Why are there large differences between models in global budgets of tropospheric ozone?

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[1] Global 3-D tropospheric chemistry models in the literature show large differences in global budget terms for tropospheric ozone. The ozone production rate in the troposphere, \( P(O_x) \), varies from 2300 to 5300 Tg yr\(^{-1}\) across models describing the present-day atmosphere. The ensemble mean of \( P(O_x) \) in models from the post-2000 literature is 35% higher than that compiled in the Intergovernmental Panel on Climate Change (IPCC) Third Assessment Report (TAR). Simulations conducted with the GEOS-Chem model using two different assimilated meteorological data sets for 2001 (GEOS-3 and GEOS-4), as well as 3 years of GISS GCM meteorology, show \( P(O_x) \) values in the range 4250–4700 Tg yr\(^{-1}\); the differences appear mostly because of clouds. Examination of the evolution of \( P(O_x) \) over the GEOS-Chem model history shows major effects from changes in heterogeneous chemistry, the lightning NOx source, and the yield of organic nitrates from isoprene oxidation. Multivariate statistical analysis of model budgets in the literature indicates that 74% of the variance in \( P(O_x) \) across models can be explained by differences in NOx emissions, inclusion of nonmethane volatile organic compounds (NMVOCs, mostly biogenic isoprene), and ozone influx from stratosphere-troposphere exchange (STE). Higher NOx emissions, more widespread inclusion of NMVOC chemistry, and weaker STE in the more recent models increase ozone production; however, the effect of NMVOCs does not appear generally sensitive to the magnitude of emissions within the range typically used in models (500–900 Tg C yr\(^{-1}\)). We find in GEOS-Chem that \( P(O_x) \) saturates when NMVOC emissions exceed 200 Tg C yr\(^{-1}\) because of formation of organic nitrates from isoprene oxidation, providing an important sink for NOx.


1. Introduction

[2] Tropospheric ozone is of importance in atmospheric chemistry as a greenhouse gas, as a precursor for the OH oxidant which controls the atmospheric lifetime of many gases, and as a surface air pollutant toxic to humans and vegetation. It is produced by photochemical oxidation of carbon monoxide, methane, and nonmethane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals (NOx = NO + NO2), and is also supplied by transport from the stratosphere. It is removed by chemical reactions and by deposition. The lifetime of tropospheric ozone varies from days to months, and the lifetimes of the precursors span an even wider range, so that quantitative accounting of the factors controlling tropospheric ozone requires a global 3-D model that couples chemistry and transport on synoptic scales.

[3] A large number of global models for tropospheric ozone have been developed over the past decade, and the pre-2000 models were reviewed by the Intergovernmental Panel on Climate Change (IPCC) Third Assessment Report (TAR) [Prather et al., 2001, Table 4.12]. More recent (post-2000) model studies are compiled in Table 1, and summary statistics across models of global tropospheric ozone budgets for present-day conditions are compiled in Table 2. Global burdens vary by only 10–20% among the models, but global production rates vary by more than 50%, suggesting that different models could give very different responses to perturbations. Global production rates averaged across all state-of-science models increased by 35% from the generation reviewed by the IPCC TAR to the post-2000 generation, and are higher still in the recent Stevenson et al. [2006] intercomparison of 21 global models. Stevenson et al. [2006] proposed that the higher ozone production rates in their study are due to several reasons including “(1) higher NOx emissions, (2) higher isoprene emissions, (3) more detailed NMHC schemes, and possibly (4) improved parameterization.
reaction and by the reactions of ozone with HO2, OH, and alkenes. Several models in this table do not report production and loss separately (‘NR’ entry in reactions of peroxy radicals with NO.

HNO3 + HNO4 (with the molecular weight of Ox assumed to be the same as O3 since O3 accounts for over 95% of Ox) following IPCC TAR.

emissions for ozone precursors.

as that of ozone only instead of Ox. We give here the correct GEOS-Chem budget for Ox.

Stevenson et al. 2001, GISS GCM output for 3 years of the present-day climate).

Stevenson et al. 2001, and the tropopause is defined as the altitude at which the temperature lapse rate drops below 2 K km⁻¹. Other models may use different definitions of the Ox family and of the tropopause, as discussed in the text. Chemical production of ozone as computed in all models is mainly from the reactions of NO with peroxy radicals, while chemical loss is mainly contributed by the O(1D) + H2O reaction and by the reactions of ozone with NO2, OH, and alkenes. Several models in this table do not report production and loss separately (‘NR’ entry in the table), reporting instead net production. However, net production is not a useful quantity for budget purposes because (1) it is a small residual between large production and loss, (2) it represents a balance between STE and dry deposition, both of which are usually parameterized to some degree as flux boundary conditions.

Chemical production and loss rates are calculated for the odd oxygen family (Ox) including species that cycle rapidly with ozone, while the other terms might be for either Ox or O3. In our work all the budget terms are for Ox, which is defined as Ox

IPCC TAR [Prather et al., 2001] 11 modelsb 3420 ± 770 770 ± 400 3470 ± 520 770 ± 180 300 ± 40 22 ± 2

Wang et al. [1998b] 4100 400

Post-2000 literature (Table 1)d 13 models 4620 ± 600 510 ± 90 4200 ± 480 1000 ± 220 330 ± 30 23 ± 4

Stevenson et al. [2006]f 4900 470

GEOS-Chem 4620 ± 600 510 ± 90 4200 ± 480 1000 ± 220 330 ± 30 23 ± 4

Stevenson et al. [2006]f 21 models 5110 ± 610 550 ± 170 4670 ± 730 1000 ± 200 340 ± 40 22 ± 2

Our work (GEOS-Chem)h 4490 510 3770 1230 290 22

GEOS-3 4250 540 3710 1080 300 23

GEOS-4 4700 520 4130 1090 300 21

GISSe 4470 ± 10 510 ± 2 3990 ± 10 990 ± 10 320 ± 3 23 ± 0.4

From global model simulations describing the present-day (post-1985) atmosphere. For the tropospheric ozone budgets reported in the literature, the chemical production and loss rates are calculated for the odd oxygen family (Ox) including species that cycle rapidly with ozone, while the other terms might be for either Ox or O3. In our work all the budget terms are for Ox, which is defined as Ox. We give here the correct GEOS-Chem budget for Ox.

