

The balance of effects of deep convective mixing on tropospheric ozone

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[1] The balance of effects that vertical transport associated with deep cumulus convection has on tropospheric O_3 is discussed. We first show theoretically that convective mixing of O_3 can substantially reduce its column mean lifetime over clean regions, while a much smaller increase is generally expected over polluted regions. The global chemistry-transport model MATCH-MPIC confirms this, computing a 6% decrease in the annual mean tropospheric O_3 burden and a 7% decrease in its lifetime due to convective transport of O_3 alone. We find, however, that the net effect of convective transport of all trace gases (O_3 and precursors together) is a 12% increase in the tropospheric O_3 burden. Thus, in contrast to previous literature, our results indicate that the enhanced O_3 production due to precursor transport from polluted regions significantly outweighs the reduction in O_3 lifetime due to mixing over clean regions. **INDEX TERMS:** 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 3314 Meteorology and Atmospheric Dynamics: Convective processes. **Citation:** Lawrence, M. G., R. von Kuhlmann, M. Salzmann, and P. J. Rasch, The balance of effects of deep convective mixing on tropospheric ozone, *Geophys. Res. Lett.*, 30(18), 1940, doi:10.1029/2003GL017644, 2003.

1. Introduction

[2] Ozone (O_3) is a strong greenhouse gas, is detrimental to plant and animal health at high concentrations, and is the main precursor of hydroxyl radicals (OH), which largely determine the atmospheric oxidizing efficiency. The factors controlling the tropospheric O_3 budget have been studied for several decades; nevertheless there are still major uncertainties regarding several physical and chemical processes.

[3] This study focuses on the role of deep convection in the tropospheric O_3 budget. Early work on this topic [e.g., Dickerson *et al.*, 1987; Pickering *et al.*, 1990] showed that the upward transport of O_3 and precursors can result in substantial local increases in the tropospheric O_3 column over polluted regions, since the lifetimes of these gases and the O_3 production efficiency (per NO_x molecule) tend to increase with altitude. On the other hand, Lelieveld and Crutzen [1994] pointed out that downward mixing of O_3 -

rich air from the upper troposphere (UT) towards the surface can reduce the column mean lifetime of O_3 ; using a simple tropospheric chemistry-transport model (CTM) they computed that, globally, this effect would outweigh the effects of mixing above polluted regions, resulting in a net 20% decrease in tropospheric O_3 . A number of studies following that have focused particularly on the ability of deep convection to transport O_3 -depleted marine boundary layer air to the UT [e.g., Kley *et al.*, 1996; Lawrence *et al.*, 1999a]. Although extreme minima in UT O_3 may be very rare [Asman *et al.*, 2003], the overall effect of convective overturning over clean regions such as the equatorial Pacific is of global relevance for reducing tropospheric O_3 , as discussed below.

[4] In the next section, we use an idealized model of the tropospheric column to examine the anticipated effects of convective mixing on O_3 and NO_x column mean lifetimes. Following that, we discuss results from several sensitivity runs with the global CTM MATCH-MPIC which quantify the global effects of convective transport on O_3 .

2. A Simple 1D Theoretical Framework

[5] The lifetime of O_3 (τ_{O_3}) increases with altitude (Table 1). The effect of convective mixing of O_3 on its column mean lifetime, T_{O_3} (defined as $T_{O_3} = \frac{\sum O_3(k)}{\sum [\tau_{O_3}(k)]^{-1} O_3(k)}$, where the sum is over all levels k), depends on the initial profile of O_3 , which differs for clean (e.g., tropical marine) and polluted (e.g., mid-latitude summertime urban) convectively active regions (Table 1). To obtain a first order estimate of how convective mixing affects T_{O_3} , we consider a simple 3-box model of the tropospheric column (Figure 1). The three boxes are initialized with the O_3 profiles from Table 1, and a small (<10%) fraction of air is mixed out of the lowest layer each step, with O_3 treated as inert during the mixing.

[6] T_{O_3} and its relative changes are plotted in Figure 2. Over time, the T_{O_3} values for the clean and polluted regions converge towards the same value for a well-mixed column. However, the relative reduction in clean regions is much greater than the increase in polluted regions. We have tested a range of different “typical” initial O_3 profiles and always obtain this asymmetry. We also find the asymmetry to hold for any amount or form of mass-conserving mixing we have tested with this simple model, and thus we expect the overall asymmetry to likely hold in 3D models regardless of the exact form of the convective mixing parameterization.

