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## Citation

Wang, Yuhang, and Daniel J. Jacob. 1998. "Anthropogenic Forcing on Tropospheric Ozone and OH Since Preindustrial Times." *Journal of Geophysical Research* 103 (D23): 31123. doi:10.1029/1998jd100004.

## Published Version

doi:10.1029/1998JD100004

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# Anthropogenic forcing on tropospheric ozone and OH since preindustrial times

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**Abstract.** A global three-dimensional model of tropospheric chemistry is used to investigate the changes in tropospheric O<sub>3</sub> and OH since preindustrial times as a result of fuel combustion and industry, biomass burning, and growth in atmospheric CH<sub>4</sub>. Model results indicate a 63% increase of the global tropospheric O<sub>3</sub> burden from preindustrial times to present (80% and 50% in the northern and southern hemispheres, respectively). Anthropogenic emissions of NO<sub>x</sub> and of CO and hydrocarbons make comparable contributions to the global O<sub>3</sub> increase (60% and 40% respectively), even though the local rate of tropospheric O<sub>3</sub> production is generally NO<sub>x</sub> limited. The rise in O<sub>3</sub> production parallels closely the rise in the emissions of CO and hydrocarbon because the O<sub>3</sub> yield per mole of CO or hydrocarbon oxidized has remained constant at 0.7-0.8 mol/mol since preindustrial times. In contrast, the O<sub>3</sub> production efficiency per mole of NO<sub>x</sub> emitted has decreased globally by a factor of 2. We find a 9% decrease in the global mean OH concentration (mass-weighted) since preindustrial times. A linear relationship is found in the model between the global mean OH concentration and the  $S_N/S_C^{3/2}$  ratio, where  $S_N$  and  $S_C$  are the sources of NO<sub>x</sub> and of CO and hydrocarbons, respectively. The relative constancy of the global mean OH concentration since preindustrial times reflects the conservation of the  $S_N/S_C^{3/2}$  ratio despite large increases in both  $S_N$  and  $S_C$ . Comparisons of model results with reconstructed nineteenth century observations of O<sub>3</sub> at continental sites indicate a systematic overestimate of about 5 ppbv. Correcting this overestimate would require either a large missing chemical sink for O<sub>3</sub> or a downward revision of the natural NO<sub>x</sub> source from lightning (3 Tg N yr<sup>-1</sup> in our model). The nineteenth century observations of O<sub>3</sub> over France show no vertical gradient between the boundary layer and the free troposphere, which is inconsistent with our current understanding of tropospheric O<sub>3</sub>. The model underestimates preindustrial CO concentrations derived from polar ice cores; these measurements are difficult to reconcile with any reasonable CO emission inventories.

## 1. Introduction

Preindustrial measurements of O<sub>3</sub> concentrations at surface sites in western Europe and South America indicate an increase of several fold from preindustrial times to present [Volz and Kley, 1988; Anfossi et al., 1991; Sandroni et al., 1992; Marengo et al., 1994]. This increase is likely driven by anthropogenic emissions of NO<sub>x</sub> (NO+NO<sub>2</sub>), CO, and hydrocarbons from fossil fuel combustion and biomass burning. Increasing concentrations of O<sub>3</sub>, NO<sub>x</sub>, CO, and hydrocarbons may have also induced significant changes in the abundance of tropospheric OH, the main atmospheric oxidant [Thompson, 1992]. Since tropospheric O<sub>3</sub> is a greenhouse gas and OH concentrations determine the lifetimes of greenhouse gases such as CH<sub>4</sub> and hydrochlorofluorocarbons (HCFCs), anthropogenic perturbations to tropospheric O<sub>3</sub> and OH have important implications for climate change [Intergovernmental Panel on Climate Change (IPCC), 1996].

A number of model studies have attempted to describe the changes of tropospheric O<sub>3</sub> and OH concentrations since preindustrial times: one-dimensional models before the early 1990s [Thompson, 1992] and two- and three-dimensional models more recently [Crutzen and Zimmermann, 1991; Thompson et al., 1993; Martinerie et al., 1995; Lelieveld and Van Dorland, 1995; Kasibhatla et al., 1996; Levy et al., 1997; Roelofs et al., 1997; Berntsen et al., 1997]. Three-dimensional model simulations suggest an increase in global O<sub>3</sub> concentrations since preindustrial times ranging from 40% [Levy et al., 1997; Roelofs et al., 1997] to 70% [Lelieveld and Van Dorland, 1995]. The estimated change of the global mean OH concentration ranges from a 20% decrease [Thompson et al., 1993] to a 6-7% increase [Marterinie et al., 1995; Berntsen et al., 1997]. The relatively small OH changes in these models reflect compensating anthropogenic influences from large increases in NO<sub>x</sub> and O<sub>3</sub>, which tend to enhance OH, and large increases in CO and hydrocarbons, which tend to deplete OH [Thompson, 1992].

We use in this work a global three-dimensional model of tropospheric O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry [Wang et al., 1998a, b, c] to better understand how anthropogenic emissions

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Paper number 1998JD100004.  
0148-0227/98/1998JD100004\$09.00

have driven changes in O<sub>3</sub> and OH concentrations since preindustrial times. A brief description of the model is given in section 2, and results for the preindustrial and present atmospheres are presented in section 3. The model has been evaluated previously with observations for the present atmosphere [Wang *et al.*, 1998b], and we extend in section 4 this evaluation to reconstructed observations of O<sub>3</sub>, CO, and OH proxies from the nineteenth century. In section 5, we interpret changes in O<sub>3</sub> and OH concentrations over the past century on the basis of changing anthropogenic emissions. Conclusions are in section 6.

## 2. Model Description

Our global three-dimensional model for tropospheric O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry is described by Wang *et al.* [1998a]. The model is driven by meteorological fields archived every 4 hours from a general circulation model developed at the Goddard Institute for Space Studies [Hansen *et al.*, 1983]. It has a spatial resolution of 4° latitude by 5° longitude with seven vertical layers extending from the surface to 150 mbar. The model transports 15 chemical tracers: odd oxygen (O<sub>x</sub> = O<sub>3</sub> + O + NO<sub>2</sub> + HNO<sub>4</sub> + 2 × NO<sub>3</sub> + 3 × N<sub>2</sub>O<sub>5</sub>), NO<sub>x</sub> (NO + NO<sub>2</sub> + NO<sub>3</sub> + HNO<sub>2</sub>), N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, HNO<sub>4</sub>, peroxyacetyl nitrates, alkyl nitrates, CO, ethane, (≥C<sub>4</sub>) alkanes, (≥C<sub>3</sub>) alkenes, isoprene, acetone, higher ketones, and H<sub>2</sub>O<sub>2</sub>. Spatially and seasonally varying flux boundary conditions are specified at 150 mbar to represent the cross-tropopause transport of O<sub>3</sub> (400 Tg O<sub>3</sub> yr<sup>-1</sup>) and of total reactive nitrogen NO<sub>y</sub> (0.48 Tg N yr<sup>-1</sup>). The present-day simulation includes anthropogenic sources from fuel combustion and industry (22 Tg N yr<sup>-1</sup> of

NO<sub>x</sub>, 520 Tg CO yr<sup>-1</sup>, and 56 Tg C yr<sup>-1</sup> of nonmethane hydrocarbons (NMHCs)), biomass burning (12 Tg N yr<sup>-1</sup> of NO<sub>x</sub>, 520 Tg CO yr<sup>-1</sup>, and 51 Tg C yr<sup>-1</sup> of NMHCs), and soil emission of NO<sub>x</sub> associated with fertilizer usage (1.3 Tg N yr<sup>-1</sup>). Natural emissions are from lightning (3.0 Tg N yr<sup>-1</sup> of NO<sub>x</sub>), soils (4.7 Tg N yr<sup>-1</sup> of NO<sub>x</sub>), and vegetation (600 Tg C yr<sup>-1</sup> of isoprene and 15 Tg C yr<sup>-1</sup> of acetone). Dry deposition is computed with a resistance-in-series scheme.

The model simulation for the present atmosphere has been evaluated extensively by Wang *et al.* [1998b] with long-term measurements of O<sub>3</sub> (surface sites and ozonesondes) and CO (surface sites) and with aircraft measurements of NO, peroxyacetyl nitrate (PAN), HNO<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, acetone, and H<sub>2</sub>O<sub>2</sub> in different regions of the troposphere. The model reproduces observed monthly mean concentrations of O<sub>3</sub> generally to within 10 ppbv and captures the observed seasonal variations of O<sub>3</sub> to within 1 month. Ozone concentrations tend to be overestimated in the tropical marine boundary layer and underestimated in the upper troposphere of the southern tropics. Observed concentrations of NO and PAN are reproduced generally to within a factor of 2; HNO<sub>3</sub> concentrations tend to be overestimated, sometimes several fold. Concentrations of CO are reproduced to generally within 10 ppbv and concentrations of H<sub>2</sub>O<sub>2</sub> are reproduced to within a factor of 2. The global mean OH concentration simulated in the model yields a lifetime of 5.1 years for CH<sub>3</sub>CCl<sub>3</sub> below 200 mbar against oxidation by OH, in agreement with the estimate of 4.9±0.3 years derived from long-term observations of CH<sub>3</sub>CCl<sub>3</sub> by Prinn *et al.* [1995].

