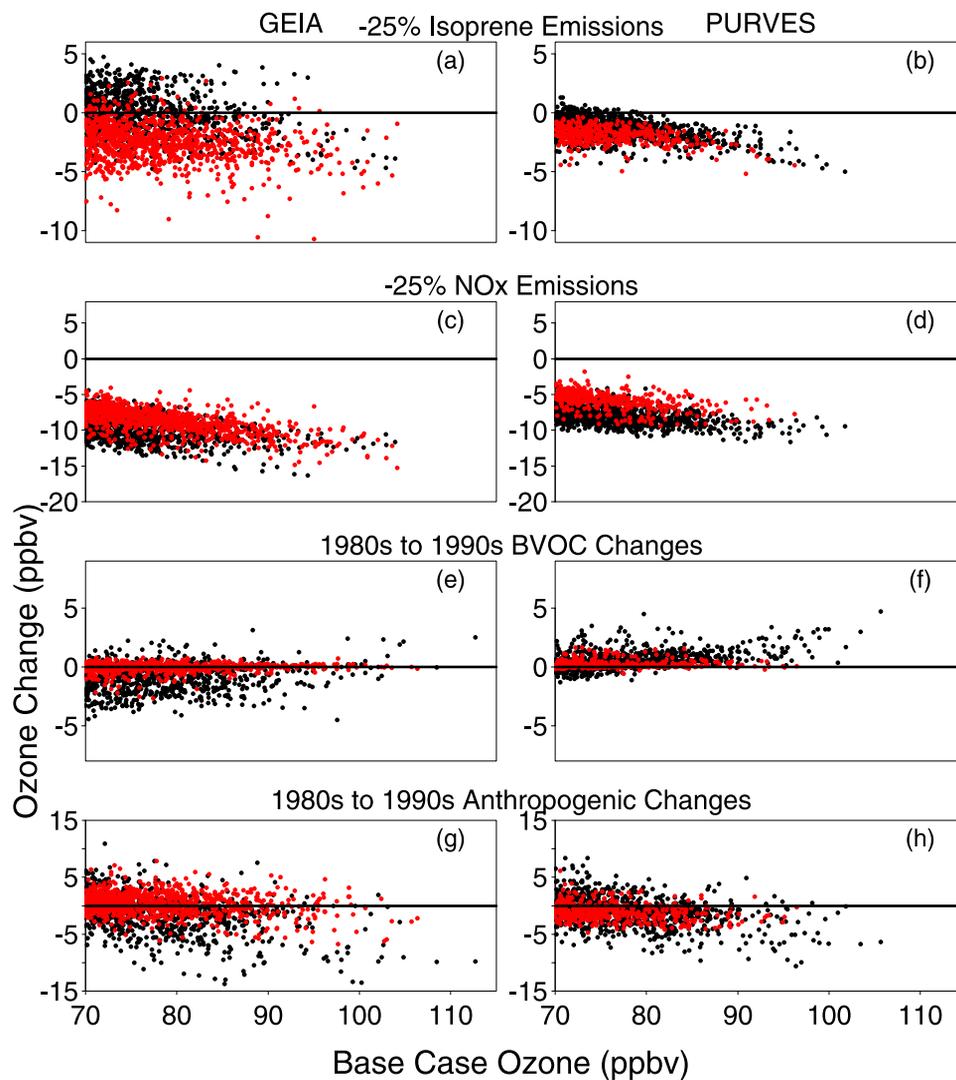
**Figure 3.** Mean afternoon (1300–1700 LT)  $\text{O}_3$  concentrations (ppbv) in surface air over the eastern United States in July 2001: (a) U.S. EPA AIRS observations averaged over a  $0.5^\circ$  latitude by  $0.5^\circ$  longitude grid, (b) GEOS-CHEM model surface layer (GSTD in Table 1), (c) 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 O<sub>3</sub> concentrations (ppbv) when isoprene and anthropogenic NO<sub>x</sub> emissions are decreased by 25% in GEOS-CHEM: (a) GISOP25-GSTD, (b) PISOP25-PSTD, (c) GNOx25-GSTD, and (d) PNOx25-PSTD. Simulations are described in Table 1.



**Figure 6.** Change in July daily mean afternoon (1300–1700 LT) high- $O_3$  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  $36^\circ\text{N}$ ) and southeastern (black; 253 total grid cells) United States, spanning  $66.5^\circ\text{W}$ – $104.5^\circ\text{W}$  and  $24.5^\circ\text{W}$ – $51.5^\circ\text{N}$ .