Modeling lightning-NOx chemistry at sub-grid scale in a global chemical transport model

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The authors thank the referees for their comments on the manuscript. Their suggestions of correction and their questions on this work are very interesting and definitely help to improve this paper.

Referee #1:

Specific comments:

- *P34100 L8-11: Is there a reason that the methods used to determine horizontal dispersion could not be used to find vertical dispersion as well? A greater understanding of vertical dispersion could be used to augment the profiles used to force the vertical distribution of LNOx given by Ott et al. If this is beyond the scope of this study as the authors indicate, that is fine, and a sentence or two explaining why would suffice. Also, is the claim that vertical diffusion is less efficient than horizontal diffusion really true for the strong convective storms that create lightning?*

We thank the referee#1 for his useful comment on the atmospheric diffusion issue. We agree that lightning triggering and NOx emissions from electrical discharges occur in the convective part of the cloud where the vertical diffusion (Dv) is stronger than the horizontal diffusion (Dh). Therefore, the vertical diffusion coefficient is a determining parameter for the LNOx distribution. However, this vertical distribution of LNOx is a priori estimated from Ott et al., 2010, as a reverse "C-shape" profile, prescribed in GEOS-Chem, and totally independent of our parameterization. It could be very interesting to estimate Dv in the cloud to improve and support the Ott et al., 2010 given LNOx vertical profile using similar methods than the one used in the present study. This is indeed beyond the scope of our study, as it would require taking over Ott et al., 2010 work. Moreover, the plume parameterization for LNOx chemistry is applied a posteriori after lightning NOx are vertically prescribed by Ott et al., 2010 and emitted in convective clouds. Our parameterization starts just after transport driven by the convective parameterization and will then mostly concerns convective outflow where the NOx are detrained in the troposphere. In this region of detrainment, the horizontal diffusion seems to be more efficient than the vertical one as mentioned by Cariolle et al., 2009. Also, future studies on the atmospheric diffusion such as in-situ measurements and meso-scale modeling calculations should be useful to better quantify Dv and Dh.

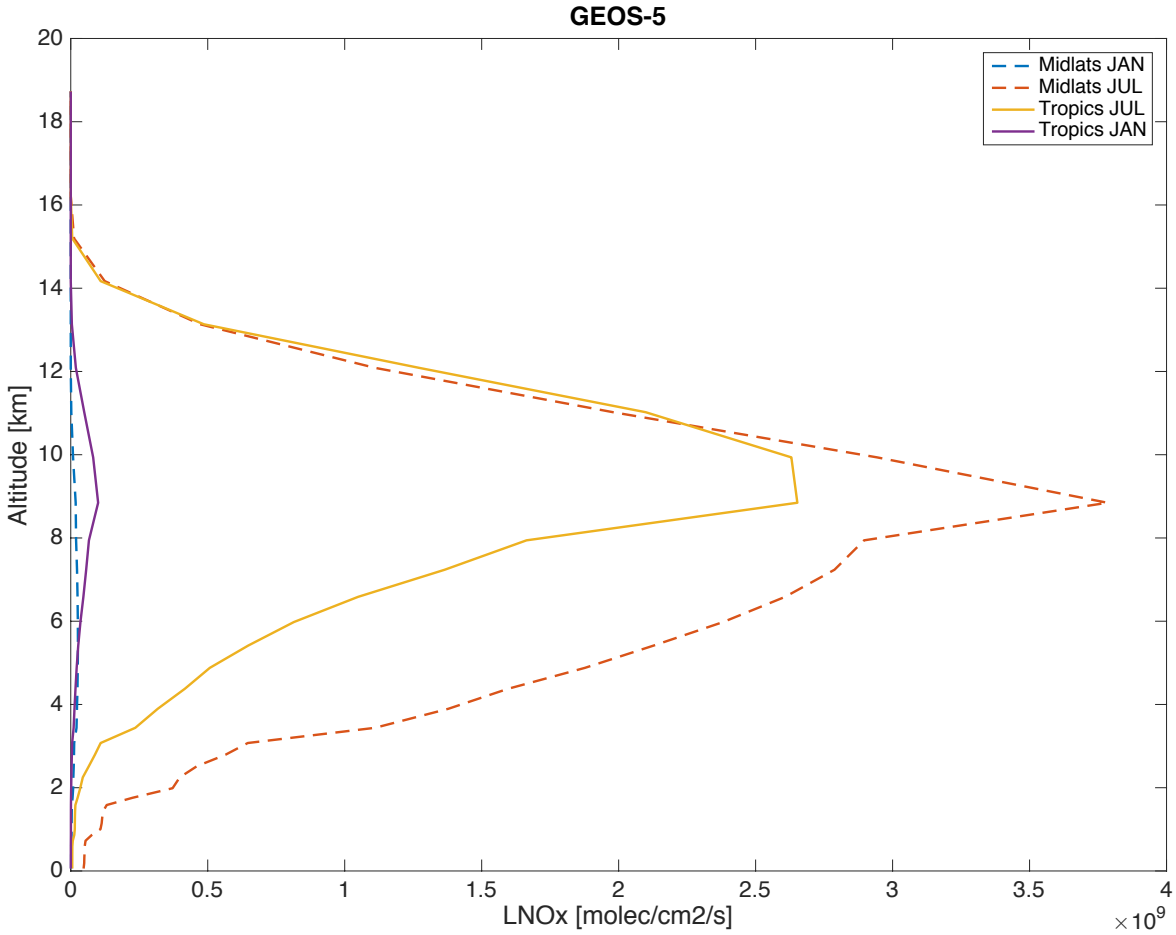
According to this explanation we have clarified this point in the text, section 3.1.1 as follows: "Note that the mean dispersion properties of the atmosphere were associated with the horizontal diffusion only. The lightning NOx emissions occur in the convective part of clouds where the vertical diffusion is strong. Therefore, the vertical diffusion coefficient is a determining parameter for the LNOx distribution in the cloud. As mentioned in section 2.1, the vertical distribution of the LNOx is a priori calculated from Ott et al. (2010) as a reverse C-shaped profile. The LNOx plume parameterization is applied a posteriori after that lightning NOx are vertically prescribed and concerns convective outflow where the NOx are detrained in the troposphere. In this region of detrainment, the horizontal dispersion may be more efficient than the vertical one as discussed in Cariolle et al., 2009. "