We simulate the preindustrial atmosphere (circa 1850) by removing anthropogenic emissions from the present-day simu-

**Table 1.** Global Sources of NO<sub>x</sub>, CO and Hydrocarbons, and Global Mean OH Concentrations

	Preindustrial <sup>a</sup>	Sensitivity Simulations Departing from the Preindustrial Atmosphere <sup>b</sup>					Present <sup>c</sup>
		A 1.7 ppmv CH <sub>4</sub>	B Present CO + NMHCs	C Present NO <sub>x</sub>	D Present Fuel + Industry	E Present Biomass Burning	
NO <sub>x</sub> (S <sub>N</sub> )	0.64	0.64	0.64	2.9	2.1	1.4	3.0
CO and Hydrocarbons							
CO <sup>d</sup>	24	34	58	29	45	43	76
CH <sub>4</sub> <sup>e</sup>	14	24	10	20	15	15	29
Nonmethane hydrocarbons (NMHCs)	10	10	13	10	12	11	13
Total (S <sub>C</sub> )	48	68	81	59	72	69	118
Global mean OH <sup>f</sup>	1.15	0.95	0.78	1.56	1.18	1.19	1.04

Sources of NO<sub>x</sub> and of CO and hydrocarbons are in Tmol yr<sup>-1</sup>; global mean OH concentrations are in 10<sup>6</sup> molecules cm<sup>-3</sup>.

<sup>a</sup>Preindustrial emissions include NO<sub>x</sub> from lightning, unfertilized soils, and 10% of present-day biomass burning, isoprene and acetone from terrestrial vegetation, and CO and NMHCs from 10% of present-day biomass burning. Methane concentration is specified at 0.8 ppmv.

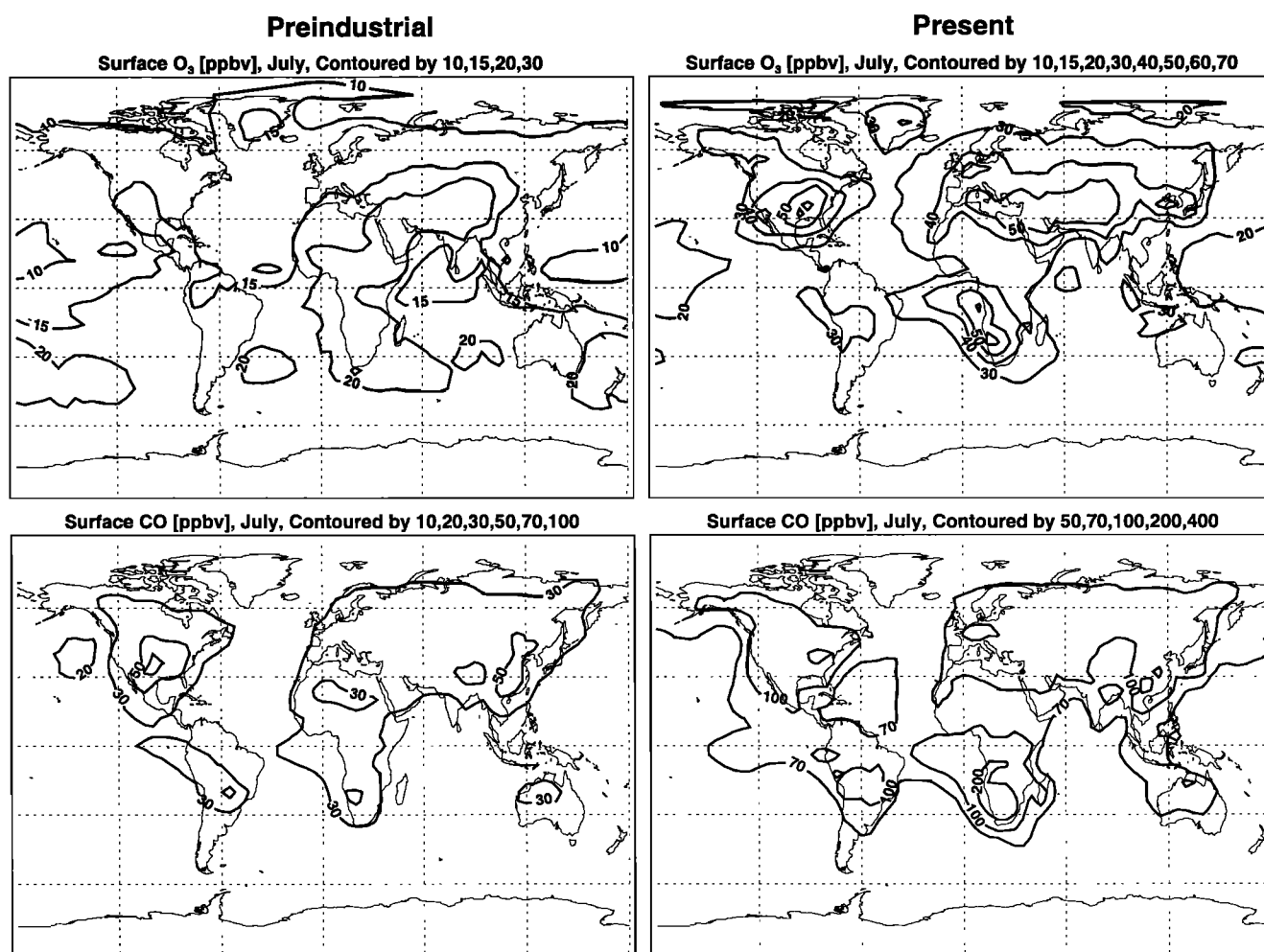
<sup>b</sup>The sensitivity cases include A, preindustrial atmosphere with present-day CH<sub>4</sub> concentration of 1.7 ppmv; B, preindustrial atmosphere with present-day emissions of CO and NMHCs from fuel combustion, industry, and biomass burning; C, preindustrial atmosphere with present-day NO<sub>x</sub> emissions from fossil fuel combustion and biomass burning (but not including soil emissions from fertilizer use of 0.1 Tmol yr<sup>-1</sup>); D, preindustrial atmosphere with present-day NO<sub>x</sub>, CO and NMHC emissions from fuel combustion and industry; E, preindustrial atmosphere with present-day biomass burning emissions of NO<sub>x</sub>, CO, and NMHCs.

<sup>c</sup>Wang *et al.* [1998a].

<sup>d</sup>Including direct CO emission and CO production from hydrocarbon oxidation.

<sup>e</sup>Source needed to sustain the specified concentration of CH<sub>4</sub> (0.8 ppmv in the preindustrial simulation and sensitivity simulations B-E, 1.7 ppmv in sensitivity simulation A and the present-day simulation).

<sup>f</sup>Weighted by atmospheric mass in the column up to 150 mbar.



**Figure 1.** Simulated July mean concentrations (ppbv) of O<sub>3</sub> and CO in the lowest model layer (0-500 m above surface) for the preindustrial and present atmospheres.

lation (Table 1). Natural emissions (vegetation, soils, and lightning) and cross-tropopause fluxes of O<sub>3</sub> and NO<sub>y</sub> are assumed to be the same as in the present atmosphere. We exclude emissions from fossil fuel combustion and industry; *Dignon and Hameed* [1989] estimated a global NO<sub>x</sub> source from fossil fuel combustion of 0.4 Tg N yr<sup>-1</sup> in 1860, as compared to 22 Tg N yr<sup>-1</sup> in 1980. We also exclude soil NO<sub>x</sub> emission from fertilizer use. The concentration of CH<sub>4</sub> is specified at 0.8 ppmv on the basis of ice core data, as compared to 1.7 ppmv for the present atmosphere [IPCC, 1996]. Changes since preindustrial times in land use, meteorology, aerosols, and stratospheric O<sub>3</sub> columns are not considered.