[7] O_3 is not only controlled by mixing, but also by the distribution of its precursors (NO_x , CO, and hydrocarbons), which in turn are also affected by convective mixing. In particular, the 3-box model indicates that the response of

Table 1. Typical Vertical Profiles for O_3 and NO_x Lifetimes (τ , in days) and Mixing Ratios (μ , in nmol/mol for O_3 and pmol/mol for NO_x), in Clean and Polluted Regions Which Have Not Recently Experienced Deep Convection, Based on Previous Work with MATCH-MPIC [e.g., von Kuhlmann et al., 2003].

| Layer | τ_{O_3} | μ_{O_3} | | τ_{NO_x} | μ_{NO_x} | |
|-------|--------------|-------------|----------|---------------|--------------|----------|
| | | Clean | Polluted | | Clean | Polluted |
| UT | 150 | 50 | 50 | 10 | 100 | 100 |
| MT | 50 | 25 | 25 | 5 | 25 | 25 |
| LT | 10 | 5 | 50 | 1 | 5 | 1000 |

NO_x to mixing is very different from O_3 - much closer to being symmetric - due to the immense enhancement of NO_x typical for polluted regions (Table 1, Figure 2). The actual change in NO_x lifetime will depend, however, on the nature of the regions being mixed, since OH (which converts NO_x to HNO_3) depends nonlinearly on the concentration of NO_x . Furthermore, the O_3 production efficiency per molecule of NO_x generally increases when NO_x is diluted, which will enhance O_3 production following convection over polluted regions. This will be facilitated by long-range transport of reservoir species, especially PAN, which is more stable in the UT and middle troposphere (MT) than in the lower troposphere (LT). Quantifying the balance of these chemical and transport effects requires a more complex model; this is done in the next section using MATCH-MPIC.

3. Global Effects on O_3

[8] We use the 3D global offline Model of Atmospheric Transport and Chemistry - Max Planck Institute for Chemistry version 3.1 (MATCH-MPIC), described and evaluated in Rasch et al. [1997], Lawrence et al. [1999b], von Kuhlmann et al. [2003], Lawrence et al. [2003], and references therein. The meteorology for these runs is driven by the NCEP reanalysis data at a reduced resolution of T21 (64×32 grid cells in the horizontal) with 28 vertical levels up to about 2 hPa and a 30-minute time step. The reduced resolution allows numerous sensitivity runs, while still providing convective mass fluxes which closely (within $\sim 10\%$) reproduce those computed at a higher resolution (T63). All runs were for 1997 with a 4-month spin-up (starting Sept. 1996), initialized with mean trace gas fields from von Kuhlmann et al. [2003] for Sept. 1998. Subgridscale transport and the hydrological cycle are diagnosed

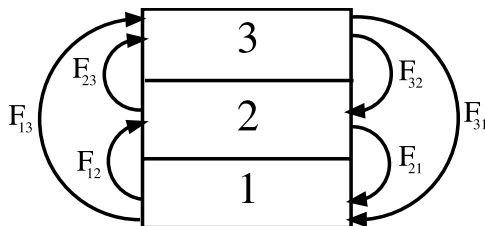


Figure 1. Schematic of the 3-box idealized model of the tropospheric column. For simplicity we assume even air masses for the regions (e.g., boundaries at 1000, 750, 500, and 250 hPa). Fluxes between the boxes represent updrafts (F_{13}), mid-level detrainment (F_{12}), entrainment (F_{23}), downdrafts (F_{31}), and mass-balance subsidence (F_{32} and F_{21}).