* *P34109 L8: I wonder about choosing the 8-11 km range. A brief explanation as to why this range was chosen would be appreciated. Is it appropriate to use the same vertical range for tropical and midlatitude storms, given the differences in their convective depth? How will this affect the parameterization of lightning outside of this range (or, how sensitive are the results to altitude)?*

Referee comment is legitimate. In a real atmosphere the detrainment region is commonly observed at higher altitude (up to 13-14km altitude, Folkins and Martin 2004, doi: http://dx.doi.org/10.1175/JAS3407.1) in the tropics than in the mid-latitudes (8-9 km altitude, DeCaria et al. 2000) In this study, the GEOS-Chem model uses GEOS-5 meteorological fields. The following figure illustrates the vertical distribution of the LNOx calculated by GEOS-Chem with GEOS-5 for the tropics and the mid-latitudes. This figure shows that the detrainment altitude is similar in both regions, i.e. around 8-11 km. GEOS-5 seems to underestimate the detrainment altitude in the tropics as shown in a previous work (Folkins et al., 2006, doi:10.1029/2006JD007325). Therefore, we decided to show vertical levels consistent with the GEOS-5 detrainment altitude level.

Outside this altitude range, our parameterization should mainly have influence between 6 and 12 km for which the calculated LNOx flux is still significant both in the tropics and in the mid-latitudes as showed by the following figure. However, the impact should be less important than between 8-10 km where the LNOx flux is the strongest.

We clarified this point in the manuscript, section 3.2.2 as follows: "The altitude range refers to the detrainment region estimated by GEOS-Chem using the GEOS-5 met fields (section 2.1) both in the tropics and in the mid-latitudes. Note that this range could vary depending on the met fields and the convection parameterization. In addition, the LNOx plume parameterization might have an impact outside of this altitude range mainly between 6 km and 12 km but in a lesser extent".