A more recent version of GEOS-Chem by Martin et al. [2003b] gives identical rates and burdens.

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GEOS-Chem Model Driven by GISS Versus GEOS Meteorological Fields

[6] The tropospheric ozone simulation in GEOS-Chem was initially described by Bey et al. [2001], with significant updates presented by Martin et al. [2002, 2003a, 2003b], Park et al. [2004a] and Evans and Jacob [2005]. We use here GEOS-Chem version 7.02.04, which includes a fully coupled treatment of tropospheric ozone-NOx-VOC chemistry and aerosols (http://www.as.harvard.edu/chemistry/trop/geos/). Cross-tropopause transport of ozone is represented by the Synoz flux boundary condition [McLinden et al., 2000] with an imposed global annual mean STE flux of 510–540 Tg yr\(^{-1}\) (this variability reflects year-to-year differences in the model circulation). The STE fluxes for NO\(_x\) and total reactive nitrogen oxides (NO\(_x\)) are 0.4 and 2.3 Tg yr\(^{-1}\) respectively.

[7] Table 3 lists the global emissions of ozone precursors used in the present work. Anthropogenic emissions are for 1995. Biomass burning emissions are climatological means [Duncan et al., 2003]. Lightning and biogenic emissions are computed locally within the model on the basis of meteorological variables, but are scaled to the same global totals in all simulations for the purpose of intercomparison. The scaling factors are globally uniform and determined by preliminary model runs calculating the unconstrained natural emissions. Lightning NO\(_x\) emissions are parameterized as a function of deep convective cloud top [Price and Rind, 1992; Wang et al., 1998a; Li et al., 2005] and are distributed vertically following Pickering et al. [1998]. Further details on the emission inventories are given by Bey et al. [2001].

[8] We present here results from GEOS-Chem driven by GEOS-3 and GEOS-4 meteorological fields (two successive versions of the GMAO assimilated product) for the same meteorological year (2001). The GEOS-3 and GEOS-4 products have 6-hour temporal resolution (3-hour for surface quantities and mixing depths), a horizontal resolution of 1\(^\circ\) × 1\(^\circ\) (GEOS-3) or 1\(^\circ\) × 1.25\(^\circ\) (GEOS-4), and 48 (GEOS-3) or 55 (GEOS-4) vertical layers. Winds are instantaneous variables in GEOS-3 and 6-hour averages in GEOS-4. More details about the GEOS-3 and GEOS-4 products can be found athttp://www.as.harvard.edu/chemistry/trop/geos/doc/man/ge_a4.html. For the simulations presented here, we use a horizontal resolution of 4\(^\circ\) × 5\(^\circ\) by spatial averaging of the meteorological fields.

[9] We also present results from GEOS-Chem driven by meteorological fields from the GISS GCM III, which is an updated version of the model used by Rind et al. [1999]. This GCM has a resolution of 4\(^\circ\) × 5\(^\circ\) with 23 layers in the vertical extending from the surface to 0.002 hPa (~85 km

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Table 3. Global Emissions of Ozone Precursors in the GEOS-Chem Model\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Emission Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_x), Tg N yr(^{-1})</td>
<td>43.8</td>
</tr>
<tr>
<td>Fossil fuel combustion</td>
<td>23.6</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>6.5</td>
</tr>
<tr>
<td>Biofuel</td>
<td>2.2</td>
</tr>
<tr>
<td>Soil</td>
<td>6.3</td>
</tr>
<tr>
<td>Lightning</td>
<td>4.7</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.5</td>
</tr>
<tr>
<td>CO, Tg CO yr(^{-1})</td>
<td>1034</td>
</tr>
<tr>
<td>Fossil fuel combustion</td>
<td>403</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>457</td>
</tr>
<tr>
<td>Biofuel</td>
<td>173</td>
</tr>
<tr>
<td>Ethane, Tg C yr(^{-1})</td>
<td>8.7</td>
</tr>
<tr>
<td>Anthropogenic emissions</td>
<td>6.8</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>1.9</td>
</tr>
<tr>
<td>Propane, Tg C yr(^{-1})</td>
<td>10.9</td>
</tr>
<tr>
<td>Anthropogenic emissions</td>
<td>10.2</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.7</td>
</tr>
<tr>
<td>(\geq)C(_2) alkenes, Tg C yr(^{-1})</td>
<td>25.8</td>
</tr>
<tr>
<td>Anthropogenic emissions</td>
<td>24.4</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.6</td>
</tr>
<tr>
<td>Biofuel</td>
<td>0.8</td>
</tr>
<tr>
<td>(\geq)C(_3) alkenes, Tg C yr(^{-1})</td>
<td>27.8</td>
</tr>
<tr>
<td>Anthropogenic emissions</td>
<td>8.8</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>7.5</td>
</tr>
<tr>
<td>Biogenic emissions</td>
<td>11.5</td>
</tr>
<tr>
<td>Isoprene from vegetation, Tg C yr(^{-1})</td>
<td>400</td>
</tr>
<tr>
<td>Monoterpenes from vegetation, Tg C yr(^{-1})</td>
<td>110</td>
</tr>
<tr>
<td>Acetone, Tg C yr(^{-1})</td>
<td>44.4</td>
</tr>
<tr>
<td>Anthropogenic emissions</td>
<td>0.7</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>3.1</td>
</tr>
<tr>
<td>Biogenic emissions</td>
<td>40.6</td>
</tr>
</tbody>
</table>

\(^{a}\)Anthropogenic emissions are for 1995. Fixed methane concentrations of 1706, 1710, 1768, and 1823 ppbv are imposed for 90–30°S, 30°S–0°, 0°–30°N, and 30–90°N.

