

Strong sensitivity of the global mean OH concentration and the tropospheric oxidizing efficiency to the source of NO_x from lightning

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[1] Production of nitrogen oxides (NO_x = NO + NO₂) by lightning (LtNO_x) is the most uncertain among the global NO_x sources, with recent estimates ranging from about 1–20 Tg(N)/yr. Previous studies of LtNO_x have focused mainly on its role in the tropospheric NO_y (reactive nitrogen) and O₃ budgets. We show that the global mean OH concentration is also very sensitive to LtNO_x. Furthermore, despite the fact that the largest changes in NO_x due to lightning are in the upper troposphere, where reactions with OH are generally slower, we find that the sensitivity of the mean tropospheric lifetime of methane (CH₄) and methylchloroform (CH₃CCl₃) to assumptions about LtNO_x are as large as the sensitivity of the tropospheric O₃ burden. Thus, an improved understanding of LtNO_x will be important for our ability to accurately simulate the tropospheric oxidizing efficiency and its changes over time. *INDEX TERMS*: 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3314 Meteorology and Atmospheric Dynamics: Convective processes; 3337 Meteorology and Atmospheric Dynamics: Numerical modeling and data assimilation. **Citation**: Labrador, L. J., R. von Kuhlmann, and M. G. Lawrence (2004), Strong sensitivity of the global mean OH concentration and the tropospheric oxidizing efficiency to the source of NO_x from lightning, *Geophys. Res. Lett.*, 31, L06102, doi:10.1029/2003GL019229.

1. Introduction

[2] Lightning plays an important role in atmospheric chemistry by producing nitric oxide (NO), a precursor of ozone. However, the violent nature of this phenomenon makes it difficult to accurately determine the global amount of lightning-produced NO_x (LtNO_x). LtNO_x still has the largest uncertainty of all NO_x sources, with estimates ranging from about 1–20 Tg(N)yr⁻¹ [Lawrence *et al.*, 1995; Price *et al.*, 1997], or ~2–30% of the total global NO_x emissions. Many factors contribute to this large difference in the estimates, among them, uncertainties in the current understanding of the fundamental processes of lightning generation itself, such as the charge separation mechanism and the partitioning between intra-cloud, inter-cloud and cloud-to-ground flashes, as well as LtNO_x-specific processes, such as the NO formation (“freeze-out”) mechanism, the number of NO molecules produced per flash, and its vertical distribution. Unlike ground sources, lightning produces NO_x in and around cumulonimbus

clouds. Convective updrafts can then carry them to the upper troposphere (UT) where they have a longer lifetime than near the surface. LtNO_x has been shown to enhance O₃ levels by up to 30% [Stockwell *et al.*, 1999]. LtNO_x also affects the budget of the hydroxyl radical (OH), and in turn the tropospheric oxidizing efficiency. These effects, however, have not received as much attention as the effect on O₃, since a large effect on the oxidizing efficiency would be somewhat counterintuitive due to the strong temperature dependence of the oxidizing reactions of gases such as CH₄ and CH₃CCl₃. In this study we investigate the effects of LtNO_x on NO_x, OH, the tropospheric oxidizing efficiency and O₃.

2. Model Description and Runs Setup

[3] For this study we employ the Model of Atmospheric Transport and Chemistry, Max-Planck Institute for Chemistry version 3.1 (MATCH-MPIC hereafter). MATCH-MPIC is an offline chemistry transport model based on the NCAR CCM2 (Community Climate Model-Version 2). It consists of a meteorology module and a chemistry module which comprises 141 gas phase reactions of 56 species, describing the major known sources and sinks of O₃ and its associated chemistry. For a comprehensive description of the model, see von Kuhlmann *et al.* [2003a], Lawrence *et al.* [1999], Rasch *et al.* [1997] and references therein. The runs for this study use the same version as Lawrence *et al.* [2003a] (except for the LtNO_x source), with input data from the NCEP/NCAR reanalysis on a reduced horizontal resolution of T21 (about 5.6° × 5.6°), 28 vertical sigma levels from the surface to ~0.2 hPa, and a timestep of 30 minutes. The runs are done for 1997, with a four month spin-up time. The deep convection scheme, on which the modeled lightning is based, is from Zhang and McFarlane [1995], and accounts for the vertical transport of a wide range of inorganic and organic precursors of OH and O₃ [Lawrence *et al.*, 2003a]. Evaluations of the vertical distribution of a number of species including CO, O₃, alkenes and CH₃OOH have not shown a clear indication of a substantial over- or underestimate of vertical transport in the model [Lawrence *et al.*, 1999; von Kuhlmann *et al.*, 2003a, 2003b; Lawrence *et al.*, 2003b]. Evaluations using radon and methyl iodide have not yet been carried out for MATCH with this scheme.