* *P34108 L16-: The authors indicate that 3-D turbulence is solved in their parameterization, and give a range of Dh values. More discussion of this would be interesting. How does Dh vary globally? Are there any trends or features in the Dh fields that are of interest? I, and I imagine other readers as well, would be interested in more details on the variability.*

The 3-D turbulence is actually not solved online in the GEOS-Chem CTM because of the fine scale characterizing this process but prescribed by the met fields (GEOS-5). Therefore, the global variability of Dh is not calculated in the model and has to be deduced a priori. For our parameterization, in order to determine Dh in the outflow region (i.e. at small scale), we have used both meso-scale modeling and in-situ measurements in the cloud anvil. The three-estimated Dh values [0.1; 15; 100] $m^2.s^{-1}$ are very dispersed. There is a real gap to fill about the knowledge in this parameter in the upper troposphere and especially in the outflow region. In the future, further meso-scale modeling studies and in-situ measurements in the scientific community should help to better define Dh variability.

We clarified this point in the revised version of the paper, section 3.2.1 as follows: “It is important to note that the 3-D turbulence is not solved online in the GEOS-Chem model because of the fine scale characterizing this process but prescribed by the GEOS-5 met fields. Therefore, the global variability of Dh is not calculated by the CTM and it is beyond the scope of this study. ”.

* *P34110 L25-: The ratio R_{LNOx} is set to be consistent with GEOS-Chem. It's good to be consistent, but I wonder if more can be said regarding this issue since this is a problem that is poorly understood. Is there anything in the parameters used in the new plume-in-grid parameterization that can shed some insight into what drives this difference between midlatitudes and tropics? This is related to my previous comment regarding variability of Dh. More discussion on the spatial variability of the various* model parameters may be enlightening.

As the referee pointed out, there are large differences in the LNOx production between the tropics and the mid-latitudes. The rate of flashes is higher in the tropics (Christian et al., 2003) but the amount of NOx molecules emitted per flash might be higher in the mid-latitudes. The amount of NOx molecules produced per flash may depend on different lightning parameters such as the number of flashes, but also the flash length, the stroke peak current and the stroke release height (Huntrieser, 2008, http://www.atmos-chem-phys.net/8/921/2008/acp-8-921-2008.pdf).

Our study aims to improve and represent the chemistry related to lightning NOx emissions in CTMs at global scale. The approach applied here is the implementation of a parameterization, which includes uncertainties regarding parameters estimate. The main parameters defined in this study could help us to get a more realistic idea of the NOx then O3 distribution at global scale. Also, the variability of these parameters may depend on latitude, as it is mainly the case for the plume lifetime. The horizontal diffusion coefficient doesn't appear directly in the plume parameterization in the CTM. It is estimated beforehand and used in the simple plume dispersion simulations. Therefore, we don't use and show the horizontal diffusion at global scale and the related variability.

The suggestion of the referee to use our results for understanding the tropics and the mid-latitudes LNOx emissions differences is interesting. However this is not easily feasible as our parameterization is linked with the convective and LNOx emission parameterizations used in the CTM, for which dependence on the tropics and mid-latitudes differences in terms of convective intensity and LNOx emissions are already considered (GEOS-Chem model, http://wiki.seas.harvard.edu/geos-chem/index.php/Lightning_NOx_emissions). Using similar LNOx emissions in the CTM (no a priori latitude dependence, RLNOx=1) with our sub-grid scales parameterizations, validated with in situ LNOx measurements, should indeed better help understand the RLNOx ratio, as suggested by referee#1. However, it would certainly require more LNOx observations in the tropics, poorly documented, as already stated in the manuscript.

* *Section 4.2: The comparisons between different model simulations (BC, P1, P2 experiments) do not include a direct comparison between the full model with and without the plume parameterization. Section 4.2.2 effectively does this by using the difference between P1 and BC experiments, but I found this to be unnecessarily confusing. A separately named direct comparison would be clearer to the reader.*

As suggested, we have changed the (P1-BC) difference by a direct comparison name (P3) in order to make the comparison clearer to the reader.

* *P34115 L5-6 "an approximate detrainment level (9 km altitude) where the LNOx are most concentrated": This sentence is a bit unclear. Is this the level where most LNOx is produced, or the level where the detrainment of LNOx from a cloud is the largest?*

We thank the referee#1 for this good remark. Regarding the results in the entire vertical, the 9 km level corresponds to the altitude where the detrainment level of LNOx is the largest.

We have clarified this point in the text in section 4.2.1 as follows: "These results are shown for an approximate detrainment level (9km altitude) where the detrainment of LNOx is the largest."