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altitude). We use archived GCM data for input to GEOS-Chem with the same temporal resolution as the GEOS data, i.e., 6-hour averages of winds, convective mass fluxes, temperature, humidity, cloud optical depths, and cloud fractions; and 3-hour averages of mixing depths and surface variables (precipitation, winds, temperature, albedo, solar radiation).

A major difference between the GEOS-3, GEOS-4, and GISS models is the treatment of wet convection. GEOS-3 uses the Relaxed Arakawa-Schubert convection scheme [Moorthi and Suarez, 1992]. GEOS-4 has separate treatments of deep and shallow convection following the schemes developed by Zhang and McFarlane [1995] and Hack [1994]. The convection scheme in the GISS GCM was described by Del Genio and Yao [1993]. Unlike the GEOS models, the GISS GCM allows for condensed water in the atmosphere (i.e., condensed water is not immediately precipitated), resulting in frequent nonprecipitating shallow convection. In the wet deposition scheme, we do not scavenge soluble species from shallow convective updrafts at altitudes lower than 700 hPa in the GISS-driven model, whereas we do in the GEOS-driven model [Liu et al., 2001]. The treatment of boundary layer turbulence is also different in GEOS and GISS. The mixing depth in GEOS is estimated from the bulk Richardson number with surface friction [Holslag and Boville, 1993] and in the GISS GCM it is estimated on the basis of the vertical profile of turbulent kinetic energy [Canuto, 1994; Canuto et al., 2001]. In either case, GEOS-Chem assumes instantaneous vertical mixing from the surface through the mixing depth [Bey et al., 2001].

3. Sensitivity to Meteorological Fields

A number of previous studies have evaluated GEOS-Chem simulations for ozone and its precursors using GEOS-3 and earlier-generation meteorological data products from GMAO [e.g., Bey et al., 2001; Martin et al., 2002; Liu et al., 2004]. No such evaluations have been reported for GEOS-Chem driven by GEOS-4 or GISS products, and we compare those here to the GEOS-3 driven simulation. Both GEOS-3 and GEOS-4 simulations are for 2001. The GISS simulation is for 3 successive years of the present-day climate; interannual differences are small (Table 2 gives interannual ranges for global ozone budgets) and all results presented from the GISS simulation refer to the 3-year averages unless otherwise specified.

Figure 1 shows the afternoon (1200–1600 local time) surface ozone concentrations simulated by GISS, GEOS-3 and GEOS-4 for January and July. Compared to GEOS-3 and GEOS-4, GISS produces higher levels of surface ozone, by up to 20% at high latitudes in winter. This appears to be largely driven by higher mixing depths and excessive high-latitude STE (D. Rind et al., Factors influencing tracer transport in GCMs, submitted to Journal of Geophysical Research, 2006).

Zonal mean concentrations of NOx, ozone, PAN, CO, and OH for January and July are compared in Figures 2a and 2b. Also shown is the rate constant for photolysis of O3 to O(1D). The most prominent difference is in the simulated wintertime concentrations of PAN in the Northern Hemisphere, which are 30–40% higher in GISS than in GEOS-3 and GEOS-4. This is largely due to the colder temperatures in GISS, suppressing decomposition of PAN. There are also significant differences in the simulated OH and J(O1D) distributions, which appear to be due largely to differences in clouds (Figure 3). A previous GEOS-Chem study by H. Liu et al. [2006] and H. Liu et al. (Radiative effect of clouds on tropospheric chemistry: Sensitivity to cloud vertical distributions and optical properties, manuscript in preparation, 2007) found that the radiative impact of clouds on global OH in July (calculated from comparison of simulations with versus without clouds) is less than 1% for GEOS-3 but yields a 14% increase in OH for GEOS-4; we find an 18% increase in OH for GISS when the radiative effect of clouds is accounted for. GEOS-3 has compensating radiative effects from low clouds (enhancing OH above cloud) and high clouds (depleting OH below cloud), while GEOS-4 has much weaker clouds in the tropical middle and upper troposphere and GISS has thicker clouds in the tropical lower troposphere (Figure 3).

Figures 4a and 4b compares the vertical profiles of simulated ozone to an ozonesonde data climatology [Logan, 1999] (with updates) at stations representative of different latitudinal bands. All three models reproduce observed ozone usually to within 10 ppb and with consistent gradients. The GISS model ozone is too high in the Arctic, particularly in winter because of excessive seasonal STE.

Global budgets of tropospheric ozone for GEOS-Chem driven by GEOS-3, GEOS-4, and GISS meteorological fields are compared in Table 2. Production rates are 4250 Tg yr−1 in GEOS-3, 4470 Tg yr−1 in GISS, and 4700 Tg yr−1 in GEOS-4. Stronger photochemical activity in GEOS-4 is also reflected in a shorter ozone lifetime, so that the global ozone burdens in GEOS-3 and GEOS-4 are almost identical. The ozone burden in GISS is 7% higher than in GEOS-3 or GEOS-4, for reasons discussed above.