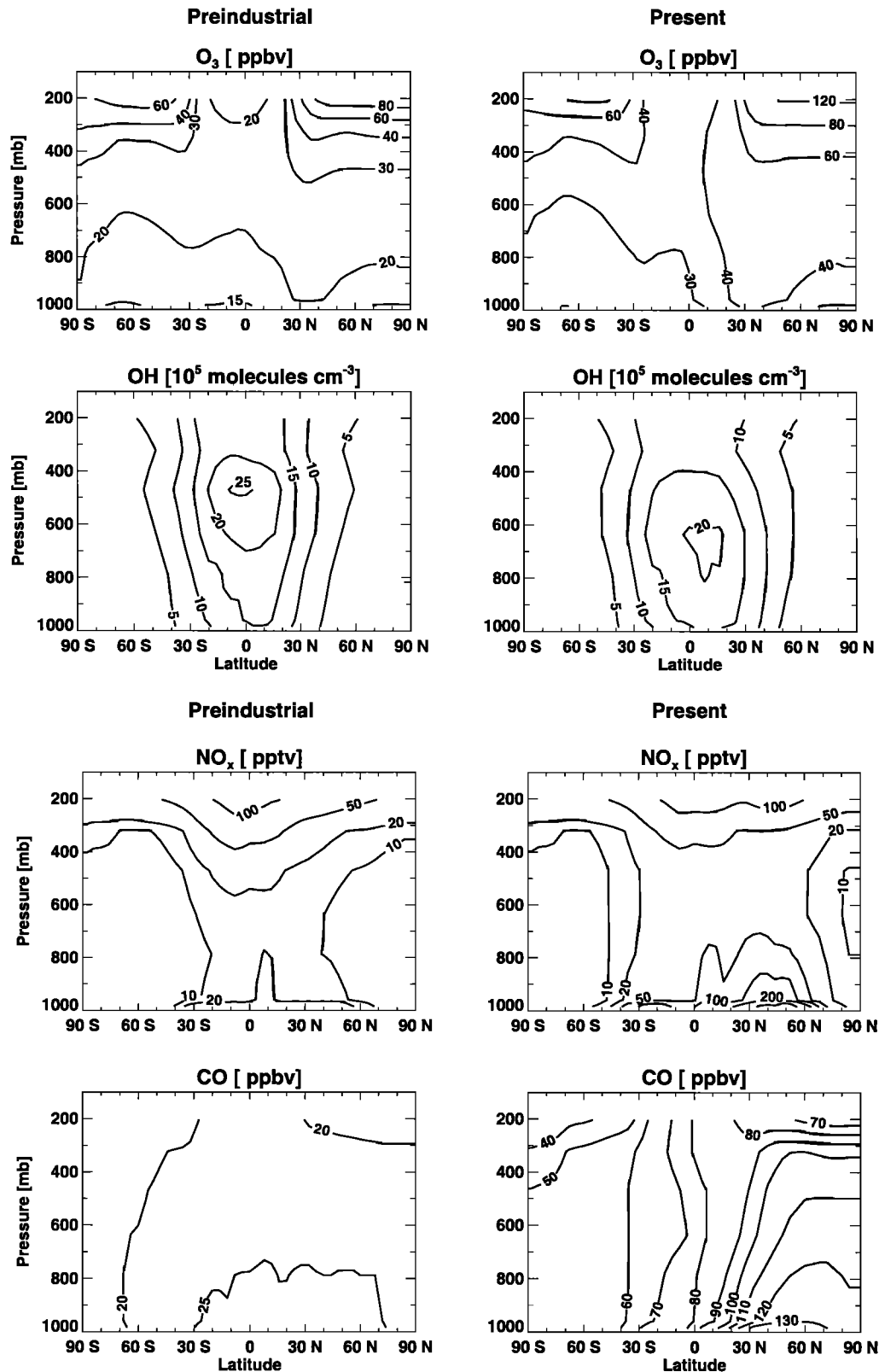
Historical trends in biomass burning are uncertain. The Greenland ice core record of ammonia does not show a systematic trend over the past 150 years [Fuhrer et al., 1996] implying a relative constant fire activity at high northern latitudes. However, biomass burning takes place principally in the tropics. As will be discussed in section 4, nineteenth century observations of O<sub>3</sub> in South America [Sandroni et al., 1992] imply a much weaker tropical biomass burning source than that of today. Following *Crutzen and Zimmermann* [1991], we assume in our standard simulation that preindustrial biomass burning emissions are 10% of the present-day value and retain

the same geographic distribution. We also conduct a sensitivity simulation assuming a preindustrial biomass burning source the same as that of today.

Nitrate records in polar ice cores offer some indication of trends in combustion since preindustrial times, but caution is necessary in interpreting these records owing to possible HNO<sub>3</sub> evaporation from snow and firn [Dibb et al., 1998]. The Greenland observations show a factor of 3 increase in nitrate deposition since preindustrial times [Mayewski et al., 1990], while our model results for Greenland give a factor of 6 increase. The Antarctic observations show large interannual variability in nitrate over the past century but no systematic trend [Mayewski and Legrand, 1990]. Our model indicates an increase of 50% in nitrate deposition over Antarctica owing to long-range transport of biomass burning emissions; such a trend could have been masked in the observations by the high interannual variability.

### 3. Ozone and OH: Preindustrial Versus Present Atmosphere

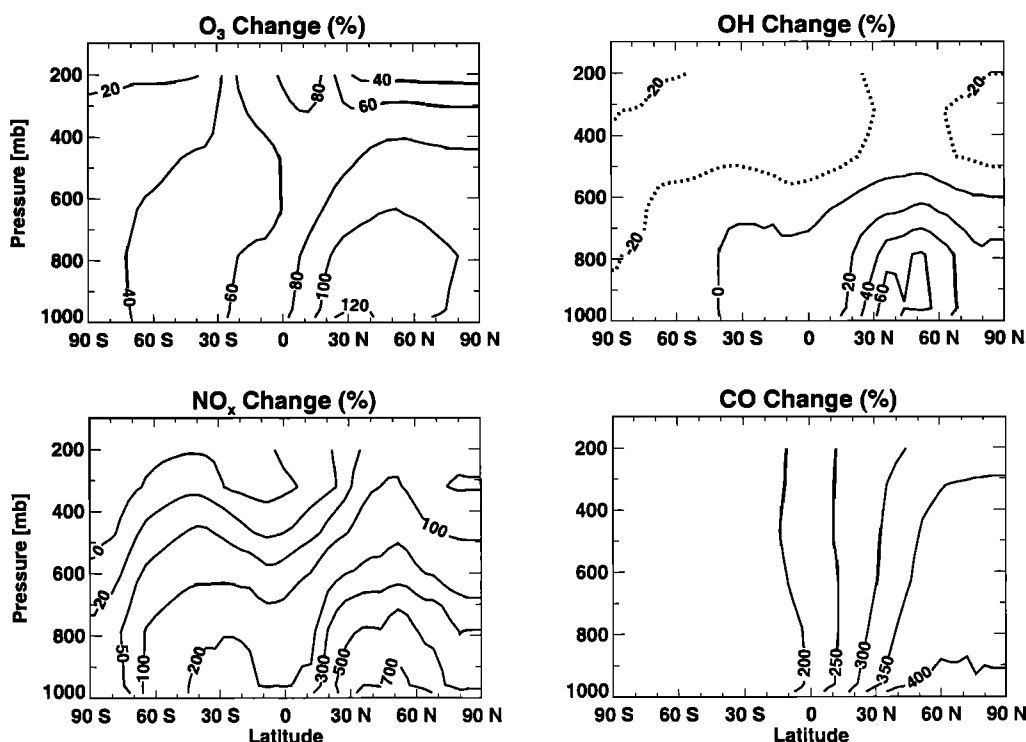
Simulated mean concentrations of O<sub>3</sub> and CO near the surface in July are shown in Figure 1 for the preindustrial and



**Figure 2a.** Zonally averaged annual mean concentrations of O<sub>3</sub> (ppbv), OH (10<sup>5</sup> molecules cm<sup>-3</sup>), NO<sub>x</sub> (pptv), and CO (ppbv) as a function of pressure and latitude for the preindustrial and present atmospheres.

present atmospheres. Preindustrial O<sub>3</sub> concentrations in the northern hemisphere are about 10-15 ppbv and are lower than in the southern hemisphere (15-20 ppbv) because of the larger amount of O<sub>3</sub> transported from the stratosphere in the winter

hemisphere and the enhanced chemical loss of O<sub>3</sub> in the summer hemisphere. In contrast, present-day O<sub>3</sub> concentrations in the northern hemisphere (20-50 ppbv) are a factor of 2 to 4 higher than in preindustrial times and are also higher than in



**Figure 2b.** Percentage changes of O<sub>3</sub>, OH, NO<sub>x</sub>, and CO concentrations (shown in Figure 2a) from preindustrial times to present.

the present southern hemisphere (20–40 ppbv) owing to enhanced summertime photochemical production associated with emissions from fuel combustion and industry. Simulated CO concentrations are a factor of 2 to 5 lower in preindustrial times than at present owing to lower preindustrial concentrations of CH<sub>4</sub> and lower direct emissions of CO. Higher CO concentrations over the continents of the northern hemisphere in preindustrial times are due to CO production from the oxidation of isoprene.

Zonally averaged annual mean concentrations of O<sub>3</sub>, OH, NO<sub>x</sub>, and CO simulated for preindustrial and present atmospheres are shown in Figure 2a; relative changes from preindustrial times to present are shown in Figure 2b. Simulated O<sub>3</sub> concentrations for the preindustrial atmosphere show a much smaller interhemispheric asymmetry than at present. Somewhat higher O<sub>3</sub> concentrations in the northern than in the southern hemisphere in preindustrial times are due mostly to a larger stratospheric source in the northern hemisphere and a larger source of NO<sub>x</sub> from soils. Model results indicate that mean tropospheric O<sub>3</sub> concentrations have increased since preindustrial times by 80% in the northern hemisphere and by 50% in the southern hemisphere. Concentrations in the upper troposphere, where O<sub>3</sub> is an effective greenhouse gas, have increased by 20–80%. This increase is largest in the tropics where O<sub>3</sub> transport from the stratosphere is negligible [Holton *et al.*, 1995].

We find that the global tropospheric O<sub>3</sub> burden (integrated from the surface up to 150 mbar) has increased by 63% from  $4.0 \times 10^{12}$  mol in preindustrial times to  $6.5 \times 10^{12}$  mol today. This increase is similar to the estimate of 70% by Lelieveld and Van Dorland [1995], but is higher than the estimates of 40% by Levy *et al.* [1997] and Roelofs *et al.* [1997]. The lower estimate by Levy *et al.* [1997] is likely due to their assumption

of present-day CH<sub>4</sub> and CO concentrations for the preindustrial atmosphere; in our preindustrial simulation, increasing the concentration of CH<sub>4</sub> from 0.8 to 1.7 ppmv alone increases the global O<sub>3</sub> burden by 13%. The lower estimate by Roelofs *et al.* [1997] is due in part to a 40% decrease in the cross-tropopause O<sub>3</sub> flux from preindustrial times to present in their simulation. Some difference among the models is also expected from adoption of different tropopause levels for budget analysis.