* *Section 4.2.1: The differences in plume lifetime for different seasons and locations are given without context. What drives these differences?*

The plume lifetime (τ) depends directly on, first, the NOx content (rl) above which the LNOx plume exists. This critical value changes mainly with the latitude since its calculation is initialized by the background concentrations of species, which are different in the tropics and in the mid-latitudes regions (see Table 1). Then, τ varies depending on the amount of LNOx emitted by lightning (NO_i, in the manuscript), which is higher in the tropics than in the mid-latitudes as mentioned previously. We do not show seasonal variations of τ (because they are negligible). However, day and night conditions strongly influence the rl calculation. Therefore, we calculate different values of τ for daytime and nighttime (Table 2). The seasonal variations are presented only for NOy and O3 distributions at global scale.

As suggested by the referee we clarified this point in the manuscript, section 4.2.1 as follows: "The plume lifetime depends on the latitude because of the different background chemical concentrations and the different amount of NOx emitted from lightning in the tropics and in the mid-latitudes. In addition, as mentioned before, we consider the influence of day and night conditions on the plume lifetime estimate. ".

* *P34115 L27: Why are some emissions "less important"? Does this just mean there are fewer emissions, or is something making them less important somehow?*

We agree with the referee that the expression "less important" is unclear to qualify the lightning NOx emissions. We mean fewer emissions and we have changed the sentence in the text, section 4.2.1, as follows: "So, the LNOx tracer is characterized by a shorter lifetime as a plume over North America than over Central Africa and around the Sahel while the model simulated fewer emissions over these regions especially in summer."

* *P34116 L5: what do you mean by "tracer is mainly reproduced"?*

We agree with the referee that this sentence is unclear and we have removed the term "mainly". Indeed, lightning NOx emissions are distributed from the surface to the cloud top height by the CTM according to the reverse "C-Shape" profile (Ott et al., 2010). Results show that the tracer mixing ratio is reproduced at the altitude where lightning emissions are calculated and detrained, mainly in the upper troposphere. This sentence aims to point out the consistency between lightning NOx emissions and the tracer distributions.

- *P34121 L1 "Significant values of B": How large does B have to be to be significant? Or does this just mean non-zero?*

We thank the referee#1 for this good comment. Our estimates of the β_1 (10^{-4}) and β_2 (10^{-3}) fractions are smaller than those from Cariolle et al., 2009 (with β_1=0.06 and β_2=0.2) in which the effects of the β fractions are non-negligible on the NOy distribution. Therefore, we assumed that if the β fractions would be higher than our estimates, their impact should be significant regarding Cariolle et al., 2009 results. Further modeling studies are needed (both box model and CTM) in order to determined what could be the significant values for the β fractions.

- *Figure 9: The hatched areas are a bit hard to read since they overlap with multiple lines. The authors may want to consider revising this figure to make it clearer.*

We agree with the referee#1 comment. The figure 9 has been modified to make it clearer.

- *P34101 L5 "than the surrounding" should be "as the surrounding"*

This has been changed in the revised version of the manuscript.

- *P34108 L22 "cover all of horizontal" should be either "cover all horizontal" or "cover all of the horizontal"*

This has been changed in the revised version of the manuscript.

- *P34110 L16 L18 "the northern Colorado" and "the Ontario". The "the" should be removed.*

This has been changed in the revised version of the manuscript.

- *P34111 L 24-25: This sentence is confusing and should probably be re-worded.*

The sentence was re-worded as suggested by the referee#1 as follows: "Our K_{eff} estimates are smaller than those calculated by Cariolle et al. (2009) for the plume chemistry related to aircraft exhausts. In this previous work, K_{eff} varies from 1.0 to $4.2.10^{-18}$ molecules^{-1} s^{-1} cm^{-3} with a mean value close to 3.10^{-18} molecules^{-1} s^{-1} cm^{-3} depending on the NO_x loading. The very low value for K_{eff} point out that the plume parameterization implies a delay of the production of ozone at the large scale rather than its destruction within the plume."

- *P34121 L8-11: The sentence beginning "That could be explained" is also confusing and needs to be re-worded.*

The sentence was re-worded as suggested by the referee#1 as follows: "Indeed, our β1 and β2 estimates are smaller than those calculated by Cariolle et al., 2009 (β1 = 0.06 and β2 = 0.2) which showed a significant impact of this mechanism in the case of aircraft NOx emissions."