Detailed accounting of the meteorological factors responsible for the differences in global ozone budgets between GEOS-3, GEOS-4, and GISS is difficult, but we identified three important factors. First is clouds, as discussed previously in the context of OH and J(O1D). Second is deep convective vertical mixing, which is stronger in GEOS-4 and GISS than in GEOS-3 and stimulates both ozone production and loss [Lawrence et al., 2003]. Third is the distribution of lightning; GEOS-4 releases 45% of lightning NOx in the Southern Hemisphere, where the ozone production efficiency per unit NOx (OPE) is higher than in the Northern Hemisphere because of lower background NOx [Wang et al., 1998b], while that fraction is only 36% in GEOS-3.

The global mass-weighted tropospheric concentration of OH in the GISS model is 1.08 × 106 molecules cm−3 on an annual mean basis, which is 5% higher than GEOS-3 (1.03 × 106 molecules cm−3) and 4% lower than GEOS-4 (1.12 × 106 molecules cm−3). The 3 year GISS simulation shows less than 1% interannual variability. These values are all consistent with the values derived by Krol et al. [1998] (1.07 ± 0.09 × 106 molecules cm−3) and Spivakovsky et al. [2000] (1.16 ± 0.17 molecules cm−3). The lifetime of methane against oxidation by tropospheric OH ranges from 9.8 years in GEOS-4 to 11.1 years in GEOS-3, all consistent with the value of 9.1 ± 2.3 years derived from the global model studies reported in IPCC TAR [Prather et al., 2001,
Table 4.3 and the value of $10.2^{+0.5}_{-0.7}$ years derived by Prinn et al. [2005].

4. Ozone Budget Evolution Over the GEOS-Chem Model History

[18] The evolution of the global tropospheric production rate of ozone, $P(O_x)$, over the history of the GEOS-Chem model lends insight into the effects of different model developments. The GEOS-Chem precursor models by Wang et al. [1998a, 1998b] and Mickley et al. [1999] had $P(O_x)$ values of 4100 and 4330 Tg yr$^{-1}$. The first GEOS-Chem model version in the literature (version 3.02) [Bey et al., 2001] calculated a higher $P(O_x)$ of 4900 Tg yr$^{-1}$, because of (1) better representation of cloud effects on UV actinic fluxes through the use of the fast-J algorithm [Wild et al., 2000], (2) removal of a default absorbing aerosol layer with optical depth of 0.1 at 310 nm, and (3) higher NOx emissions (45.6 Tg N yr$^{-1}$ versus 42 Tg N yr$^{-1}$ in the work by Wang et al. [1998a] and 40 Tg N yr$^{-1}$ in the work by Mickley et al. [1999]), reflecting the use of 1994 versus 1985 anthropogenic inventories. Martin et al. [2002] used version 4.11 as a base for additional updates that included (1) reducing biomass burning NOx emission from 12 to 6 Tg N yr$^{-1}$, which decreased $P(O_x)$ to 4760 Tg yr$^{-1}$; (2) accounting for the radiative and heterogeneous chemical effects of mineral dust, which further decreased $P(O_x)$ to 4440 Tg yr$^{-1}$; and (3) increasing lightning NOx emission.
Figure 2a. January zonal mean concentrations of NOx, ozone, PAN, CO, OH, and rate constant $J_{O_3/\text{p}}$ for photolysis of O₃ to O(1D), as simulated by the GISS, GEOS-3 and GEOS-4 models.
Figure 2b. Same as Figure 2a but for July.
from 3 to 6 Tg N yr\(^{-1}\), which increased \(P(O_3)\) back to 4920 Tg yr\(^{-1}\).

[19] Starting with version 4.13 (January 2001), a benchmarking process has been in place in which successive standard versions of GEOS-Chem are tested and documented with 1-month simulations for July, always starting from the same initial conditions. Figure 5 shows a 5-year history of the temporal evolution of \(P(O_3)\) in these 1-month benchmarks. Details on each version are at http://www.as.harvard.edu/chemistry/trop/geos/geos_versions.html. \(P(O_3)\) decreased from version 4.17 to 4.22 because of accounting of heterogeneous chemistry on mineral dust. The increase from version 4.22 to 4.23 reflects the doubling of lightning NO\(_x\) emission from 3 to 6 Tg N yr\(^{-1}\) to better reproduce observed ozone concentrations in the tropics [Martin et al., 2002]. The decrease from version 4.26 to 4.27 is due to increase in the yield of organic nitrates from isoprene oxidation (hereinafter, isoprene nitrates), from 4\% [Chen et al., 1998] to 12\% [Sprengnether et al., 2002]. The peroxy radicals produced from oxidation of NMVOCs by OH react with NO by two branches:

\[
\begin{align*}
\text{RO}_2 + NO &\rightarrow \text{RO} + \text{NO}_2 \\
\text{RO}_2 + NO + M &\rightarrow \text{RONO}_2 + M
\end{align*}
\]
(R1a) results in $O_3$ production via subsequent NO$_2$ photolysis while (R1b) is a sink for NO$_x$ by organic nitrate formation. The branching ratio (R1b)/(R1a) is determined by the number of carbon atoms in RO$_2$ and by temperature [Atkinson, 1990]. Isoprene nitrates have a hydroxy group that greatly enhances their water solubility, and we assume in GEOS-Chem that they are removed from the atmosphere by wet and dry deposition [Chen et al., 1998; Horowitz et al., 1998; Liang et al., 1998; Giacopelli et al., 2005; Fiore et al., 2005].