Table 2 shows our global budgets of tropospheric O<sub>3</sub> for the preindustrial and present-day simulations. Our budget for the present atmosphere is discussed by Wang *et al.* [1998b, c] and is consistent with results from other recent three-dimensional models. Our estimate for chemical production of O<sub>3</sub> in the preindustrial troposphere is almost identical to the estimates by Crutzen [1994] and Roelofs *et al.* [1997], while our estimate for chemical loss of O<sub>3</sub> is 10% higher than Crutzen [1994] and 14% lower than Roelofs *et al.* [1997]. The lower estimate of chemical loss by Crutzen [1994] is due to a 40% higher O<sub>3</sub> loss to dry deposition than in our model; the higher estimate by Roelofs *et al.* [1997] is due to a 30% lower loss to dry deposition and a 50% higher cross-tropopause flux than in our model.

We find that the budget of tropospheric O<sub>3</sub> is dominated by chemical production and loss within the troposphere for both the present and preindustrial atmospheres. The globally averaged lifetime of O<sub>3</sub> has decreased by 20% since preindustrial times because most of the increase of O<sub>3</sub> concentrations has been in the lower troposphere (Figure 2b) where the lifetime of O<sub>3</sub> is shorter than in the middle and upper troposphere [Wang *et al.*, 1998c]. As a result, although chemical production of O<sub>3</sub> at present is more than twice that in preindustrial times, the O<sub>3</sub> burden in the troposphere is only 63% higher.

**Table 2.** Global Sources, Sinks, and Production Efficiencies for Tropospheric O<sub>3</sub>

	Sensitivity Simulations Departing from the Preindustrial Atmosphere						Present
	Preindustrial	A 1.7 ppmv CH <sub>4</sub>	B Present CO + NMHCs	C Present NO <sub>x</sub>	D Present Fuel + Industry	E Present Biomass Burning	
<b>Sources (Tmol yr<sup>-1</sup>)</b>							
Chemical production	39	46	45	65	59	55	85
Transport from strato- sphere	8.4	8.4	8.4	8.4	8.4	8.4	8.4
<b>Sinks (Tmol yr<sup>-1</sup>)</b>							
Chemical loss	38	44	44	60	54	52	77
Dry deposition	8.7	9.8	9.6	13	13	11	17
O <sub>3</sub> burden (Tmol)	4.0	4.5	4.4	5.2	5.1	4.7	6.5
O <sub>3</sub> lifetime (days)	31	31	31	26	28	27	25
O <sub>3</sub> production efficiency α <sub>N</sub> per of NO <sub>x</sub> emitted (mol/mol)	60	71	70	22	28	39	28
O <sub>3</sub> yield α <sub>C</sub> per unit of CO or hydrocarbon oxidized (mol/mol)	0.80	0.67	0.56	1.1	0.81	0.80	0.72

The budgets and production efficiencies are for odd oxygen (O<sub>x</sub> = O<sub>3</sub> + O + NO<sub>2</sub> + HNO<sub>4</sub> + 2 x NO<sub>3</sub> + 3 x N<sub>2</sub>O<sub>5</sub> + organic nitrates + HNO<sub>3</sub>) in the model air column from the surface to 150 mbar (specified as the tropopause). Over 95% of O<sub>x</sub> is O<sub>3</sub>. Chemical production of O<sub>x</sub> is by reactions of peroxy radicals with NO, and chemical loss is principally through the reactions O<sup>1</sup>D+H<sub>2</sub>O, O<sub>3</sub>+HO<sub>2</sub>, and O<sub>3</sub>+OH. Sensitivity cases are the same as in Table 1.

Our model results for OH indicate that concentrations have either increased or decreased since preindustrial times depending on the region (Figure 2b). This variability reflects largely the regional variability in the enhancements of NO<sub>x</sub> and O<sub>3</sub>, which tend to increase OH. Enhancements of CO and CH<sub>4</sub>, which tend to decrease OH, are much more uniform in the troposphere. In the lower troposphere of the northern hemisphere, where NO<sub>x</sub> and O<sub>3</sub> are strongly enhanced, OH concentrations show a 20-60% increase. In the middle and upper troposphere where NO<sub>x</sub> and O<sub>3</sub> enhancements are modest, OH concentrations show a 20% decrease.

Preindustrial OH concentrations are almost symmetric across the equator, while present-day OH concentrations are higher in the northern than in the southern hemisphere. The impact of anthropogenic emissions on OH concentrations is asymmetric because the lifetimes of CO (a few months) and CH<sub>4</sub> (about 10 years) are much longer than that of NO<sub>x</sub> (hours to days) allowing CO and CH<sub>4</sub> but not NO<sub>x</sub> to be transported to the southern hemisphere from the northern hemisphere where 90% of the fossil fuel combustion source and most of CH<sub>4</sub> sources are located. The interhemispheric asymmetry in the change of OH concentrations was previously simulated by Crutzen and Zimmermann [1991]; the increase of OH concentrations in the lower troposphere of the northern hemisphere is larger and broader in our model than in theirs.

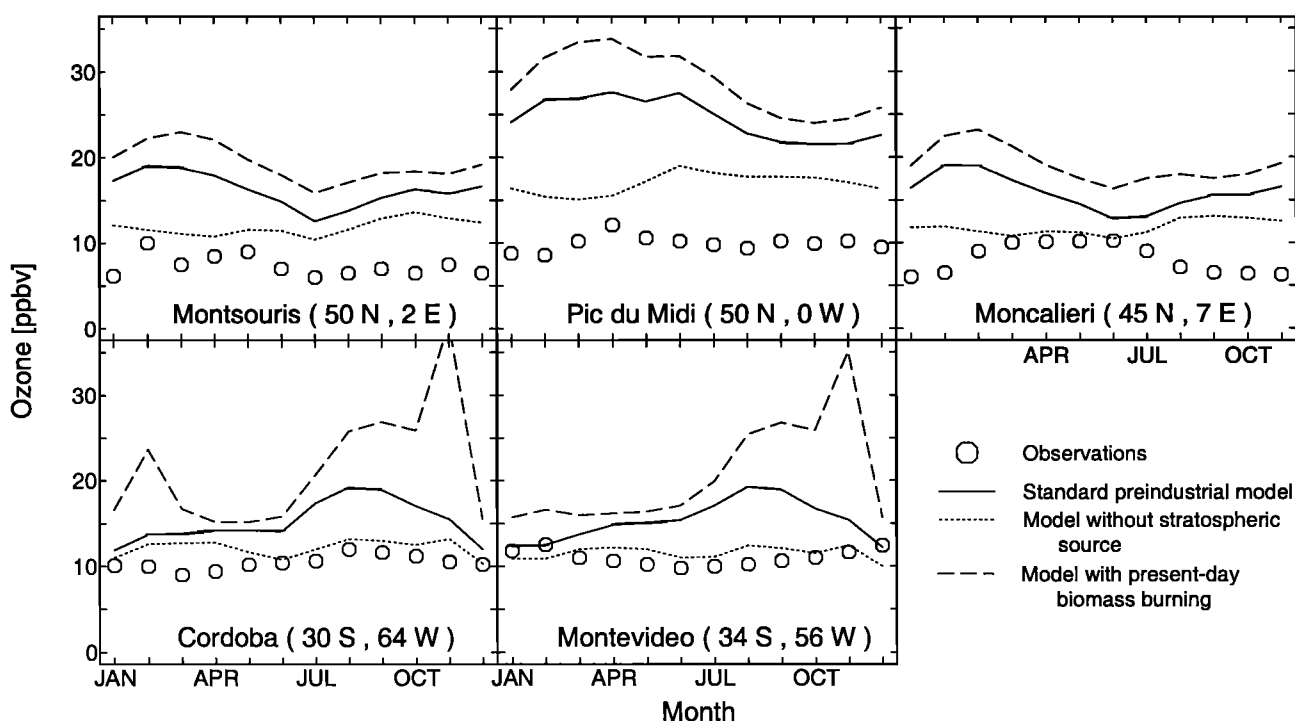
We find that the mass-weighted global mean OH concentration below 150 mbar has decreased by 9% from 1.15 x 10<sup>6</sup> molecules cm<sup>-3</sup> (preindustrial) to 1.04 x 10<sup>6</sup> molecules cm<sup>-3</sup> (present). However, the lifetime of CH<sub>3</sub>CCl<sub>3</sub> against OH oxidation has remained at 5.1 years; the increase of OH concentrations in the lower troposphere, where the rate constant for CH<sub>3</sub>CCl<sub>3</sub> oxidation is higher owing to warmer temperatures,

has compensated for a lower present-day global mean OH concentration. Previous model calculations of the trend in the mass-weighted global mean OH concentration from preindustrial times to present indicated a 6-7% increase [Martinierie *et al.*, 1995; Bernsten *et al.*, 1997], a 3% decrease [Lelieveld and Van Dorland, 1995], a 10-15% decrease [Crutzen and Zimmermann, 1991], and a 22% decrease [Roelofs *et al.*, 1997]. Earlier estimates based largely on one-dimensional models indicated a 10-30% decrease [Thompson, 1992]. The general consensus among the current generation of models is that the global mean OH concentration has remained to within 20% of the present-day value since preindustrial times.