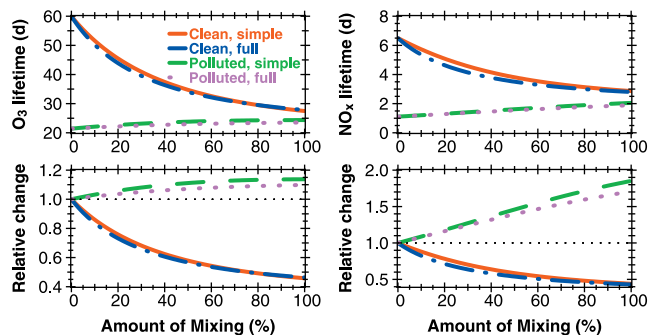


Figure 2. Mean T_{O_3} (left panels) and T_{NO_x} (right panels) and relative changes for the 3-box model as a function of the total amount of air mass mixed out of box 1. Two cases are shown, one assuming that $F_{12} = F_{23} = F_{31} = 0$ (“simple”), and one with $F_{12} = F_{23} = F_{31} = 0.5 F_{13}$ (“full”).

online. The model uses a combination of two convection parameterizations focusing on deep and shallow mixing [Zhang and McFarlane, 1995; Hack, 1994]. The photochemical scheme includes a parameterization of non-methane hydrocarbon (NMHC) oxidation covering up to C5 molecules (especially isoprene). Further details can be found via <http://www.mpch-mainz.mpg.de/~lawrence>.

[9] We performed about 20 sensitivity runs for this study; the main ones considered here are listed in Table 2. In the test runs we completely shut off the convective transport of O_3 or of all trace gases (by both the Zhang-McFarlane and Hack schemes), so that comparing the results to the respective BASE run indicates the net effect of each process. Very similar results (within a few %) are obtained when we only shut off the Zhang-McFarlane convection. We do not modify the convective transport of water vapor or potential temperature, so that the modeled meteorology remains the same in all runs. We also do not modify the lightning NO_x source or precipitation scavenging, which we are examining in separate studies. Note that these runs are not intended to suggest that the atmosphere would actually operate without convection or the convective transport of individual gases, but rather they are “Gedankenexperiments” which allow us to quantify the net contributions of convective transport of trace gases to the O_3 budget.

[10] As could be anticipated from the previous section, the effect of convective transport of O_3 alone is to reduce its column amounts (Figures 3 and 4, Table 3). MATCH-MPIC indicates that this reduction is significant, about 6% globally, exceeding 3 DU annually throughout much of the tropics (monthly mean differences exceed 8 DU in some regions). The overturning reduces the O_3 amounts in the UT and causes an increase near the surface, particularly in the tropics (Figure 4). This results in an increase in both the dry deposition loss and the gradient-driven stratosphere-troposphere exchange (STE) source (Table 3; the values are based on the model budget routines, with the tropopause diagnosed each timestep based on the WMO lapse rate definition; see von Kuhlmann et al. [2003] for details). The absolute change in the tropospheric O_3 column is largest over the central Atlantic. A maximum in the tropospheric O_3 column is present in this region, which has been studied extensively, and has been attributed to the convective

Table 2. Sensitivity Simulations Considered in This Study

| Run | Description |
|------------|---|
| BASE | Base run with MATCH-MPIC v3.1, based on <i>von Kuhlmann et al.</i> [2003] |
| NO_CONV_O3 | No convective transport of O ₃ |
| NO_CONV_T | No convective transport of all chemical tracers |
| CH4_BASE | Like BASE but without NMHC chemistry |
| CH4_NCT | Like CH4_BASE, but no convective transport of all chemical tracers |

uplifting of precursors along with lightning NO_x production over Africa and South America, followed by O₃ production in the UT outflow plumes over the central Atlantic [e.g., *Moxim and Levy*, 2000]. Convective mixing of O₃ over the ocean weakens this precursor-driven maximum. In contrast, we compute that the relative changes in O₃ mixing ratios are largest over the Pacific warm pool (not shown), where convection is prevalent and surface O₃ levels are low due to high loss rates.

[11] Is the effect of convective transport of precursors large enough to overcome these reductions due to the transport of O₃? According to our simulations (Figures 5 and 6, Table 3), it is: the global O₃ burden increases by 12% due to convective transport of all gases, and the annual mean column increases over nearly the entire globe, in large regions by more than 5 DU. This is accompanied by an increase of more than 15% in the tropospheric photochemical activity (both gross production and destruction); we also compute a 14% increase in the global tropospheric NO_x burden and lifetime. The largest increases in O₃ are not directly in the source regions but rather in the outflow of North America (northern Atlantic), Europe (Mediterranean), eastern Asia (Pacific) and southern Asia (Indian Ocean). This is because of the time needed for photochemical processing of polluted continental air before significant amounts of O₃ are produced. The relative change in zonal mean mixing ratios (Figure 6) is again greatest in the tropics, particularly in the mid-troposphere (in the UT the increase due to precursors has to compete with the decrease shown in Figure 4 due to the transport of O₃).