$P(O_x)$ slowly decreased from version 4.32 to 5.07.06 because of a succession of minor changes including the dry deposition of N$_2$O$_5$. The increase from version 5.07.06 to 5.07.07 resulted from the decrease in the N$_2$O$_5$ reaction probability ($\gamma_{N_2O_5}$) from a constant value of 0.1 to a value dependent on local aerosol composition with a global mean of 0.02 [Evans and Jacob, 2005]. The increase from version 6.02.02 to 6.02.03 is mainly due to reduced dust loadings associated with an updated dust mobilization scheme [Zender et al., 2003; Fairlie et al., 2007].

5. Variation Across Models in Global Tropospheric Ozone Budgets

5.1. Factors of Variability

[21] We now examine the variability in tropospheric ozone budgets for the ensemble of models reported in the literature. Values of $P(O_x)$ vary from 2300 to 4300 Tg yr$^{-1}$ in the 1996–2000 literature reviewed by IPCC TAR and from 3300 to 5300 Tg yr$^{-1}$ in the post-2000 literature compiled in Table 1. Compared to the older generation of models compiled in IPCC TAR, the ensemble of post-2000 models shows significant mean differences in global ozone budgets, including a 35% increase of ozone production, a 34% decrease of STE ozone flux, and a 10% increase of ozone burden (Table 2). The recent intercomparison of 21 current-generation models (including different versions

Figure 4a. Comparison of January monthly mean $O_3$ vertical profiles simulated by GISS (black solid lines), GEOS-3 (red dashed lines) and GEOS-4 (green dash-dotted lines) to climatological ozonesonde observations from Logan [1999] (open circles with horizontal bars for interannual standard deviation).
of the same models) by Stevenson et al. [2006] shows a 10% further increase in mean $P(O_x)$ relative to the post-2000 literature (Table 2). All models in that intercomparison were constrained to use the same ozone precursor emissions from anthropogenic sources and biomass burning, while natural emissions were allowed to vary from model to model.

[22] The definitions for the tropopause and for the odd oxygen family ($O_x$) used to compute tropospheric ozone budgets may vary from one model to another, and this is a factor of variability in the budgets in Table 2. Most model studies use the thermal tropopause as determined by the temperature lapse rate, while some use a chemical tropopause ($[O_3] = 150$ ppb) [e.g., Prather et al., 2001; Stevenson et al., 2004, 2006]. Logan [1999] showed from ozonesonde data that the mixing ratio of ozone is usually less than 150 ppbv at the thermal tropopause, except in summer at middle and high latitudes. We find in GEOS-Chem that the tropospheric ozone burden is 10% higher if we use the chemical versus thermal tropopause definition. Stevenson et al. [2004] previously found that $P(O_x)$ is relatively insensitive to the definition of the tropopause but that the ozone burden and lifetime are more affected. Some model budgets include peroxyacetyl nitrates (PANs) and HNO$_3$ in their definition of the $O_x$ family, while others do not, but this has little importance since peroxy radicals + NO reactions are the main contributors to $P(O_x)$ and are included in all models [Stevenson et al., 1997; Wauben et al., 1998; Wang et al., 1998a; Crutzen et al., 1999]. We find in our model that excluding PANs and HNO$_3$ from the $O_x$ family causes a 10% increase in $P(O_x)$. These effects are relatively small, and there is no trend in their use that could explain the mean difference in budgets between the IPCC TAR and post-2000 models.

[23] The STE ozone fluxes in the older IPCC TAR models ranged from 390 to 1440 with a mean of 770 ±
400 Tg yr$^{-1}$. It is now recognized that many of these fluxes were too high, driven by artifacts in the vertical winds at the tropopause, particularly when using assimilated meteorological fields [Tan et al., 2004; van Noije et al., 2004]. Robust constraints from observed NO$_x$-N$_2$O-O$_3$ correlations in the lower stratosphere impose an STE ozone flux of $540 \pm 140$ Tg yr$^{-1}$ [Murphy and Fahey, 1994; Olsen et al., 2001]. The STE ozone flux in the current generation of global models in Table 2 ($510 \pm 90$ Tg yr$^{-1}$) reflects that constraint, often through the use of a flux boundary condition (as in GEOS-Chem) or by relaxation to observed ozone concentrations above the tropopause region [Horowitz et al., 2003].

The lower STE ozone flux in the newer models leads to stronger tropospheric ozone production by reducing the NO$_x$/NO concentration ratio in the upper troposphere. We conducted a sensitivity study using our GISS-driven GEOS-Chem simulation with the STE ozone flux increased by 25% to 625 Tg yr$^{-1}$ (Table 4). The 25% increase resulted in a 5% increase of O$_3$ burden, a 3% increase of O$_3$ lifetime, and a 1% decrease of $P(O_3)$. The increase in $P(O_3)$ between the IPCC TAR models and more recent ones is much larger, and the trend in O$_3$ burden is positive, so this cannot be a dominant effect.