## 4. Model Evaluation With Preindustrial Observations

### 4.1. Ozone

Nineteenth century concentrations of O<sub>3</sub> at a number of continental sites have been reconstructed from old measurements made with impregnated papers and a colorimetric scale. A detailed review is given by Marenco *et al.* [1994]. According to this review, some early reconstructions including by Linvill *et al.* [1980] (15-50 ppbv in Michigan), Bojkov [1986] (15-26 ppbv at sites in North America and Europe), and Lissac and Grubisich [1991] (30-36 ppbv in Yugoslavia) have positive biases due to incorrect calibrations. For comparison with our model results, we use the reconstructed data by Anfossi *et al.* [1991] and Marenco *et al.* [1994] for France and Italy and those by Sandroni *et al.* [1991] for Argentina and Uruguay. These reconstructions used similar calibrations [Marenco *et al.*, 1994].



**Figure 3.** Simulations and reconstructed observations of preindustrial O<sub>3</sub> concentrations (ppbv) in surface air over Europe and South America: Montsouris, France (1876-1886) [Anfossi *et al.*, 1991], Pic du Midi, France (1874-1881, the Plantade Station, Elevation 2.4 km) [Marenco *et al.*, 1994], Moncalieri, Italy (1868-1893) [Anfossi *et al.*, 1991], Cordoba, Argentina (1886-1892) [Sandroni *et al.*, 1992], and Montevideo, Uruguay (1883-1885) [Sandroni *et al.*, 1992]. Reconstructed observations are open circles; results from the standard preindustrial simulation (with biomass burning source reduced to 10% of the present-day value) are solid lines; results from a preindustrial simulation without the O<sub>3</sub> source from the stratosphere are dotted lines; and results from a preindustrial simulation with the present-day biomass burning source (NO<sub>x</sub>, CO, and NMHCs) are dashed lines.

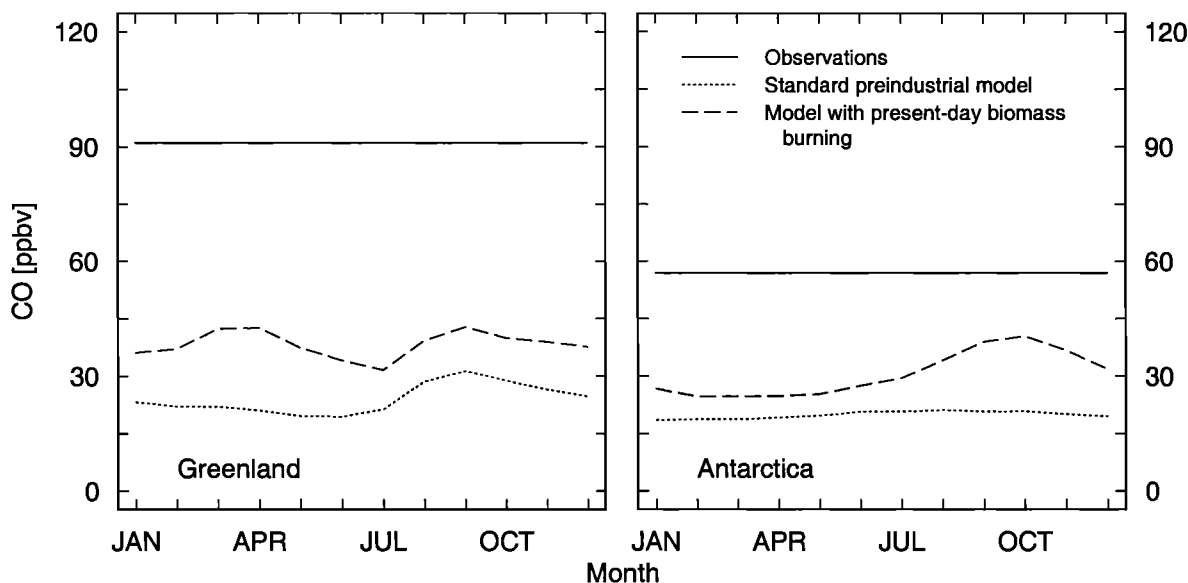
Figure 3 compares the reconstructed observations with model simulations of surface O<sub>3</sub> concentrations for the preindustrial atmosphere. The reconstructed data generally show O<sub>3</sub> concentrations of 7-12 ppbv. The weak winter-spring maximum in the European observations is reproduced by the model, where it reflects the stratospheric influence (Figure 3). Observations from South America show no significant spring-time enhancement from biomass burning, in contrast to the present atmosphere [Kirchhoff and Rasmussen, 1990], implying a much weaker biomass burning source in preindustrial times than that of today. Including the present-day biomass burning source in our standard preindustrial simulation leads to a 10-20 ppbv increase of O<sub>3</sub> concentrations in northern Argentina and Uruguay during the austral burning season of August-November (Figure 3).

Figure 3 shows that our standard preindustrial simulation overestimates the reconstructed observations consistently by 0-20 ppbv. The discrepancies are particularly large in the winter season of both hemispheres, reflecting a greater seasonal amplitude in the model (driven by the stratospheric influence). The preindustrial observations in Figure 3 were typically taken around the clock, and some of the model overestimate may be due to nighttime O<sub>3</sub> depletion by dry deposition in a shallow stable surface layer sampled by the observations but not resolved by the model [Jacob *et al.*, 1993]. Negative interference to O<sub>3</sub> measurements by NH<sub>3</sub> or SO<sub>2</sub> could also contribute [Anfossi and Sandroni, 1997]. Loss of O<sub>3</sub> to natural organic

aerosols or to a denser preindustrial vegetation canopy could further mitigate some of the overestimates in summer. These effects are, however, unlikely to explain the seasonal pattern of the overestimates and should not be an issue at Pic du Midi, a mountain site [Marenco *et al.*, 1994]. Model results from a sensitivity simulation in which O<sub>3</sub> transport from the stratosphere is excluded are in much better agreement with the reconstructed observations (Figure 3). However, there is no physical basis to suspect that O<sub>3</sub> transport from the stratosphere to the troposphere in preindustrial times was much less or had a different seasonal variation from present [Holton *et al.*, 1995].

Previous global three-dimensional model simulations of the preindustrial atmosphere show similar tendencies to overestimate observations. Roelofs *et al.* [1997] find mean surface O<sub>3</sub> concentrations over Europe of 10-15 ppbv in summer and 15-20 ppbv in winter, in good agreement with ours, while Levy *et al.* [1997] find corresponding values of 7-9 ppbv in summer and 20 ppbv in winter (H. Levy II., personal communication, 1997). The best simulation would appear to be that of Berntsen *et al.* [1997] which yields surface O<sub>3</sub> concentrations of 10 ppbv at Paris with little seasonal variation. However, that simulation assumes excessive O<sub>3</sub> deposition velocities: 0.5 cm s<sup>-1</sup> in summer and 0.4 cm s<sup>-1</sup> in winter over Europe referenced to 200 m altitude (lowest model layer) [Berntsen and Isaksen, 1997]. These values are about a factor of 2 too high when compared to resistance-in-series models which account for the





**Figure 4.** Measured and simulated preindustrial CO concentrations (ppbv) over Greenland and Antarctica. Ice core measurements by *Haan et al.* [1996] (annual averages) represented in solid lines are for the periods of 1802-1862 (Greenland) and 1860-1916 (Antarctica). Dotted lines are results from the standard preindustrial simulation with the biomass burning source reduced to 10% of the present-day value, and dashed lines are results from a preindustrial simulation with the present-day biomass burning source (NO<sub>x</sub>, CO, and NMHCs).

effect of nighttime stability in the 0-200 m column and a lack of stomatal uptake of O<sub>3</sub> in winter [*Jacob et al.*, 1993; *Ganzeveld and Lelieveld*, 1995; *Munger et al.*, 1998; *Wang et al.*, 1998a].

The most troubling discrepancy in Figure 3 is at Pic du Midi (2.4 km altitude), where the preindustrial data should not be affected by chemical interferences from NH<sub>3</sub> or SO<sub>2</sub> and where local surface effects should be minimal [*Marenco et al.*, 1994]. Matching the nineteenth century Pic du Midi observations in our model, assuming the same stratospheric source as that of today and some natural NO<sub>x</sub> emissions (lightning and soils), would require a large missing chemical sink of O<sub>3</sub> in the troposphere. A perplexing aspect of the Pic du Midi preindustrial observations is the lack of vertical gradient relative to Montsouris (Figure 3). Present-day vertical profiles of O<sub>3</sub> concentrations at remote continental sites typically show differences of 10-20 ppbv between the sea level and 2-3 km altitude as a result of chemical loss and dry deposition in the boundary layer [*Anderson et al.*, 1994; *Mauzerall et al.*, 1996]. *Anfossi et al.* [1991] found in the nineteenth century Moncalieri data that O<sub>3</sub> concentrations associated with downslope winds from the Alps (foehn) were 5-10 ppbv higher than average, suggesting an increase of O<sub>3</sub> concentrations with altitude which is at odds with the Pic du Midi data.

#### 4.2. Carbon Monoxide

A recent analysis of ice core CO records shows concentrations of 91 ppbv in central Greenland for the period of 1802-1862 and 57 ppbv in Antarctica for the period of 1860-1916 [*Haan et al.*, 1996]. Figure 4 compares these data with model results for Greenland and Antarctica. The standard model for the preindustrial atmosphere is too low by a factor of 4 and does not show the observed interhemispheric asymmetry. When the present-day biomass burning source is included, model results are still a factor of 2 too low and exhibit little

interhemispheric asymmetry. As discussed in section 4.1, the reconstructed O<sub>3</sub> observations in South America imply a biomass burning source in the nineteenth century much less than that of today.

