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The global impact of human activity on tropospheric ozone

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Abstract. Within a conceptual framework of stratospheric injection, CO-CH_4 background tropospheric chemistry, parameterized pollution production in the continental boundary layer and surface deposition, we use an 11 level GCTM to simulate global distributions of present and pre-industrial tropospheric O_3. The chemistry is driven by previously simulated present and pre-industrial NOx fields, while prescribed fields of CO, CH_4 and H_2O are held constant. An evaluation with measurements from 12 surface sites, 21 ozonesonde sites and 1 aircraft campaign finds agreement within ±25% for 73% of the observations while identifying systematic errors in the wintertime high-latitude Northern Hemisphere (NH), the Southern Hemisphere (SH) tropics during biomass burning, and the remote SH. We predict that human activity has increased the annual integral of tropospheric ozone by 39% with 3/4's of that increase in the free troposphere, though the boundary layer [BL] annual integral has increased by 66%. The 2 largest components of the global O_3 budget are stratospheric injection at 696 TgO_3/yr, and loss through dry deposition, which increases from 459 TgO_3/yr to a present level of 825 TgO_3/yr. While tropospheric chemistry's net contribution is relatively small, changing from a pre-industrial destruction of -236 TgO_3/yr to a present production of +128 TgO_3/yr, it is a balance between two much larger terms, -558 TgO_3/yr of destruction in the background troposphere and +686 TgO_3/yr of production in the polluted boundary layer. Human impact on O_3 predominates in the summertime extratropical NH and in the tropics during their biomass burning seasons [increases of 50%-100% or more]. Conversely, there has been little increase in most of the upper troposphere [<20%], where ozone's influence on tropospheric climate is strongest.

1. Introduction

Tropospheric O_3, which dominates tropospheric chemistry and may influence climate, crop production and human health, has increased by more than a factor of two in the last 100 years in the polluted boundary layer [BL] of Europe [*Volz and Kley*, 1988] and is frequently elevated above the natural background in the eastern US BL [e.g., *Logan*, 1989]. It has been speculated that such increases have occurred throughout the NH.

Both downward transport from the stratosphere [e.g., *Junge*, 1962] and in situ photochemical production [e.g., *Chameides and Walker*, 1973; *Crutzen*, 1974] are believed to be important sources of tropospheric O_3. Previous observation-based [e.g. *Parrish et al.*, 1993; *Moody et al.*, 1995] and model-based [e.g. *Crutzen and Zimmermann*, 1991; *Jacob et al.*, 1993; *Roelofs and Lelieveld*, 1995] studies have attempted to determine the relative importance of transport and chemistry. We change the focus and present a systematic global analysis that quantifies the impact of human activity on tropospheric O_3 and identifies key mechanisms.

2. Global Chemical Transport Model (GCTM)

Our GCTM simulation is based on a conceptual model with four components controlling tropospheric O_3: 1. irreversible transport of stratospheric O_3 into the troposphere; 2. NOx-dependent, CO-CH_4 based O_3 chemistry throughout the free troposphere and clean BL; 3. photochemical production of O_3 in the polluted continental BL; 4. seasonal and vegetation-dependent surface deposition of tropospheric O_3.

The GCTM has a horizontal resolution of ~265 km, 11 sigma levels in the vertical at standard pressures of 10, 38, 65, 110, 190, 315, 500, 685, 835, 940, and 990 mb and is driven by twelve months of 6-hour time-averaged wind, temperature, and precipitation fields from a general circulation model. See *Kasibhatla et al.* [1996] and references therein for details.

Component 1, the irreversible injection of stratospheric O_3, which enters the troposphere primarily at mid- and high latitudes during winter and spring [see *Mahlman et al.*, 1980 and *Levy et al.*, 1985 for details], and Component 4, the seasonal and vegetation-dependent surface dry deposition of O_3, are treated as described in *Kasibhatla et al.* [1996]. Pre-industrial mid-stratospheric ozone levels remain unchanged and increased pre-industrial forestation, which may increase pre-industrial dry deposition, is neglected.