Tropospheric ozone production is highly sensitive to the supply of NO$_x$. Stevenson et al. [2006] pointed out that the higher NO$_x$ and isoprene emissions used in their model intercomparison study were two important factors for their much higher ozone production rates compared to IPCC TAR values, with each factor accounting for about half of the increase of $P(O_3)$ in one specific model (FRSGC/UCI). Comparison of the older global models compiled by IPCC TAR [Prather et al., 2001] versus the post-2000 literature of Table 1 shows a mean increase across models in global surface NO$_x$ emission (excluding lightning and aircraft) from 34.9 to 38.8 Tg N yr$^{-1}$, and an increase in lightning

### Table 4. GEOS-Chem Model Sensitivities of Global Tropospheric Ozone and OH Budgets$^a$

<table>
<thead>
<tr>
<th>Sensitivity</th>
<th>Chemical Production Rate of Ozone, Tg yr$^{-1}$</th>
<th>Chemical Loss Rate of Ozone, Tg yr$^{-1}$</th>
<th>Ozone Burden, Tg</th>
<th>Ozone Lifetime, days</th>
<th>OH, $1 \times 10^6$ molecules cm$^{-3}$</th>
<th>Methane Lifetime, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard simulation</td>
<td>4487</td>
<td>3999</td>
<td>319</td>
<td>23.3</td>
<td>1.08</td>
<td>10.6</td>
</tr>
<tr>
<td>STE +25%</td>
<td>4445</td>
<td>4065</td>
<td>335</td>
<td>24.1</td>
<td>1.08</td>
<td>10.5</td>
</tr>
<tr>
<td>Fossil fuel NO$_x$ emission +25%</td>
<td>4649</td>
<td>4113</td>
<td>325</td>
<td>23.0</td>
<td>1.11</td>
<td>10.3</td>
</tr>
<tr>
<td>Lightning NO$_x$ emission +25%</td>
<td>4672</td>
<td>4158</td>
<td>328</td>
<td>23.2</td>
<td>1.14</td>
<td>10.1</td>
</tr>
<tr>
<td>Isoprene emission –25%</td>
<td>4486</td>
<td>3991</td>
<td>319</td>
<td>23.4</td>
<td>1.13</td>
<td>10.1</td>
</tr>
<tr>
<td>No isoprene emission</td>
<td>4394</td>
<td>3900</td>
<td>315</td>
<td>23.5</td>
<td>1.28</td>
<td>8.8</td>
</tr>
<tr>
<td>No NMVOCs emissions</td>
<td>3986</td>
<td>3566</td>
<td>298</td>
<td>24.3</td>
<td>1.31</td>
<td>8.7</td>
</tr>
</tbody>
</table>

$^a$All simulations are for 1 year (with 6-month initialization) driven by the same GISS meteorology.

$^b$Standard simulation as presented in the text including stratosphere-troposphere exchange (STE) of 500 Tg yr$^{-1}$, NO$_x$ emission from fossil fuel combustion of 23.6 Tg N yr$^{-1}$, lightning NO$_x$ emission of 4.7 Tg N yr$^{-1}$, and isoprene emission of 400 Tg C yr$^{-1}$ (Table 3). All sensitivity simulations are relative to the standard simulation.
NOx emission from 4.0 to 4.9 Tg yr\(^{-1}\) (Table 5). The former reflects an actual rise in Asian NOx anthropogenic emissions between the ca. 1985 inventories used by the IPCC TAR models versus the early 1990s inventories used in the more recent models [Fusco and Logan, 2003]. There is large uncertainty associated with lightning NOx emissions. State-of-science estimates range from 1 to 20 Tg yr\(^{-1}\) [Price et al., 1997; Boersma et al., 2005], though global models use values in the range 2−7 Tg yr\(^{-1}\) to reproduce observed ozone and NOx concentrations in the tropics [e.g., Levy et al., 1996; Martin et al., 2002; Tie et al., 2002; Li et al., 2005].

[26] Another significant difference between the newer and older generation of global models is the treatment of NMVOCs. Only about half of the models compiled in IPCC TAR included NMVOC chemistry while almost all models in the post-2000 literature do. Isoprene from vegetation generally accounts for most of total NMVOC emissions in the post-2000 literature do. Isoprene from vegetation generally accounts for most of total NMVOC emissions in the post-2000 literature [Wang and Jacob, 1998; Poissant et al., 2000; von Kuhlmann et al., 2004] found a somewhat weaker effect, ranging from 16% to 24%. Changing methane would also have a major effect on global tropospheric ozone budgets [Wang and Jacob, 1998; Fiore et al., 2002], but models simulating present-day conditions all use sensibly the same methane levels constrained by observations.

5.2. Regression Analysis for Global Ozone Production in Models

[27] To explore these issues further, we conducted a multivariate regression analysis of present-day \(P(O_x)\) versus model parameters for the ensemble of 32 models compiled in Table 2 for which sufficient information was available. This included 18 models from the literature plus the 14 models from the Stevenson et al. [2006] intercomparison that reported a model STE (Table 5). We find that 74% of the variance of \(P(O_x)\) across models can be explained by the global total NOx emissions \(E_{NOx}\), STE, and NMVOC emissions \(E_{NMVOC}\) through the following regression

\[
P(O_x) = 104 E_{NOx} + 0.96 E_{NMVOC} - 0.47 STE - 581 \tag{1a}
\]

where \(P(O_x)\) and STE are in Tg yr\(^{-1}\), \(E_{NOx}\) is in Tg N yr\(^{-1}\), and \(E_{NMVOC}\) is in Tg C yr\(^{-1}\). The 85% confidence intervals for the coefficients of \(E_{NOx}\), \(E_{NMVOC}\) and STE are [73, 136], [0.48, 1.45] and [−0.93, −0.01] respectively.

[28] We also find that an alternative regression model with on/off dependence on NMVOC emissions can equally explain \((R^2 = 0.74, n = 32)\) the variation of \(P(O_x)\) across models:

\[
P(O_x) = 106 E_{NOx} + 672 \delta(NMVOC) - 0.40 STE - 753 \tag{1b}
\]

where \(\delta(NMVOC)\) is 1 if NMVOCs are included in the model and 0 otherwise. The step dependence on NMVOCs will be discussed below. The success of equations (1a) and (1b) in reproducing the \(P(O_x)\) for each of the 32 models included in the regression analysis is shown in Figures 6a and 6b. Differences are less than 500 Tg yr\(^{-1}\) for most of the models. Higher-order terms in the regression, including the product \(E_{NOx} \delta(NMVOC)\), did not improve the regression results.