[4] The parameterization for the horizontal distribution of lightning used in MATCH-MPIC is based on Price and Rind [1992]: $F = 3.44 \times 10^{-5} H^{4.9}$ for continental convective clouds, and $F = 6.4 \times 10^{-4} H^{1.73}$ for marine clouds, where F is the flash frequency (flashes/min/8 × 10 box) and H is the modeled cloud top height in km. Although widely used, deficiencies with this simple approach have to be acknowledged. In preliminary results of a parallel study, comparing

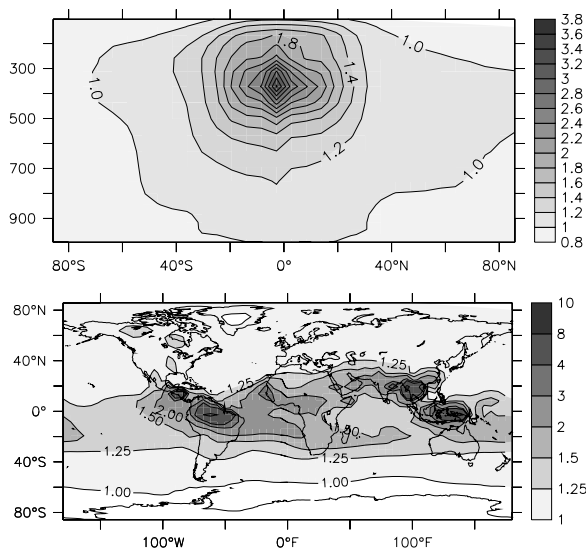


Figure 1. Ratios of the annual zonal mean NO_x mixing ratios (top) and of the horizontal distributions at 300 hPa (bottom) for the L5 versus L0 run.

to satellite observations, we have found that the parameterization captures the main features of lightning activity (land/sea, tropics/extratropics and seasonal patterns); however, it also tends to overestimate (underestimate) flash activity for the tropical (extratropical) latitudes, and within the tropics, modeled flash densities over Africa are lower than over South America. It is not yet clear whether this is due to the lightning parameterization, including neglected effects such as aerosols, or the convection parameterization. The vertical distribution of LtNO_x in MATCH-MPIC for this study is based on the C-shaped vertical profiles developed by *Pickering et al.* [1998].

[5] We have carried out 5 different runs in which we have only varied the LtNO_x source strength and kept all other model parameters the same. The LtNO_x production rates are 0, 2, 5, 10 and 20 Tg(N)yr⁻¹ (hereafter the L0, L2, L5, L10 and L20 runs, respectively), which reflects the extremes of the uncertainty range (the L0 run is not realistic, but rather is used to help illustrate the net effect of any other given LtNO_x source strength). We will focus our discussion on the L5 run, since it best reflects the currently most accepted production estimate for the LtNO_x source.

3. Results

3.1. Effects on NO_x

[6] We first examine how NO_x itself is affected by LtNO_x by comparing the L5 and L0 runs. The largest effects of

Table 1. OH Mass- and Volume-Weighted Tropospheric Mean Concentrations and Lifetimes of CH₄ and MCF for the 5 Different Model Runs

	L0	L2	L5	L10	L20
(OH) _m (×10 ⁶)	0.82	0.89	1.0	1.1	1.23
(OH) _v (×10 ⁶)	0.73	0.83	0.94	1.05	1.19
τ(CH ₄) (yrs.) ^a	10.26	9.47	8.79	8.07	7.34
τ(CH ₄) (yrs.) ^b	10.82	9.93	9.13	8.39	7.59
τ(MCF) (yrs.) ^b	6.6	6.04	5.55	5.09	4.6

^aCalculated using online budgets.