[12] The previous study of *Lelieveld and Crutzen* [1994] used the MOGUNTIA model to compute a 20% decrease in the global O₃ burden due to O₃ and precursor transport, opposite of the 12% increase computed here. Their results were driven largely by the response of their UT (see their

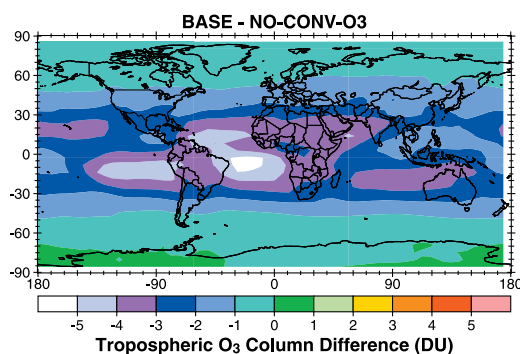
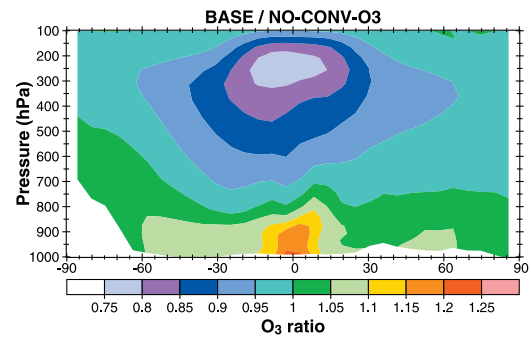
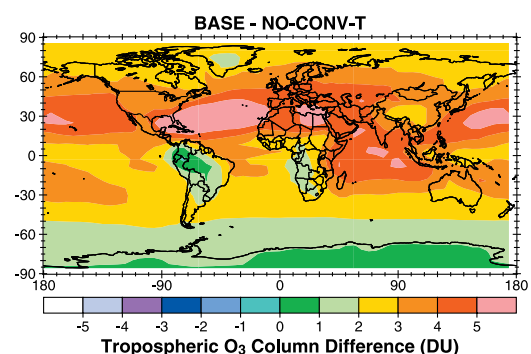
**Figure 3.** Difference in the annual mean O₃ column below a climatological tropopause of $P(\text{hPa}) = 300 - 215 \times [\cos(\phi)]^2$ for the base run minus the NO_CONV_O3 run.**Figure 4.** Ratio of the annual zonal mean O₃ in the BASE run versus the NO_CONV_O3 run.

Figure 1), where convective transport decreased their zonal mean O₃ and NO_x mixing ratios by more than a factor of two, compared with the much smaller changes computed by MATCH-MPIC (Figure 6). In the MT, on the other hand, they computed an increase similar to that shown in Figure 6. We have done several sensitivity runs to try to resolve the difference in the UT. The largest effect was obtained by neglecting NMHCs (not included in MOGUNTIA). Since NMHCs are shorter-lived than CH₄ and thus more susceptible to convective mixing, they would be expected to lead to more UT O₃ production following uplifting. Figure 7 shows, however, that we nevertheless compute an increase in the O₃ column nearly everywhere, though less than when we include NMHCs (compare Figure 5). Other parameters had smaller effects, such as the uptake of HNO₃ by ice (only included in MATCH-MPIC), which provides an important removal mechanism for NO_y from the UT even when convective mixing is turned off, and various effects due to differences in the convective transport parameterizations, tested by varying parameters such as the detrainment levels and downdraft strength. Possibly the differences are due to the low vertical resolution of MOGUNTIA (with layer thicknesses of 100 hPa) and the treatment of upper boundary conditions (fixed fluxes for O₃ and fixed mixing ratios at 100 hPa for HNO₃ [*Dentener*, 1993]); in particular, the prescribed HNO₃ at 100 hPa in MOGUNTIA may have resulted in an unrealistic response for UT NO_y, NO_x and O₃ when convective mixing was turned off. Finally, we cannot be certain that the MATCH-MPIC results are more realistic; hopefully similar sensitiv-