Referee #2:

- *Lightning emissions are of NO, not NOx. It would be helpful if the paper discussed this from the beginning and not waiting until Section 4 to clarify this.*

We agree with the referee#2 comment and we have clarified this point at the beginning of the Introduction as follows: "Lightning emissions are one of the most important sources of nitrogen oxides (NOx ≡ NO + NO2) in the upper troposphere (WMO, 1999; Hudman et al., 2007). Lightning primarily produce NO and may also induce a negligible quantity of NO2 with a ratio NO2/NOx of 0.5 to 0.1 (Franzblau, 25 1991; Stark et al., 1996)."

- *p. 34101: the Ox family is O + O3 + NO2 (not O2!)*

This has been changed in the revised version of the manuscript.

- *The English needs to be corrected throughout the paper - there are numerous mismatches of plural-singular, and extraneous or missing articles (the, a). Also, for example, on p. 34106, 'allows to form' should be 'allowing formation of'.*

We thank the referee#2 for his/her comment. We have corrected the English throughout the paper.

Referee #3:

General comments:

1. *The plume parameterization uses both mixing ratios (molecules/molecules; all the variables that start with "r") and concentrations (molecules/cm3) in its equations, so it is important that the text correctly refer to each to avoid confusion. However, the original C09 equations have not had their units correctly translated to this paper. For example, Equation (2) labels r_p as a concentration (molecules cm^{-3}), but it needs to be a mixing ratio in order for its integration with air density (ρ) to yield molecules. The subsequent continuity equations, especially the d(rO3)/dt equation, are also dependent on a careful distinction of concentration versus mixing ratio in its components. The authors will either need to maintain the original units from C09 in all their equations (a mix of both mixing ratios and concentrations), or reformulate them such that they are all concentrations as they are currently described (e.g., removing _ where necessary, changing rO3 to [O3], etc.). I also recommend removing the multiplication crosses in the equations, and think it would be easier for the reader if standard square brackets were used for the concentrations in Equations (5)-(7), e.g., d([O]+[O3])/dt = k2 [NO2] - k3[NO][O3] ...*

We agree with the suggestion of the referee#3. The related changes have been made in the text for describing the equations with the appropriate terms according to Cariolle et al., 2009.

2. *It is not clear to me what model is being used to estimate τ and K_{eff}, which requires resolving chemistry and transport on spatiotemporal scales finer than the plume itself. I think the model section needs an additional part that describes the "simple plume dispersion" model referenced in Sections 3.2.3 and 3.2.4., in particular how the chemistry was included that was used to determine Keff .*

We agree with the referee comment. We have added the section 2.4 to the manuscript in order to present the simple plume dispersion model for determining τ and K_{eff} as follows:

"To model the dispersion of lightning NOx emissions we use a simple dispersion model similar to the plume model used for aircraft NOx emissions, except that the plume is supposed to be oriented along a vertical axis. The plume is represented as a cylinder that encompass horizontal diffusion with a constant coefficient Dh (section 3.2.1). This simple model is composed of 30 horizontal circles with spacing increasing progressively from the center axis. The discretization of the diffusion equation is mass conservative.

The chemistry scheme and associated reaction rate constants is adapted from the large-scale chemical model MOCAGE (Teyssedre2007). It includes the main reactions involved in the NOx-HOx system. Simple plume simulations were performed in order to estimate the physical and chemical characteristics of plumes related to lightning NOx emissions. "

3. *The formulation of Keff in C09 assumes that only NOx is elevated in the plumes relative to the diluted background mean (whereas other species are assumed to match the background at the initialization of the plume). This is a decent assumption for aircraft and ships, but less so for lightning. Lightning NOx is released during active deep convection, by which sub-grid-scale processes rapidly mix air from non-local locations, yielding complex*

mixtures of ozone, VOC, HOx and H2O observed in convective outflows that would be atypical relative to the background grid cell. For example, the recent DC3 campaign saw complex mixtures of surface and stratospheric air masses alongside lightning NOx plumes (doi:10.1175/BAMS-D-13 00290.1). I think that the authors should briefly acknowledge these uncertainties and how they might affect their conclusions.