[29] Applying equation (1a) to the values of \(E_{NOx}\), \(E_{NMVOC}\), and STE in the individual models yields a mean \(P(O_x)\) increase of 870 Tg yr\(^{-1}\) from the IPCC TAR models to the post-2000 literature, which is 72% of the actual increase shown in Table 2 (1200 Tg yr\(^{-1}\)). Additive increases of 520, 230 and 120 Tg yr\(^{-1}\) result respectively from the increases of NOx and NMVOC emissions and from the decrease of STE. The other 28% of the \(P(O_x)\) increase may be due to other changes in models over the past decade including better parameterizations of convection [Chatfield and Delany, 1990; Pickering et al., 1992;
Horowitz et al., 2003], cloud radiative effects [Wild et al., 2000], and aerosol extinction [Martin et al., 2002; Bian et al., 2003; Tie et al., 2005], as well as equatorward shift of anthropogenic emissions [Gupta et al., 1998; Stevenson et al., 2006]. Similarly, 1510 Tg yr\(^{-1}\) or 89% of the actual increase (1690 Tg yr\(^{-1}\), Table 2) of \(P(O_x)\) in the work by Stevenson et al. [2006] relative to IPCC TAR models can be explained with equation (1a). Equation (1b) yields similar results. The higher \(P(O_x)\) in the Stevenson et al. [2006] intercomparison relative to the ensemble mean of post-2000 models can be largely explained by higher NO\(_x\) emissions.

5.3. Interpretation of the Regression Analysis

We now offer a physical interpretation for the individual terms in the regression equation (1) that successfully describe global tropospheric ozone production in models. The coefficient of \(E_{NOx}\) represents the ozone production efficiency (OPE = \(\partial P(O_x)/\partial E_{NOx}\)), and is 30 mol mol\(^{-1}\) in (1a) and 31 mol mol\(^{-1}\) in (1b). Fossil fuel combustion accounts for about half of total NO\(_x\) emission in the models (Table 3). We conducted a sensitivity analysis in GEOS-Chem increasing the global NO\(_x\) emission from fossil fuel combustion by 25%, which raises \(E_{NOx}\) by 13% or 5.9 Tg N yr\(^{-1}\) (Table 4). We found that the global ozone production increased by 162 Tg yr\(^{-1}\). The OPE derived from this perturbation (8 mol mol\(^{-1}\)) is much smaller than the OPE derived from equation (1). In a separate sensitivity test, we increased the global lightning NO\(_x\) emission by 25% (1.2 Tg N yr\(^{-1}\), representing a 2.7% increase of \(E_{NOx}\)) and found that \(P(O_x)\) increased by 185 Tg yr\(^{-1}\) (Table 4). The OPE derived from this perturbation (45 mol mol\(^{-1}\)) is much larger than the OPE derived from equation (1). Thus lightning NO\(_x\) is about 6 times more efficient in driving ozone production than anthropogenic NO\(_x\). Separating lightning from other sources of NO\(_x\) in the linear regression (1) does not however produce a significantly higher correlation.

The dependence of \(P(O_x)\) on STE is expressed in equation (1) by a linear sensitivity coefficient \(\partial P(O_x)/\partial STE\), which is \(-0.47\) mol mol\(^{-1}\) in (1a) and \(-0.40\) mol mol\(^{-1}\) in (1b). We find in GEOS-Chem that \(P(O_x)\) decreases by 45 Tg yr\(^{-1}\) when we increase STE by 25% (Table 4), yielding a sensitivity coefficient of \(-0.36\) mol mol\(^{-1}\) which is consistent with the result from the linear regression.

Equations (1a) and (1b) can explain the differences of \(P(O_x)\) across global models equally well but imply different sensitivities to \(E_{NMVOC}\). Equation (1a) implies a linear dependence while (1b) implies a step dependence
where \( P(O_x) \) increases by 670 Tg yr\(^{-1}\) when NMVOC emissions are included but does not increase further within the typical range of 500–900 Tg C yr\(^{-1}\) used in models (isoprene being the dominant contributor).

[34] We conducted further analysis to reconcile the discrepancy between equations (1a) and (1b). Figure 7 shows the sensitivity of \( P(O_x) \) to NMVOC emissions for the ensemble of models used in the regression analysis, after standardizing to the same values of STE (510 Tg yr\(^{-1}\)) and \( E_{NO_x} \) (45 Tg N yr\(^{-1}\)) using equation (1a). We see that the models results can be classified into two groups, with versus without NMVOCs. Models with NMVOCs tend to have higher ozone production, with the exception of two outliers [Hauglustaine et al., 1998; Lelieveld and Dentener, 2000]. Among the models including NMVOC chemistry, however, there is no clear dependence of \( P(O_x) \) on NMVOC emission. Although it is well known from regional ozone models that ozone production is often NMVOC-saturated, this refers to the local ozone production rate [e.g., Stillman et al., 1990], not to the ultimate ozone production as computed in a global model. Increasing NMVOCs would be expected to increase the OPE both by decreasing OH levels (and hence increasing the lifetime of \( NO_x \)) and by promoting the sequestration of \( NO_x \) as PAN and its eventual release in regions of high OPE [Lin et al., 1988; Houweling et al., 1998; Wang et al., 1998c; Poisson et al., 2000; Roelofs and Lelieveld, 2000; Hudman et al., 2007; von Kuhlmann et al., 2004].