^bApproximated with monthly mean model output (see text).

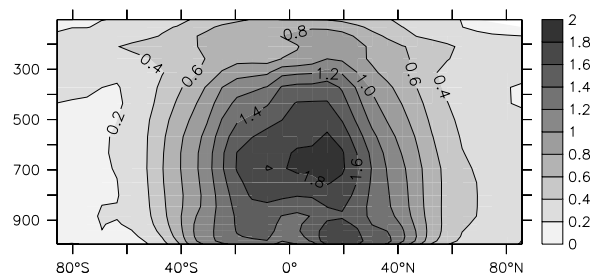


Figure 2. Annual zonal mean OH concentration (in ×10⁶ molec/cm³) for the L5 run.

LtNO_x are in the tropical UT (Figure 1), particularly over equatorial South America and eastern Indonesia and, to a lesser extent, over central Africa, which is consistent with observations that show that lightning activity is heavily weighted towards the tropics and continental regions [*Christian et al.*, 2003], though as noted above, the effect over Africa is likely underestimated and over South America and Indonesia overestimated. Despite the fact that 20% of the total LtNO_x mass is released in the first 2 km above the continental landmasses, the increase in the tropical lower troposphere (LT) is relatively small, since there LtNO_x must compete against the other major surface NO_x sources, namely soil emissions, biomass burning and industrial emissions.

3.2. Effects on OH, The Tropospheric Oxidizing Efficiency and O₃

[7] LtNO_x has a substantial effect on the global mean OH mass and volume-weighted concentrations ([OH]_m and [OH]_v hereafter) [*Lawrence et al.*, 2001]. Table 1 shows that [OH]_m ([OH]_v) increases by about 50% (>63%) from the L0 to the L20 run. For every 5Tg(N)yr⁻¹ increase in the LtNO_x source strength, [OH]_m ([OH]_v) increases by about 22% (29%) between the L0 and L5 runs, 10% (12%) between the L5 and L10 runs, and 6% (6%) between the L10 and L20 runs, indicating a tendency towards saturation. The vertical distribution of OH and its regional changes due to LtNO_x are depicted in Figures 2–4. While the largest absolute increases in the OH concentration occur in the middle troposphere (MT) to UT (~300–500 hPa) (Figure 3), the largest relative enhancement occurs higher up (~200–300 hPa) (Figure 4). The reason for this is twofold; first, the extremely low OH concentrations in the cold and dry tropical UT in the L0 run cause even a small absolute increase in OH to translate into a large relative increase in that region. Second, near the tropopause, OH production by

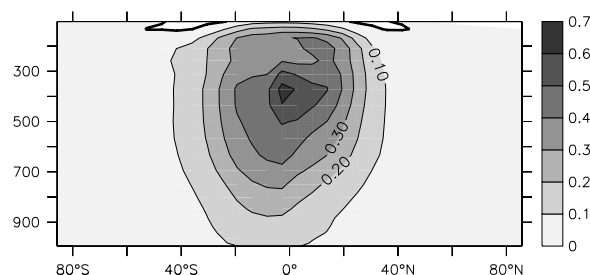


Figure 3. Absolute difference of the annual zonal mean OH concentration (in ×10⁶ molec/cm³) of the L5 and L0 runs.

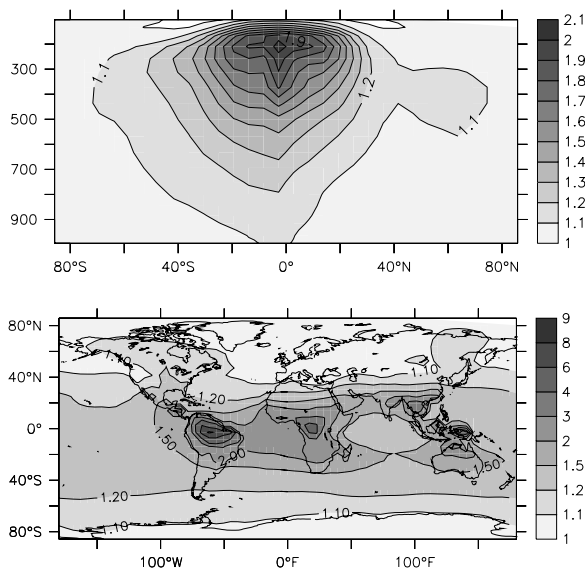


Figure 4. Ratios of annual zonal mean OH concentrations (top) and of the horizontal distributions at 300 hPa (bottom) for the L5 versus L0 run.