**Figure 5.** Like Figure 3 except for the BASE run minus the NO_CONV_T run.

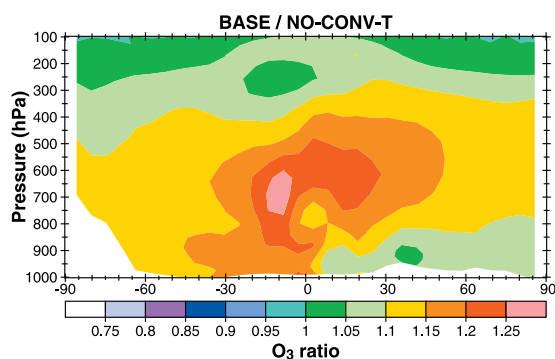


Figure 6. Like Figure 4 except for the BASE run versus the NO_CONV_T run.

ity studies with other models will eventually help resolve this issue.

4. Conclusions

[13] Convective mixing of O_3 alone reduces its column mean lifetime over clean regions, countered by a much smaller increase in its lifetime over polluted regions. We compute that this results in a 7% decrease in its global average total lifetime (including dry deposition), and a 6% decrease in the tropospheric O_3 burden. The decrease is particularly pronounced in the UT, indicating that convective transport of O_3 acts to reduce its efficiency as a greenhouse gas. On the other hand, the transport of precursors tends to enhance the O_3 production efficiency and amount in the column. We find that this effect outweighs the O_3 reduction effect nearly everywhere, especially in the outflow of major industrialized regions, resulting in a 12% increase in the tropospheric O_3 burden. This effect is primarily driven by the transport of NO_x , as is suggested by the fact that the addition of NMHCs is only responsible for a relatively small part of the overall effect of precursor transport (compare Figure 3, 5, and 7); we have confirmed this key role of NO_x with a run in which we turn off transport only of O_3 and NO_x (not shown). However, convectively transported NMHCs and CO also make an important contribution, and further sensitivity runs to quantify the individual effects would be interesting after it is determined whether other contemporary models with different formulations of convective transport and of upper and lower boundary processes (especially STE and dry deposition) confirm our basic results.

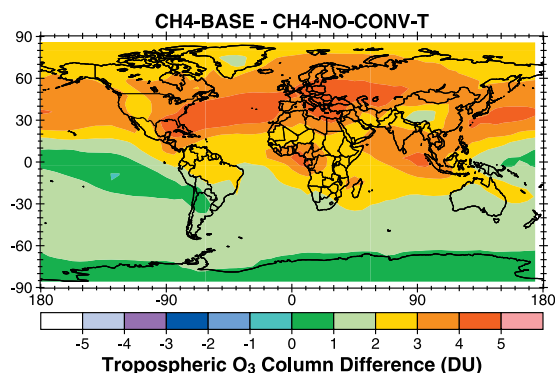


Figure 7. Like Figure 3 except for the CH4_BASE run minus the CH4_NCT run.

Table 3. Tropospheric O_3 Budgets for the MATCH-MPIC Sensitivity Runs, and Relative Changes (in parentheses), Computed as $100 \times (\frac{BASE}{NO_CONV_X} - 1)$ in Order to Directly Indicate the Changes Due to Convective Transport of O_3 Alone and of All Gases

| | BASE | NO CONV O3 | NO CONV T |
|-----------------------|-------|---------------|---------------|
| Burden (Tg) | 328 | 350 (-6.3%) | 293 (11.9%) |
| Total Lifetime (d) | 25.7 | 27.6 (-6.9%) | 26.1 (-1.5%) |
| Chemical Lifetime (d) | 30.7 | 32.5 (-5.5%) | 31.5 (-2.5%) |
| Production (Tg/yr) | 4062 | 4051 (0.3%) | 3481 (16.7%) |
| Loss (Tg/yr) | -3902 | -3933 (-0.8%) | -3393 (15.0%) |
| Net Chem. (Tg/yr) | 160 | 118 (35.6%) | 88 (81.8%) |
| STE (Tg/yr) | 609 | 587 (3.7%) | 622 (-2.1%) |
| Dry Dep. (Tg/yr) | -761 | -695 (9.5%) | -711 (7.0%) |

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