The NOx-mediated O_3 chemical tendencies in each gridbox in the unpolluted free troposphere and clean BL [Component 2] are interpolated each time-step from pre-calculated tables using the model's instantaneous O_3 levels and 6-hour average NOx levels for present and pre-industrial atmospheres taken from previous GCTM simulations. Both O_3 chemical tendency tables are constructed with a standard CO-CH_4-NOx reaction scheme using the same climatological water vapor, temperature, CO and CH4 data [*Kasibhatla*, 1996; *Klonecki and Levy*, 1997]. Detailed analyses of individual Production and Loss terms are given in *Klonecki and Levy* [1997]. We also include a pre-calculated O_3 loss from the heterogeneous nighttime conversion of NOx to HNO_3 on sulfate aerosol.

While pre-industrial decreases in CO, CH_4, H_2O, and sulfate aerosol are neglected in this study, we find that NOx dominates the O_3 chemical tendencies and that pre-industrial ozone tendencies are primarily destruction and not very sensi-

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tive to CO and CH_4 [*Klonecki and Levy*, 1997]. The NOx simulations, which use the same pre-calculated conversion rates among NOx, PAN and HNO_3, are primarily influenced by differences between pre-industrial [~8 TgN/yr] and present [~40 TgN/yr] NOx emissions. The primary anthropogenic NOx emissions, fossil fuel combustion and biomass burning, are released in the BL of the NH midlatitudes and tropics, respectively, and produce greatly enhanced NOx levels in those regions and enhanced background levels throughout the NH. In general, the present simulated NOx levels are in good agreement with available observations [Appendix in *Kasibhatla et al.*, Table 1 and Section 3 in *Levy et al.*, 1996].

For both present and pre-industrial O_3, simulated isoprene and anthropogenic NOx concentrations are used as proxies for anthropogenic and natural reactive hydrocarbons, respectively. In each grid-box, the model switches from the simple CO-CH_4 reaction scheme to Component 3, smog production of O_3, when either NOx exceeds 200pptv or isoprene exceeds 100pptv and NOx exceeds 50 pptv. The simulation is quite insensitive to the exact magnitudes of the switches.

Because our goal is to quantify the impact of pollution O_3 on the global troposphere and not to simulate its local behavior in detail, we expand a simple summertime parametrization [*Kasibhatla et al.*, 1996] to reproduce seasonal-average O_3 levels in the polluted BL and provide a realistic source for regional and global transport. Guided by empirical relationships between NO_y species and O_3 and theoretical calculations of O_3 produced per NOx consumed [e.g., *Liu et al*, 1987; *Trainer et al.*, 1993], we relate the net rate of O_3 production to the rate of NO_2 oxidation to HNO_3 by OH [see *Kasibhatla et al.*, 1996]. The proportionality constant (k) is chosen to be:

k(NOx) = 8.5 for NOx > 1 ppbv, and
k(NOx) = [8.5 - 60*$\log_{10}$(NOx)], for NOx < 1 ppbv.

In the extratropics [30N-90N and 30S-90S], we scale k(NOx) by S(month), which is specified using the seasonal variation of the net ozone production efficiency (OPE) calculated by *Hirsch et al.* [1996] for Harvard Forest. In the tropics [30N-30S], S is set to 1.0 throughout the year. The values of the individual parameters [8.5, 60] in k(NOx) and S(month), while constrained by our current understanding of regional smog chemistry, are chosen to reproduce the observed seasonal levels of O_3 in the polluted boundary layer of the midlatitude NH and of the tropics. Significant biogenic emissions of NOx and reactive hydrocarbons induce pre-industrial BL production of O_3 by "pollution" Component 3, primarily in the tropics. The same k(NOx) and S(month) are used.

The parameterization is based on analyses from only a few specific geographic locations. While attempting to extrapolate to the whole globe in a rational manner, we recognize that a more global set of data and analyses is needed.