O(¹D) + H₂O is slow, so that secondary sources such as the reaction of NO with HO₂ become relatively more important than at lower altitudes. Furthermore, HO_x yields for reactions such as photolysis of acetone and oxidation of methane are enhanced in the presence of NO_x [Folkins and Chatfield, 2000].

[8] How do these changes in OH affect the oxidizing efficiency of the troposphere? We examine this with respect to two long-lived trace gases, methane (CH₄) and methylchloroform (CH₃CCl₃, or MCF for short). Their lifetimes ($\tau_{(CH_4)}$ and $\tau_{(MCF)}$) for the five runs are given in Table 1. While $\tau_{(CH_4)} = 10.26$ years is computed for the L0 run, the L5 run yields $\tau_{(CH_4)} = 8.79$ years, a reduction of nearly 15%. A similar relative reduction in $\tau_{(MCF)}$ is also computed. Note that since CH₄ is simulated in the model, we can use the online model budget routines to compute $\tau_{(CH_4)}$ (using the tropopause based on the temperature lapse rate criterion). However, since we do not simulate MCF, we approximate $\tau_{(MCF)}$ using monthly mean OH and temperature fields from the model output, a climatological tropopause, and a uniform distribution in the troposphere. We verify that the error in this approximation is small by doing the same for $\tau_{(CH_4)}$ and comparing to the online budget values (Table 1), showing that the offline estimates are biased $\sim 5.5\%$ and $\sim 3.9\%$ high in the L0 and L5 run, respectively; thus, $\tau_{(MCF)}$ values in Table 1 are also expected to be slightly overestimated.

Table 2. Lifetimes of CH₄ and MCF and Their Corresponding LtNO_x Production Range According to Various Studies

Reference	$\tau_{(CH_4)}$ yrs	LtNO _x Tg/yr	$\tau_{(MCF)}$ yrs	LtNO _x Tg/yr
Spivakovsky et al. [2000]	9.6	~ 2	4.6	10–20
Prinn et al. [1995] ^a	$8.9^{+1.6}_{-0.8}$	0–10	4.6 ± 0.3	10–20
Prinn et al. [2001] ^a	$10.1^{+1.7}_{-1.2}$	0–5	$6.0^{+1}_{-0.7}$	0–5
Krol et al. [1998]	$8.6^{+1.6}_{-0.8}$	0–10	4.5 ± 0.1	10–20
Montzka et al. [2000]	—	—	$5.2^{+0.2}_{-0.3}$	5–10
Dentener et al. [2003]	9.0	~ 2 –5	—	—

^aLower atmospheric lifetime values, rounded to one decimal point.

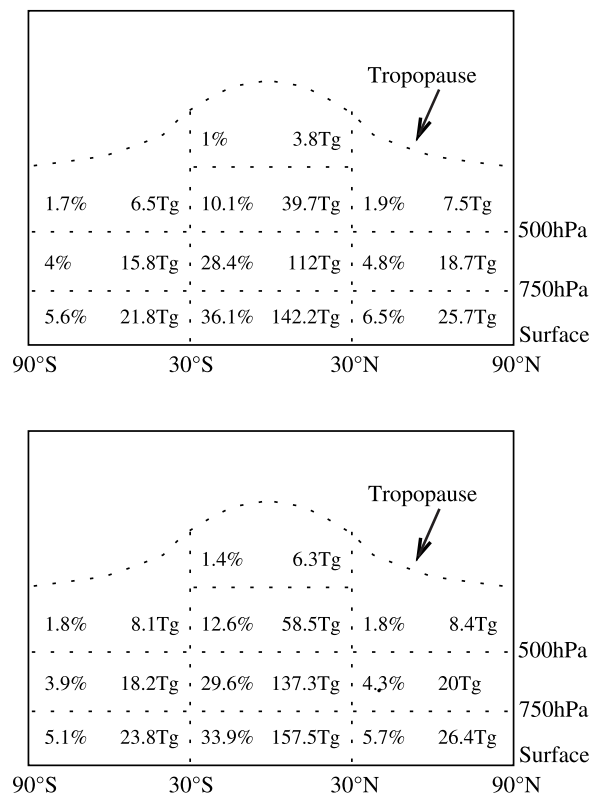


Figure 5. Percentages and total CH₄ oxidized in tropospheric subdomains in the L0 run (top) and the L5 run (bottom).