[35] We conducted three GEOS-Chem sensitivity simulations with NMVOC emissions modified from the standard values in Table 3: one with isoprene emission reduced by 25%, one with isoprene emission set to zero, and one with all NMVOC emissions set to zero (Table 4). The sensitivity simulations show saturation (Figure 7) for NMVOC emissions greater than 200 Tg C yr\(^{-1}\). We find that the saturation is due to the formation of organic nitrates, especially isoprene nitrates, providing a significant sink for \( NO_x \) as discussed in section 4. The importance of this sink for \( NO_x \) has been discussed in previous model studies [Horowitz et al., 1998; Liang et al., 1998; von Kuhlmann et al., 2004; Fiore et al., 2005]. As shown in Figure 8, increasing isoprene emissions in GEOS-Chem saturates PAN as well as ozone, while causing sharp decreases in \( NO_x \) and OH.

[36] Although it is most likely (as assumed in GEOS-Chem) that isoprene nitrate formation is a terminal sink for \( NO_x \) [Giacopelli et al., 2005], some models recycle isoprene nitrate to \( NO_x \) through reaction with OH [Grossenbacher et al., 2001] or do not include isoprene nitrate formation. Those models would have greater positive response of \( P(O_x) \) to the magnitude of isoprene emissions [Fiore et

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Figure 6b. Same as Figure 6a but the ozone production rates are derived from equation (1b) instead of (1a).
We find in GEOS-Chem that $P(O_3)$ decreases by 11% in the absence of NMVOCs. This sensitivity is at the low end of values reported in the literature, e.g., 16% [Roelofs and Lelieveld, 2000], 22% [von Kuhlmann et al., 2004], 22% [Poisson et al., 2000], 27% [Houweling et al., 1998]. Roelofs and Lelieveld [2000] viewed isoprene nitrate as a terminal NOx sink, as we do here, while the other studies allowed it to recycle to NOx.

We find that the annual mean, mass-weighted tropospheric OH concentration in GEOS-Chem increases by 21% and the methane lifetime against oxidation by tropospheric OH decreases by 18% in the absence of NMVOCs. This sensitivity is at the high end of model results reported in literature: Houweling et al. [1998] found that including NMVOCs hardly affected the tropospheric OH burden; Roelofs and Lelieveld [2000] viewed isoprene nitrate as a terminal NOx sink, as we do here, while the other studies allowed it to recycle to NOx.

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[37] Global models of tropospheric ozone show large differences in their global ozone budget terms. The production rate $P(O_3)$ of ozone in the troposphere varies from 2300 to 5300 Tg yr$^{-1}$ across models documented in the literature since 1996. The ensemble mean of $P(O_3)$ in post-2000 models has increased by 35% relative to the older generation compiled by the IPCC TAR. A recent 21-model intercomparison by Stevenson et al. [2006] reports even higher $P(O_3)$. Trends in the mean global burden of tropospheric ozone computed by these models have been much weaker, about 10%, reflecting compensating effects from weaker stratosphere-troposphere exchange (STE) and shorter ozone lifetimes. Better understanding of the factors driving the variability in $P(O_3)$ across models is important because of its implications for the computed sensitivity of tropospheric ozone to perturbations.

We investigated this issue by using a global tropospheric chemistry model (GEOS-Chem) driven by three different sets of meteorological fields: assimilated data for 2001 (GEOS-3 and GEOS-4) and GISS GCM III present-day climate. The interface with GCM fields is a new development for GEOS-Chem designed to enable study of the effects of climate change on atmospheric composition. The GISS GCM fields provide a simulation of tropospheric ozone and its precursors that is consistent with the established GEOS-driven simulations. The simulated wintertime concentrations of PAN in the Northern Hemisphere in GISS are 30–40% higher than in GEOS-3 and GEOS-4, largely because of colder temperatures. The GISS simulation overestimates surface ozone by up to 20% over the high latitudes in winter, because of excessive STE at high latitudes.
and lightning NOx emissions in global models of tropospheric chemistry. The importance of better describing cloud processes sensitivity highlights, especially in the context of climate warming source is kept the same in all simulations. This convection) also contribute, even though the global lightning NOx emissions show a saturation of P(Ox) with increasing NMVOCs. Either regression form can largely explain the 25% increase in the ensemble mean P(Ox) for the post-2000 models relative to the IPCC TAR models. This increase is driven by higher NOx emissions (15%), more widespread inclusion of NMVOC emissions (7%), and weaker STE (3%).

Although P(Ox) is sensitive to the inclusion of NMVOC chemistry in models, it does not appear generally sensitive to the magnitude of NMVOC emissions within the typical range used by the models (500–900 Tg C yr⁻¹). GEOS-Chem sensitivity simulations with variable NMVOC emissions show a saturation of P(Ox) when emissions exceed 200 Tg C yr⁻¹. This saturation effect is due to the formation of isoprene nitrates, providing a significant sink for NOx. Models that do not include isoprene nitrate formation or that allow the recycling of NOx from isoprene nitrate would not show such a saturation effect.

Our analysis of the factors determining the variability of P(Ox) has been for the present-day atmosphere, with known levels of methane. For past or future atmospheres, changing methane needs to be accounted as an additional factor affecting the tropospheric ozone budget [Wang and Jacob, 1998; Fiore et al., 2002]. This could be included as an additional linear term in the regression analysis (1); Wang and Jacob [1998] find an ozone production efficiency of 0.7 moles per mole of methane oxidized in a model perturbation to the preindustrial atmosphere, with little variation of this efficiency over a range of conditions. Unlike isoprene, oxidation of methane does not produce organic nitrates with significant yield.

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