3. Evaluation

We compare surface, lower troposphere [surface - 800mb] and mid-troposphere[600mb - 400mb] simulations with surface, ozonesonde and aircraft measurements from around the globe. Examining the O_3 scatter plots in Figure 1, we see that simulation and observation agree within ±25% for 144 or 73% of the cases. Another 34 or 17% fall just outside of that range. Only 20, or 10%, of the comparisons are significant outliers, and they fall into three specific categories. The first occurs during the SH biomass burning season when O_3 levels

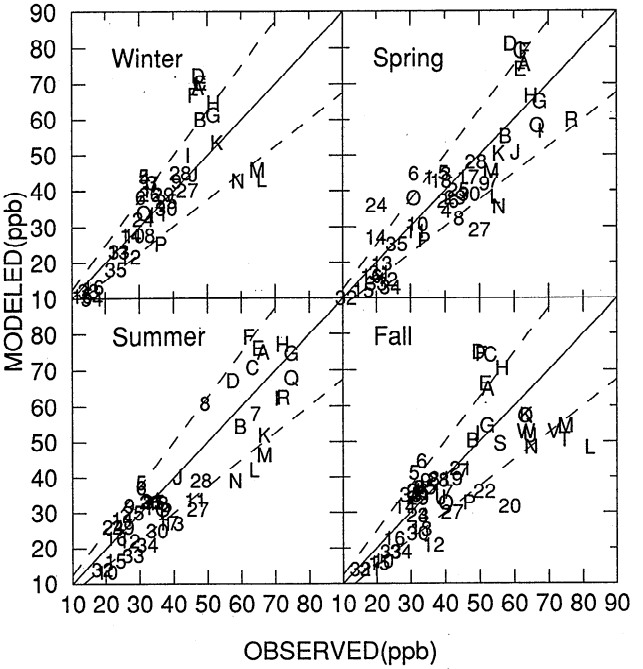

Figure 1. Scatter plot of simulated ozone vs. observations from 21 ozonesonde sites, 12 surface sites and the TRACE-A aircraft mission. The surface and lower troposphere [surface - 800mb] comparisons are numbers and the mid-troposphere [600 - 400mb] comparisons are letters. The sites are: Barrow, AK [1,A]; Boulder, CO [2,B]; Churchill, Can. [3,C]; Edmonton, Can. [4,D]; Goose Bay, Can. [5,E]; Resolute, Can. [6,F]; Wallops, MD [7,G]; Hohenpeissenberg, GER. [8,H]; Bermuda [9,I]; Hilo, HI [10,J]; Brazzaville, Congo [11,K]; Natal, BRZ. [12,L]; Ascension Island [13,M]; Irene, SA [14,N]; Samoa [15,O]; Lauder, NZ [16,P]; Azores [17,Q]; Canary Islands [18,R]; Cuiaba, BRZ [19,S]; Porto, BRZ [20,T]; Etosha, SA [21,U]; TRACE-A(0-30S over land) [22,V]; TRACE-A (0-30S over ocean) [23,W]; Pt. Barrow, AK [24]; Westman Island [25]; Mace Head, IR [26]; Niwot, CO [27]; Izania [28]; Bermuda [29]; Mauna Loa, HI [30]; Barbados [31]; Samoa [32], Cape Pt., SA [33]; Cape Grim, Taz. [34]; S. Pole [35].

at Natal, Porto, and from TRACE-A aircraft over land are seriously underestimated throughout the troposphere. However, during this same period, simulated O_3 at Cuiaba, Etosha and over the South Atlantic compares reasonably well with measurements. The other two model biases are excess mid-troposphere O_3 at NH high-latitudes from September - February, which distorts the simulated seasonal cycle in that region, and the deficit at a number of island sites in the SH, particularly during the SH winter and spring. Both biases are primarily the result of stratospheric transport biases in the GCTM [*Mahlman et al.*, 1986; *Levy et al.*, 1985; and references therein].

A quantitative evaluation of the pre-industrial simulation is limited to the Paris data from the late 1800's [*Volz and Kley*, 1988]. While our summertime minimum is in excellent agreement, our seasonal cycle is larger.