Previous model simulations for the preindustrial atmosphere, reviewed by *Haan et al.* [1996], also underestimate the ice core data. *Haan et al.* [1996] suggested that the underestimate could reflect the neglect of nineteenth century industrial emissions in the models. However, these emissions would have to be unrealistically large. As *Haan et al.* [1996] noted, the ice core record for 1860-1916 over Antarctica indicates CO concentrations similar to those observed today. The background CO concentration from CH<sub>4</sub> oxidation, however, has increased by 15 to 20 ppbv since preindustrial times. The ice core data for 1802-1862 over Greenland are not much lower than an annual mean concentration of 115 ppbv simulated in our model for the present atmosphere. The ice core data of *Haan et al.* [1996] would thus imply higher CO and NMHC emissions in the nineteenth century than at present in the southern hemisphere and comparable emissions in the northern hemisphere. Such a scenario is inconsistent with historical trends in fossil fuel combustion and is also inconsistent with the observed increase in tropospheric CO over Jungfraujoch (Switzerland) from 1950 to present [*Zander et al.*, 1989]. The Jungfraujoch measurements for 1950-1951 indicate 67 ppbv CO, which is lower than the Greenland ice core concentration of 91 ppbv reported by *Haan et al.* [1996] for the nineteenth century.

#### 4.3. Hydrogen Oxide Radicals

Trends in the concentrations of hydrogen oxide radicals (HO<sub>x</sub>=OH+HO<sub>2</sub>) since preindustrial times have been estimated by *Staffelbach et al.* [1991] and *Anklin and Bales* [1997] using CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> records from Greenland ice cores. Interpretation of these records is subject to caution

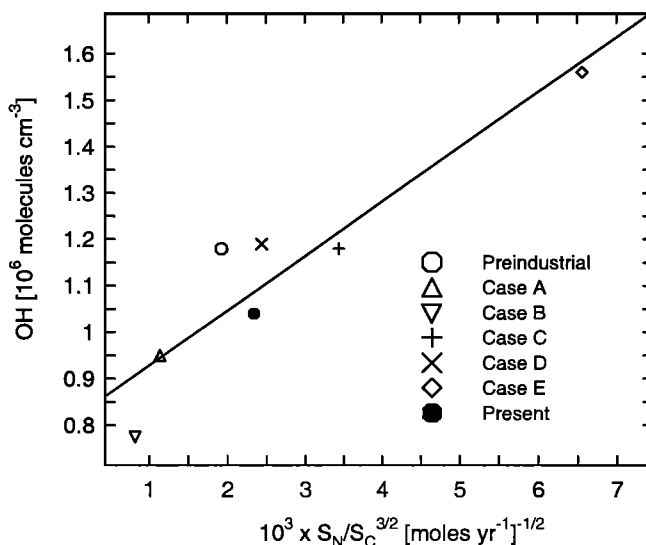
because of possible post-depositional exchange with the atmosphere, reactions within the ice, and secular changes in the seasonal accumulation of snow [Nefel *et al.*, 1995]. The record of CH<sub>2</sub>O suggests a 30% decrease in OH concentrations since preindustrial times [Staffelbach *et al.*, 1991]; our corresponding model results over Greenland show a 12% decrease. Data for H<sub>2</sub>O<sub>2</sub> in Greenland ice cores show constant concentrations from preindustrial times until about 1970 and a doubling of concentrations since then which would suggest a rise in HO<sub>x</sub> concentrations [Sigg and Nefel, 1991; Anklin and Bales, 1997]. Our model shows a factor of 2.5 increase of H<sub>2</sub>O<sub>2</sub> concentrations over Greenland from preindustrial times to today because of the increasing source of HO<sub>x</sub> radicals as tropospheric O<sub>3</sub> concentrations increase.

## 5. Ozone and OH: Relationship to Anthropogenic Emissions

The major forcings of O<sub>3</sub> and OH concentrations since preindustrial times in our model are (1) the increase of CH<sub>4</sub> concentrations from 0.8 to 1.7 ppmv, (2) emissions of CO, NMHCs, and NO<sub>x</sub> from fuel combustion and industry, and (3) emissions from biomass burning. We conducted three sensitivity simulations in which each forcing was individually added to the standard preindustrial simulation. We also conducted two additional sensitivity simulations in which the changes in emissions from preindustrial times to today were applied to either CO and NMHCs or to NO<sub>x</sub>. The global mean OH concentrations for these simulations are shown in Table 1, and global budgets of tropospheric O<sub>3</sub> are shown in Table 2.

As discussed in section 3, OH concentrations reflect a balance between sources of CO and hydrocarbons ( $S_C$ ) which deplete OH and sources of NO<sub>x</sub> ( $S_N$ ) which enhance OH. Table 1 shows values of  $S_C$  and  $S_N$  for our different simulations. In an analytical solution to a simple box model, we find that OH concentrations vary as  $S_N/S_C^{3/2}$  (appendix). Our global three-dimensional model indeed exhibits a linear dependence of the global mean OH concentration on the  $S_N/S_C^{3/2}$  ratio for the range of simulations conducted (Figure 5), but the large intercept of the linear regression line implies a much smaller OH sensitivity to  $S_N/S_C^{3/2}$  than implied by the box model analysis. This dampening of the OH sensitivity to  $S_N/S_C^{3/2}$  in the global model reflects short lifetimes of NO<sub>x</sub> and fast-reacting NMHCs. Anthropogenic NO<sub>x</sub> and NMHCs emitted at the surface are mostly removed from the atmosphere within the continental boundary layer [Liang *et al.*, 1998], which limits their impact on the global mean OH concentration. As seen in Table 1, increasing preindustrial CO and NMHC emissions to those of today (case B) increases  $S_C$  by 70% but decreases the global mean OH concentration by only 30%; increasing preindustrial NO<sub>x</sub> emissions to present-day values (case C) increases  $S_N$  by a factor of 4.5 but only increases OH by 40%. The less than 10% change of the global mean OH concentration since preindustrial times in our standard model reflects the relative constancy of the  $S_N/S_C^{3/2}$  ratio (Figure 5) despite factors of 4.7 and 2.5 increases in  $S_N$  and  $S_C$ , respectively.

The global increase of O<sub>3</sub> production in the model from preindustrial times ( $39 \times 10^{12}$  mol yr<sup>-1</sup>) to present ( $85 \times 10^{12}$  mol yr<sup>-1</sup>) reflects a combination of increasing emissions of NO<sub>x</sub>, CO, and hydrocarbons. Although the O<sub>3</sub> production rate is NO<sub>x</sub> limited throughout the troposphere [Chameides *et al.*, 1992], we find that the increase of NO<sub>x</sub> emissions alone (case C) accounts for only 57% of the increase in O<sub>3</sub> production.



**Figure 5.** Global mean OH concentration as a function of  $S_N/S_C^{3/2}$ , where  $S_N$  and  $S_C$  are the tropospheric sources of NO<sub>x</sub> and of CO and hydrocarbons (mol yr<sup>-1</sup>), respectively. The solid line shows a least squares fit. Model sensitivity simulations are described in Table 1.

Increases in CO and NMHC emissions (case B) and in the concentration of CH<sub>4</sub> (case A) make significant contributions of about 15% each, because increasing CO and hydrocarbons enhances the O<sub>3</sub> production efficiency per unit NO<sub>x</sub> emitted [Lin *et al.*, 1988; Crutzen, 1994].

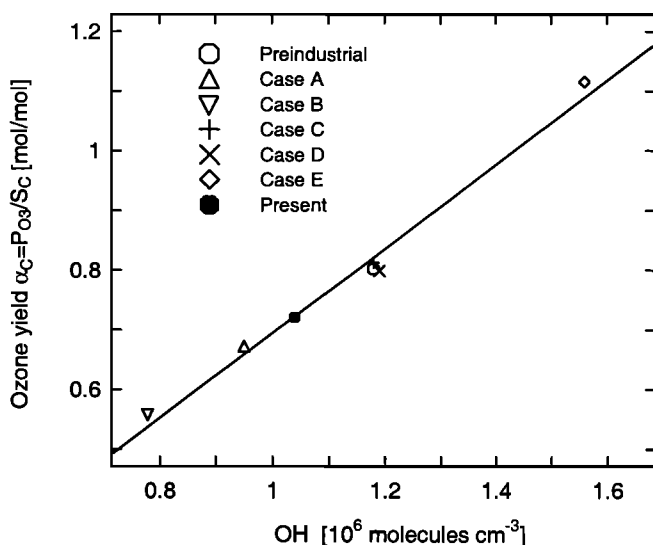
One can separate the effects of anthropogenic emissions by source category. We find that emissions from fuel combustion and industry (case D) and from biomass burning (case E) each explain about 40% of the total increase of O<sub>3</sub> production in the model, while the increase of CH<sub>4</sub> concentrations (case A) explains most of the remaining 20%. This near-additivity reflects the constancy in the O<sub>3</sub> yield per unit of CO or hydrocarbon emitted, as discussed below. Fuel combustion and biomass burning make similar contributions to the rise in O<sub>3</sub> production even though the fossil fuel source of NO<sub>x</sub> is larger (Table 1) because of a higher O<sub>3</sub> production efficiency in the tropics where most of the biomass burning source is located.