[9] Comparing our computed lifetimes to recent estimates given in the literature (Table 2), we see that at both extremes of the LtNO_x source magnitude range, the computed $\tau_{(CH_4)}$ and $\tau_{(MCF)}$ values are still barely within the current range of uncertainty. A tendency is hard to discern, indicating the uncertainty in factors other than LtNO_x that also affect OH and therefore $\tau_{(CH_4)}$ and $\tau_{(MCF)}$. However, we notice that $\tau_{(CH_4)}$ in all five references corresponds to or includes the 2–5 Tg yr⁻¹ LtNO_x production range. $\tau_{(MCF)}$ values correspond to the higher end of the spectrum, even after accounting for the slight high bias in our offline estimates. The inconsistency between the implied LtNO_x source magnitudes based on $\tau_{(CH_4)}$ and $\tau_{(MCF)}$ is related to the different OH spatial distributions used in the different studies as well as to the different temperature dependencies of the reaction rates of the two gases with OH.

[10] Which part of the atmosphere is mainly responsible for the computed changes in the lifetime? We divided the troposphere into compartments (following Lawrence et al. [2001]) and computed the amounts of oxidized CH₄ as well as the fraction (in %) of the total tropospheric CH₄ burden oxidized in each compartment for both the L0 and L5 runs (Figure 5). In absolute as well as relative terms, most of the CH₄ is oxidized in the tropical troposphere, especially in the LT. The largest absolute increase in the amount of CH₄ oxidized occurs in the two lowermost compartments of the tropical troposphere due to the strong temperature dependence of the oxidation reaction despite the only moderate increase in OH there, whereas the largest relative increases occur above 500 hPa (with increases of ~ 65 and $\sim 47\%$,

respectively, in the upper two tropical compartments) due to the larger relative increase in OH there (Figure 4).

[11] Finally, we can compare these effects to the effects of LtNO_x on O₃. In our runs, we find that the tropospheric burden of O₃ increases from 377 to 430 Gg, or ~14%, between the L0 and L5 runs. Thus, the effects of LtNO_x on the tropospheric oxidizing efficiency are similar in magnitude to the effects on O₃, while the effects on [OH]_m and [OH]_v are even larger.

4. Discussion and Conclusions

[12] Our results show that the OH concentration and the tropospheric oxidizing efficiency are strongly sensitive to the global LtNO_x source magnitude, comparable to, or larger than, the effect of LtNO_x on O₃. For our model, the uncertainty in LtNO_x alone translates into an uncertainty in our simulated $\tau_{(CH_4)}$ and $\tau_{(MCF)}$ which is about as large as their overall uncertainty based on other recent studies using various approaches to estimate their lifetimes. Based on this, it is tempting to suggest that improved estimates of the lifetimes of trace gases such as CH₄ and MCF could be used to constrain the global source of NO_x from lightning. However, this is currently impractical, due to the many other uncertainties involved. For instance, the LtNO_x parameterization introduces an unquantified error in both its horizontal and vertical distribution, which is important because the sensitivity of OH to additional NO_x varies regionally. The competition of LtNO_x with other NO_x sources (e.g., biomass burning) will be influenced by uncertainties in their magnitudes and in their convective lofting to the upper troposphere; this also applies to other competing HO_x precursors (e.g., acetone). Finally, there are still uncertainties in many key reaction rates, such as PAN formation and thermal degradation. Reduction in these uncertainties will lead to quantitative changes in the effects of LtNO_x on OH and on the oxidizing efficiency computed with improved models in future studies. We do not expect, however, that this will result in a qualitative change in our main conclusion, that is, that the strong effect of LtNO_x on OH and the tropospheric oxidizing efficiency should be considered alongside its effects on O₃, and reinforces the need for a more accurate determination of the source of NO_x from lightning in future studies.

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