Though far from perfect, these 3-dimensional GCTM simulations, are in harmony with the observations and capture the complex coupling between tropospheric chemistry and transport. They provide an appropriate tool for quantitative global analyses of anthropogenic impact, of transport vs. chemistry and of natural vs. pollution chemistry.

Table 1. Annual Integrals of Tropospheric O_3

Annual Integrated O_3	Present	Pre-industrial	Human Impact	
	[TgO_3]	[TgO_3]	[TgO_3]	[%]
Global Troposphere	298	215	83	39%
Free Troposphere	245	183	62	32%
NH extraTropics	93	67	26	39%
SH extraTropics	42	34	8	24%
Tropics	110	82	28	36%
Boundary Layer	53	32	21	66%
NH extraTropics	19	11	8	73%
SH extraTropics	10	7	3	43%
Tropics	24	14	10	71%

4. Results and Discussion

In Table 1 we predict that the total mass of tropospheric ozone has increased by 39% [83 TgO_3] from a pre-industrial level of 215 TgO_3. This increase, which is almost equally divided between the NH extratropics and the tropics with only a small contribution from the SH extratropics, is quite consistent with the location of human activity and related emissions. While the largest percentage increase [~70%] occurs in the BL, almost 3/4's of the actual increased mass is found in the free troposphere, requiring either export of O_3 from the polluted BL or enhanced background O_3 production.

For a more detailed picture of human impact, we examine maps of the ratios of present to pre-industrial O_3 for the surface and 500mb in Figures 2 and 3, respectively. The more than doubling of July surface O_3 over the NH mid-latitude pollution regions and of January surface O_3 over tropical biomass burning regions, both shown in Figure 2, should be no surprise. The doubling of July O_3 over most of the surface

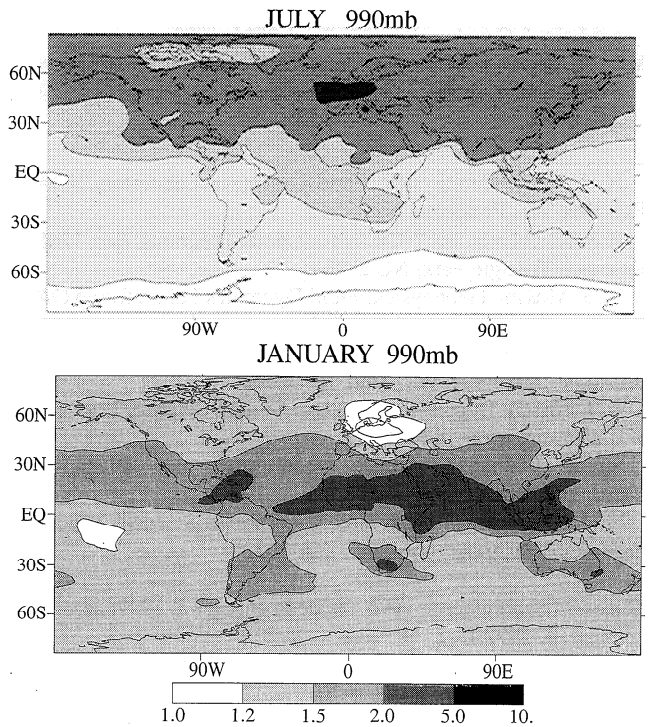

Figure 2. Simulated ratios of present to pre-industrial surface O_3 for July and January.