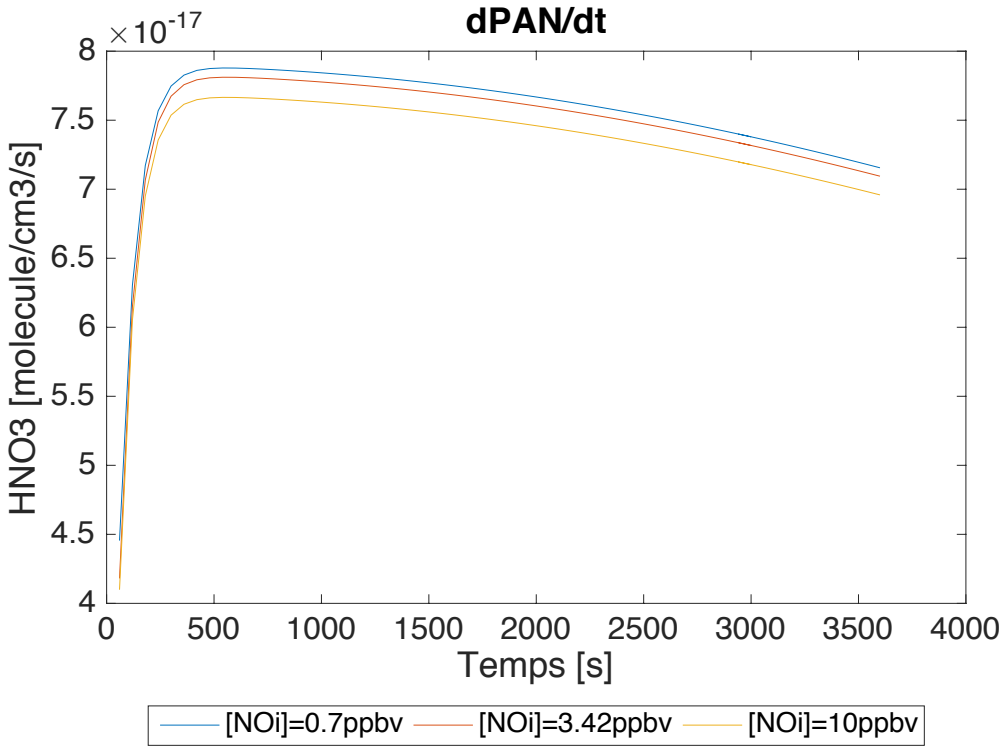
The comment about the K_{eff} calculation from the referre#3 is very interesting. We agree that in the case of lightning emissions other species like VOCs, HOx and H2O may be uplifted from the surface in the convective region. Nevertheless, Sauvage et al., 2007 showed that, in the upper troposphere, NOx rather than VOCs mainly influence O3 mixing ratio. In other words, the OPE in the UT is controlled by NOx. We assumed that our plume parameterization is a first estimate of the LNOx chemistry focused on NOx.

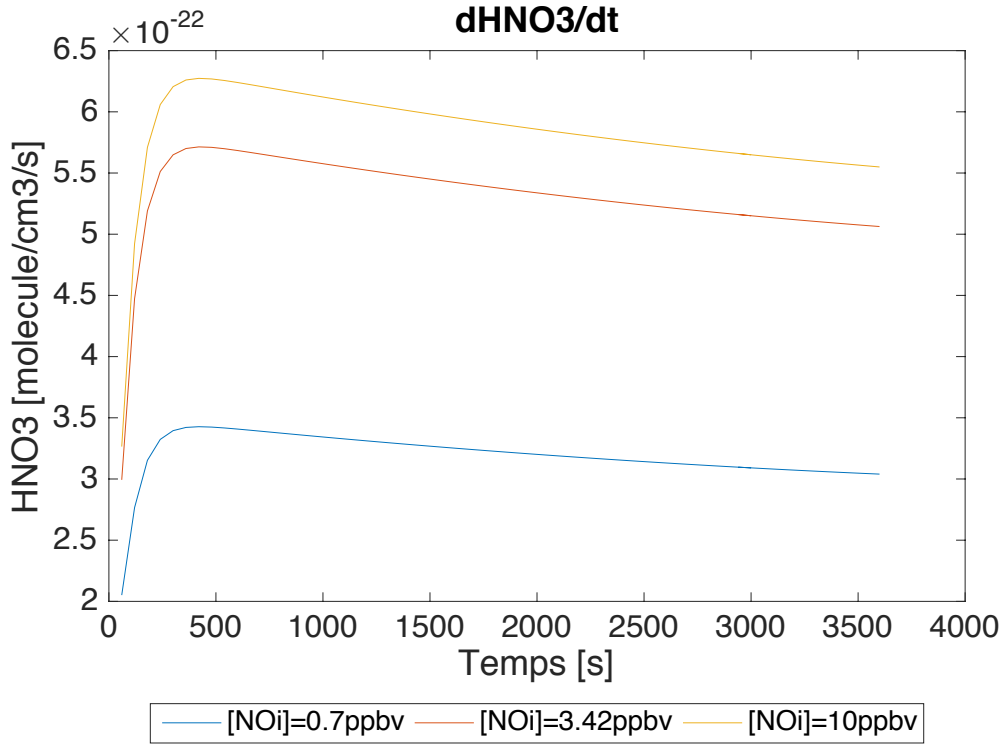
As suggested by the referee, we have clarified this point in the manuscript in section 3.2.4 as follows: ‘‘Note that in the case of lightning emissions other species like VOCs, HOx and H2O may be uplifted in the convective region that could bring uncertainties in our approach. However, we assumed that the OPE is mainly controlled by NOx in the upper troposphere as previously showed by Sauvage et al. (2007b). Therefore, K_{eff} calculation is here mainly dependent on NOx content. Future studies should try to investigate this issue for lightning emissions mixed with strong surface emissions in order to sharpen our parameterization”