The increase of O<sub>3</sub> production since preindustrial times can be related quantitatively to emissions of O<sub>3</sub> precursors by using as diagnostic the O<sub>3</sub> production efficiency ( $\alpha_N$ ) per unit NO<sub>x</sub> emitted [cf. Liu *et al.*, 1987] and the O<sub>3</sub> yield ( $\alpha_C$ ) per unit of CO or hydrocarbons oxidized [Crutzen, 1988]. The losses of CO and hydrocarbons are in balance with their sources on a global scale. The global rate of chemical O<sub>3</sub> production ( $P_{O_3}$ ) is therefore

$$P_{O_3} = \alpha S \quad (1)$$

where  $\alpha$  is  $\alpha_N$  or  $\alpha_C$  and  $S$  is the source of NO<sub>x</sub> ( $S_N$ ) or of CO and hydrocarbons ( $S_C$ ), respectively. We obtain  $S_C$  from Table 1 by adding the sources of CO, CH<sub>4</sub>, and NMHCs. Table 2 shows global values of  $\alpha_N$  and  $\alpha_C$  for all the model simulations.

We find that the O<sub>3</sub> production efficiency  $\alpha_N$  has decreased by a factor of 2 since preindustrial times because of its sensitivity to NO<sub>x</sub> concentrations [Liu *et al.*, 1987]. By contrast, the O<sub>3</sub> yield  $\alpha_C$  has changed little since preindustrial times; as a result, O<sub>3</sub> production has increased proportionally to  $S_C$ .



**Figure 6.** The O<sub>3</sub> yield  $\alpha_C$  (mol/mol) per unit CO or hydrocarbon oxidized as a function of the global mean OH concentration ( $10^6$  molecules  $\text{cm}^{-3}$ ). The solid line shows a least squares fit. Model sensitivity simulations are described in Table 1.

Increasing CO and NMHCs emissions alone (cases A and B) decreases  $\alpha_C$ , whereas increasing NO<sub>x</sub> emissions alone (case C) increases  $\alpha_C$ . We find, however, that the mix of NO<sub>x</sub>, CO, and hydrocarbon emissions from anthropogenic sources is such that it leaves  $\alpha_C$  unchanged. The conservation of  $\alpha_C$  explains the additivity of the forcings from fuel combustion and industry (case D), biomass burning (case E), and increasing CH<sub>4</sub> concentrations (case A) in increasing O<sub>3</sub> production since preindustrial times. Figure 6 shows a tight linear relationship between  $\alpha_C$  and the global mean OH concentration in the model. A rise in  $\alpha_C$  implies greater O<sub>3</sub> production per molecule of CO or hydrocarbon emitted and hence a net increase in OH concentrations.

We find in the model that the dependence of O<sub>3</sub> production on emissions of precursors is more linear when referenced to hydrocarbon rather than to NO<sub>x</sub> emissions; that is, the variability of  $\alpha_C$  is less than that of  $\alpha_N$  (Table 2). As shown in the appendix,  $\alpha_C$  is theoretically constrained to remain between 0.2 and 3; the lower limit reflects the minimum O<sub>3</sub> production necessary to avoid titration of OH, while the upper limit reflects the maximum O<sub>3</sub> yield from oxidation of a typical CO and hydrocarbon mix in a high-NO<sub>x</sub> atmosphere [Crutzen, 1988].

The lower limit of  $\alpha_C$  has two implications. Recent global three-dimensional models indicate that the budget of tropospheric O<sub>3</sub> is dominated by O<sub>3</sub> production in the troposphere, as opposed to transport from the stratosphere [Wang *et al.*, 1998b, and references therein]. This result can be simply explained by considering the lower limit of 0.2 for  $\alpha_C$ . Our values of  $S_C$  are  $120 \times 10^{12}$  mol  $\text{yr}^{-1}$  and  $48 \times 10^{12}$  mol  $\text{yr}^{-1}$  for the present and preindustrial atmospheres, respectively (Table 1), implying minimum O<sub>3</sub> chemical production of  $24 \times 10^{12}$  mol  $\text{yr}^{-1}$  (present) and  $10 \times 10^{12}$  mol  $\text{yr}^{-1}$  (preindustrial). In comparison with a source of  $8 \times 10^{12}$  mol  $\text{yr}^{-1}$  transported from the stratosphere [Wang *et al.*, 1998a, b], tropospheric O<sub>3</sub> production must be much larger (by a factor of 3) at present and no less in preindustrial times.

Using a lower limit of 0.2 for  $\alpha_C$ , we can also demonstrate simply that the rate of O<sub>3</sub> production must be NO<sub>x</sub> limited on a global scale. Ozone production is NO<sub>x</sub> limited if the source  $S_{HO_x}$  of HO<sub>x</sub> radicals is larger than the source  $S_N$  of NO<sub>x</sub>; it is hydrocarbon limited if the opposite holds [Jacob *et al.*, 1995; Kleinman *et al.*, 1997]. The dominant global source of HO<sub>x</sub> in the troposphere is O<sub>3</sub> photolysis to O(<sup>1</sup>D) followed by reaction of O(<sup>1</sup>D) with H<sub>2</sub>O; this reaction is also a major sink for O<sub>3</sub> and amounts to 50-60% of the tropospheric O<sub>3</sub> source [Crutzen, 1994]. We thus estimate a minimum  $S_{HO_x}$  of 0.2  $S_C$  with an  $\alpha_C$  of 0.2. In comparison,  $S_N=0.013 S_C$  for the preindustrial atmosphere,  $S_N=0.061 S_C$  for fossil fuel combustion, and  $S_N=0.036 S_C$  for biomass burning (Table 1). The dominance of  $S_{HO_x}$  over  $S_N$  implies that tropospheric O<sub>3</sub> production has remained NO<sub>x</sub> limited since preindustrial times and will stay so in the future as long as the global  $S_N/S_C$  ratio remains below 0.1.

## 6. Conclusions

We examined the changes in tropospheric O<sub>3</sub> and OH concentrations since preindustrial times using a global three-dimensional model. The model has been shown previously to provide a generally good simulation of O<sub>3</sub>, CO, NO<sub>x</sub>, and the global mean OH concentration for the present atmosphere [Wang *et al.*, 1998b]. Our simulation of the preindustrial atmosphere assumes 0.8 ppmv CH<sub>4</sub>, no emissions from fuel combustion and industry, 10% of the present-day biomass burning source, and the same natural emissions (lightning, soils, and vegetation) as in the present.

Comparison of model results for the preindustrial atmosphere with reconstructed observations of O<sub>3</sub> in the nineteenth century shows significant discrepancies. The reconstructed data for O<sub>3</sub> over Europe and South America show concentrations of 7-12 ppbv; model results are about 5 ppbv higher and show a stronger seasonal variation. Previous global model simulations of O<sub>3</sub> in preindustrial times show similar overestimates. Allowing for some emissions from fossil fuel combustion in the nineteenth century would worsen the overestimates.

Of particular concern is the failure of the model to reproduce the low preindustrial O<sub>3</sub> observations at Pic du Midi (2.4 km altitude) which should not be affected by depositional effects or negative measurement interference by SO<sub>2</sub> or NH<sub>3</sub>. A remarkable feature of the Pic du Midi observations is the lack of vertical gradient relative to sea level observations during the same period at nearby Montsouris. This lack of vertical gradient is inconsistent with our current understanding of tropospheric O<sub>3</sub>. Matching the Pic du Midi observations in the model would require an important missing sink for O<sub>3</sub> in the preindustrial atmosphere or a downward revision of lightning NO<sub>x</sub> emissions (presently 3 Tg N  $\text{yr}^{-1}$ ) which provide the principal source of preindustrial O<sub>3</sub>.

Polar ice core data for preindustrial times are available for CO, CH<sub>2</sub>O (proxy of OH), and H<sub>2</sub>O<sub>2</sub> (proxy of HO<sub>x</sub>). The model underestimates the ice core measurements of nineteenth century CO concentrations and corresponding interhemispheric gradient [Haan *et al.*, 1996]. These measurements cannot be reconciled with any reasonable CO emission inventories for the nineteenth century. Model results for OH concentrations over Greenland indicate a decrease of 12% since preindustrial times, comparable with the 30% decrease derived from ice core records of CH<sub>2</sub>O. Model results for

H<sub>2</sub>O<sub>2</sub> concentrations over Greenland indicate a factor of 2.5 increase since preindustrial times; ice core records show little change of H<sub>2</sub>O<sub>2</sub> concentrations until 1970 and a doubling since then.

We find that anthropogenic emissions since preindustrial times have caused an increase of 120% in tropospheric O<sub>3</sub> production and a doubling of the total tropospheric O<sub>3</sub> source (including transport from the stratosphere). The increase in the global tropospheric O<sub>3</sub> burden is only 63% because O<sub>3</sub> production due to anthropogenic emissions takes place preferentially in the lower troposphere, where the lifetime of O<sub>3</sub> is shorter than in the middle and upper troposphere.

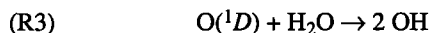
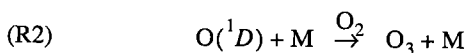
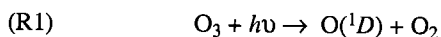
Although the local rate of O<sub>3</sub> production in the troposphere is NO<sub>x</sub> limited in general, we find that increasing NO<sub>x</sub> emissions alone from preindustrial times to present explains only 57% of the rise in O<sub>3</sub> production of the global troposphere. Increasing emissions of CH<sub>4</sub>, CO, and NMHCs accounts for the rest because the O<sub>3</sub> production efficiency per mole of NO<sub>x</sub> emitted increases with increasing CO and hydrocarbons. Separating the effects of anthropogenic emissions by source category, we find that fossil fuel combustion and the increase of biomass burning each contribute about 40% of the global increase of O<sub>3</sub> production since preindustrial times in the model and that the increase of atmospheric CH<sub>4</sub> contributes about 20%.