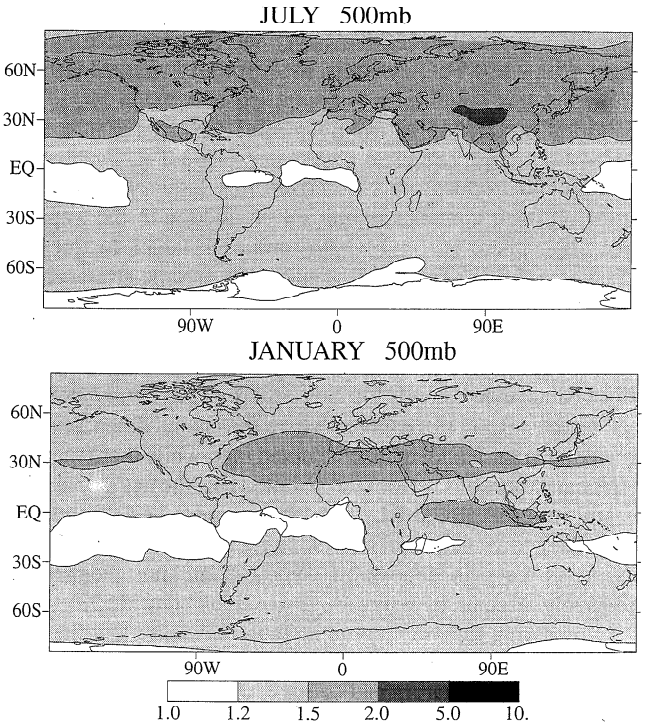

Figure 3. Simulated ratios of present to pre-industrial 500 mb O_3 for July and January.

layer of the NH, including the remote oceans, was less expected, though it is consistent with earlier speculation by *Fishman and Crutzen* [1978] and with *Volz and Kley's* [1988] extrapolation of their European data to the NH. The anthropogenic impact in the mid-troposphere shown in Figure 3 is primarily in the summer NH where O_3 is enhanced by more than 50%. While a NH subtropical belt of >50% enhancement remains in January, much of the wintertime NH and almost all of the SH in both July and January show only moderate levels of enhancement [20 - 50%]. Even during the SH biomass burning season [not shown] the enhancement at 500mb is <50% with the exception of a band [25S - 40S] stretching from South Africa to Australia. Human impact in the upper troposphere [not shown] is quite weak [<20%] with the exception of a 20-50% enhancement in the tropics.

In Table 2 we identify and quantify specific components or processes that control the present level of O3 and that drive its increase from pre-industrial times. At present, we see that the 2 non-chemical terms, dry deposition and stratospheric injec-

Table 2. Annual Tropospheric O_3 Budget

Annual O_3 Budget Components	Present	Pre-industrial	Human Impact
	[TgO_3/yr]	[TgO_3/yr]	[TgO_3/yr]
Stratospheric Injection	+696	+696	0.0
CO-CH4 Background Chem.	-558	-435	-123
Tropical Free Trop.	+163	+176	-13
extraTropical Free Trop.	-72	-129	+57
Boundary Layer	-649	-482	-167
B.L. Pollution Production	+686	+199	+487
Dry Deposition	-825	-459	-366

tion, still dominate, while the global integral of all chemistry is relatively small [+128 TgO_3/yr] and in reasonable agreement with +170 TgO_3/yr from *Roelofs and Lelieveld* [1995]. However, this small term is composed of a much larger BL pollution production of +686 TgO_3/yr which is almost balanced by a large chemical destruction [-558 TgO_3/yr] in the background troposphere. Moreover, this large chemical destruction itself contains significant production in the tropical free troposphere [+163 TgO_3/yr] and even larger destruction elsewhere [-721 TgO_3/yr]. Unlike the middle-stratosphere where ozone production [P] and destruction [L] tend to be in close balance [*Mahlman et al.*, 1980; *Levy et al.*, 1985], most of the troposphere is dominated by one term or the other. A close balance between P and L is only found in narrow boundary regions of the troposphere where the chemical tendency is changing sign. It should also be noted that, while there may be regional export of O_3 from the polluted BL, the net global flux is still into the global BL, even with present levels of pollution. The global troposphere is strongly buffered from BL pollution as long as deposition velocities are not themselves adversely affected by rising O_3 [e.g., *Jacob et al.*, 1993].

Considering the 4th column in Table 2. we see that the primary human impacts, assuming no significant changes in stratospheric circulation and ozone levels, are a large increase in both BL pollution production and, as a result of increased surface O_3 levels, in surface deposition. There is also a significant though smaller increase in chemical destruction in the background troposphere. Essentially, the global troposphere changes from a chemically destructive environment for O_3 to a mildly productive one. This leads to significant, though regionally and seasonally variable, increases in O_3 levels.

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