The global impact of human activity on tropospheric ozone


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 NO$_x$ fields, while prescribed fields of CO, CH$_4$ and H$_2$O 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 [Volk 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 Zimmerman, 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 GCM 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 CH$_4$ 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$_2$O, 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-
tive to CO and CH$_4$ [Klöneki and Levy, 1997]. The NOx simulations, which use the same pre-calculated conversion rates among NO$_x$, PAN and HNO$_3$, are primarily influenced by differences between pre-industrial [-8 TgN yr$^{-1}$] and present [-40 TgN yr$^{-1}$] NOx emissions. The primary anthropogenic NOx emissions, fossil fuel combustion and biomass burning, are released in the BL of the NII 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 200 pptv or isoprene exceeds 100 pptv 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$_x$, 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$_x$ oxidation to HNO$_3$ by OH [see Kasibhatla et al., 1996]. The proportionality constant (k) is chosen to be:

$$k(\text{NOx}) = 8.5 \text{ for NOx > 1 pptv, and}$$

$$k(\text{NOx}) = (8.5 - 60 \log_{10}(\text{NOx})) \text{, for NOx < 1 pptv.}$$

In the extratropics [30N-90N and 30S-90S], we scale k(\text{NOx}) by S(month), which is specified using the seasonal variation of the net ozone production efficiency (OPD) 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(\text{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 - 800 mb] and mid-troposphere [600 mb - 400 mb] 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 at Natal, Portim, and from TRAC-A aircraft over land are seriously underestimated throughout the troposphere. However, during this same period, simulated O$_3$ at Cuiaba, Etoha 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 [Vols 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

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

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 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 O_3 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

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Stratospheric Injection</td>
<td>+696</td>
<td>+696</td>
<td>0.0</td>
</tr>
<tr>
<td>CO-CH4 Background Chem.</td>
<td>-558</td>
<td>-435</td>
<td>-123</td>
</tr>
<tr>
<td>Tropical Free Trop.</td>
<td>+163</td>
<td>+176</td>
<td>13</td>
</tr>
<tr>
<td>extraTropical Free Trop.</td>
<td>-72</td>
<td>-129</td>
<td>+57</td>
</tr>
<tr>
<td>Boundary Layer</td>
<td>-649</td>
<td>482</td>
<td>167</td>
</tr>
<tr>
<td>B.L. Pollution Production</td>
<td>+686</td>
<td>+199</td>
<td>+487</td>
</tr>
<tr>
<td>Dry Deposition</td>
<td>-825</td>
<td>-459</td>
<td>-366</td>
</tr>
</tbody>
</table>
tion, still dominate, while the global integral of all chemistry is relatively small [+128 TgO3/yr] and in reasonable agreement with +170 TgO3/yr from Roelofs and Lelieveld [1995]. However, this small term is composed of a much larger BL pollution production of +686 TgO3/yr which is almost balanced by a large chemical destruction [-558 TgO3/yr] in the background troposphere. Moreover, this large chemical destruction itself contains significant production in the tropical free troposphere [+163 TgO3/yr] and even larger destruction elsewhere [-721 TgO3/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 O3 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 O3 [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 O3 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 O3 to a mildly productive one. This leads to significant, though regionally and seasonally variable, increases in O3 levels.

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