The global O<sub>3</sub> production efficiency  $\alpha_N$  per unit NO<sub>x</sub> emitted decreases in the model from 60 mol/mol in preindustrial times to 28 mol/mol at present reflecting a greater relative increase of NO<sub>x</sub> emissions (factor of 4.7) than of CO and hydrocarbons (factor of 2.5). The global O<sub>3</sub> yield  $\alpha_C$  per unit CO or hydrocarbon oxidized has, however, remained nearly constant at 0.7-0.8 mol/mol; the emission mixes of NO<sub>x</sub>, CO, and hydrocarbons from fuel combustion and industry and from biomass burning are such that they conserve  $\alpha_C$  but not  $\alpha_N$ . The increase of tropospheric O<sub>3</sub> production since preindustrial times has therefore largely followed that of CO and hydrocarbon emissions.

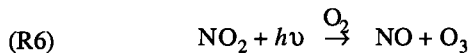
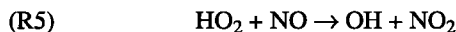
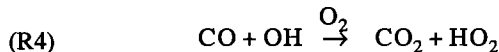
Model results indicate that the global mean OH concentration (weighted by air mass) has decreased by 9% since preindustrial times. However, the lifetime of CH<sub>3</sub>CCl<sub>3</sub> against OH oxidation has remained at 5.1 years because of the temperature dependence of the oxidation rate constant; the increase of OH concentrations in the warmer lower troposphere has compensated for a lower global mean OH concentration. We find that the global mean OH concentration varies linearly with the  $S_N/S_C^{3/2}$  ratio, where  $S_N$  and  $S_C$  are the total tropospheric sources of NO<sub>x</sub> and of CO and hydrocarbons, respectively. The relative constancy of the global mean OH concentration since preindustrial times reflects conservation of the  $S_N/S_C^{3/2}$  ratio by anthropogenic emissions.

## Appendix: A Simple Schematic for Tropospheric O<sub>3</sub> and HO<sub>x</sub> Chemistry

We consider here a simple schematic of tropospheric O<sub>3</sub>-NO<sub>x</sub>-CO chemistry derived from currently accepted mechanisms [Logan *et al.*, 1981]. The primary supply of HO<sub>x</sub> (OH + HO<sub>2</sub>) radical is the photolysis of O<sub>3</sub> to O(<sup>1</sup>D) and subsequent reaction of O(<sup>1</sup>D) with H<sub>2</sub>O,



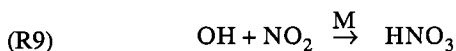
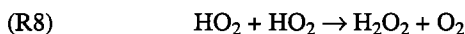
Cycling of HO<sub>x</sub> by oxidation of CO in the presence of NO<sub>x</sub> leads to production of O<sub>3</sub>,



The oxidation of NO to NO<sub>2</sub> also takes place by the reaction NO + O<sub>3</sub>,



Loss of HO<sub>x</sub> radicals takes place mostly by self-reaction of HO<sub>2</sub> and oxidation of NO<sub>2</sub> by OH,



We consider in this system the steady state equations for HO<sub>x</sub>, OH, O<sub>3</sub>, NO<sub>x</sub>, and CO concentrations, respectively,

$$2 \frac{J_1 k_3 [H_2O]}{k_2 [M]} [O_3] = 2k_8 [HO_2]^2 + k_9 [OH][NO_2][M] \quad (A1)$$

$$k_5 [HO_2][NO] + 2 \frac{J_1 k_3 [H_2O]}{k_2 [M]} [O_3] = k_4 [OH][CO] \quad (A2)$$

$$k_5 [HO_2][NO] + F_{O_3} = \frac{J_1 k_3 [H_2O]}{k_2 [M]} [O_3] + k_d [O_3] \quad (A3)$$

$$S_N = k_9 [OH][NO_2] \quad (A4)$$

$$S_C = k_4 [OH][CO] \quad (A5)$$

where  $k_i$  or  $J_i$  is the reaction or photolysis rate constant for reaction  $i$ ,  $k_d$  is a deposition rate constant for O<sub>3</sub>,  $F_{O_3}$  is the net transport rate of O<sub>3</sub> from the stratosphere, and  $S_N$  and  $S_C$  are the sources of NO<sub>x</sub> and CO, respectively. Hydrocarbons react similarly to CO and their sources are lumped into  $S_C$  for the purpose of this simple model. Since  $S_C$  is much larger than  $S_N$  in either the present or preindustrial atmosphere (Table 1), loss of OH radicals through reaction (R9) is negligible compared to reaction (R4) and is neglected in equation (A2).

We can now derive the chemical production rate of O<sub>3</sub> as that of the odd-oxygen family ( $O_x \equiv O_3 + O + NO_2$ ) by using equations (A2), (A3), and (A5),

$$P(O_3) = k_5 [HO_2][NO] = \frac{1}{3} (S_C - 2(F_{O_3} - k_d [O_3])) \quad (A6)$$

This chemical system is stable only if sufficient OH is available to oxidize CO. Methane observations show that the atmosphere has been stable in this manner over at least the 200,000 year extent of the ice core records [IPCC, 1996]. To satisfy this stability in our simple model, the production of O<sub>3</sub> must be at least

$$P_{O_3}(\min) = \frac{1}{3} (S_C - 2F_{O_3}) \quad (A7)$$

At this limit, all O<sub>3</sub> molecules produced in the troposphere or transported from the stratosphere are used to generate OH radicals (R3) for the oxidation of CO (R4). In the real atmosphere, the lower limit for P(O<sub>3</sub>) is higher than that given by equation (A7) because (1) additional O<sub>3</sub> sinks include the reactions of O<sub>3</sub> with OH and HO<sub>2</sub>, (2) additional OH sinks include the reactions of OH with O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and H<sub>2</sub>, and (3) additional O<sub>3</sub> production takes place through the reaction of NO and organic peroxy radicals in which no OH production takes place unlike in reaction (R5). Another stable chemical regime may also exist when NO<sub>x</sub> emission is extremely low and the HO<sub>x</sub> sources from photolysis of carbonyl compounds and the chemical recycling of peroxides become more important than the HO<sub>x</sub> source from O<sub>3</sub> (reactions (R1)-(R3)). The concentrations of O<sub>3</sub> and OH would be extremely low under these conditions. Such a regime is not considered in this analysis.

Equation (A7) implies the existence of a lower limit for the O<sub>3</sub> yield  $\alpha_C$  per unit of CO or hydrocarbons emitted,

$$\alpha_C(\min) = \frac{1}{3} (1 - 2 F_{O_3} / S_C) \quad (\text{A8})$$

Estimates of  $S_C$  and  $F_{O_3}$  for preindustrial and present atmospheres (Table 1) yield a lower limit of 0.2 for  $\alpha_C$ .

The maximum value of  $\alpha_C$ , corresponding to high-NO<sub>x</sub> conditions, is 1 for oxidation of CO to CO<sub>2</sub>, 1.7 for oxidation of CH<sub>4</sub> to CO, and about 1 per atom C for oxidation of NMHCs to CO [Crutzen, 1988]. For the CO and hydrocarbon emission mixes corresponding to the preindustrial and present atmospheres, we obtain a maximum value of 3 for  $\alpha_C$ . The total source of O<sub>3</sub> in the troposphere thus scales to  $S_C$  with a factor of  $\alpha_C$  that may vary theoretically from 0.2 to 3.

The above schematic also yields a relationship between OH concentrations,  $S_N$ , and  $S_C$ . Considering equations (A1)-(A5) and assuming O<sub>3</sub>-NO-NO<sub>2</sub> photochemical steady state by reactions (R6)-(R7), we obtain

$$[\text{OH}] = \frac{3^{3/2} J_1 k_3 k_5 J_6}{k_2 k_7 k_8^{1/2} k_9 [\text{M}]} \times \frac{[\text{H}_2\text{O}] \times S_N}{(S_C - 2(F_{O_3} - k_d[\text{O}_3]))(S_C + F_{O_3} - k_d[\text{O}_3])^{1/2}} \quad (\text{A9})$$

Since  $S_C$  is much larger than  $F_{O_3}$  in both preindustrial and present atmospheres (Table 1), this equation can be reduced to a simple dependence of [OH] on  $S_N$  and  $S_C$

$$[\text{OH}] = K \frac{S_N}{S_C^{3/2}} \quad (\text{A10})$$

where  $K$  is a constant. Results from our global three-dimensional model show a linear relationship between the global mean OH concentration and the  $S_N/S_C^{3/2}$  ratio, but the actual dependence of [OH] on  $S_N/S_C^{3/2}$  is much less than implied by the present simple box model analysis (section 5).

**Acknowledgments.** We thank Jennifer Logan and Clarisa Spivakovsky for helpful discussions. We also thank Bill Chameides for his comments. This work was supported by the National Aeronautics and Space Administration (EOS/IDS, ACMAP, and GTE programs).

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(Received June 8, 1998; revised August 21, 1998; accepted August 31, 1998.)