4. *I would expect lightning plumes to be highly efficient PAN producers, since the convection in which lightning occurs would also loft short-lived peroxyacetyl radicals from the surface to react with the elevated NOx, and the temperatures in the cold free and upper troposphere will guarantee that PAN does not thermally decompose and it will outlast the plume. However, because the plume formulation does not allow NOx to be converted into PAN in the plume, it is released as NOx away from the regions of elevated peroxyacetyl radicals, and therefore global PAN decreases, as the authors correctly explain in Section 4. However, unless the ratio of PAN production to HNO3 production is relatively suppressed in the high-NOx plumes (which I would not expect), then this is likely an error in the PAN budget introduced by the plume parameterization. I think the authors should comment based on their DSMACC results whether relative PAN production is stable, enhanced or suppressed in the high-NOx conditions. Unless it is suppressed, then I think that a conclusion of this paper should be a recommendation that future studies with a similar lightning plume parameterization include an additional β term that characterizes the conversion of NOx to PAN, and associated d([PAN]/dt) and d([CH3C(O)OO])/dt continuity equations alongside those for HNO3, O3, and NOx.*

This is an excellent comment from the referee#3. As showed in the manuscript, our LNOx plume parameterization implies a decrease in PAN mixing ratio at global scale, which is mainly explained by the storage of NOx in the plume form along the transport.

The following two figures show d[PAN]/dt and d[HNO3]/dt implied by high NO concentration (0.7ppb, 3.42ppb and 10ppbb) as results from DSMACC box model simulations (example for the mid-latitudes conditions at daytime). These figures show that high NO condition implies a significant increase in PAN, which is higher by a factor 10^5 than the HNO3 production.





Therefore, we agree with the referee#3 about the potential gap for PAN chemistry in our LNOx plume parameterization. It could be of great interest to add the PAN and CH3C(O)OO continuity equations and a new term to describe the NOx conversion to PAN within the plume.

A discussion about the PAN chemistry was added in the manuscript, in section 4.2.2, as follows: "Note that the production of PAN is limited by the supply of NO_x or non-methane volatile organic compounds (NMVOCs). Above continental lightning sources regions, NMVOCs are uplifted by deep convection but with lower NO_x due to the activation of the plume parameterization. That implies a less efficient PAN production in these regions. Downwind of lightning sources regions (oceanic regions), NO_x increases because of the LNO_x transport in the plume form but there is less NMVOCs available to produce PAN. Therefore, both in regions of LNO_x emissions and downwind the PAN production is limited leading to overall lower PAN mixing ratios at large scale in P1 experiment. However, this may be nuanced by considering the PAN chemistry in future studies using similar LNO_x plume parameterization by introducing the PAN and CH3C(O)OO continuity equations and a new term to consider the fraction of NO_x converted to PAN within the plume. This should allow the PAN production during the plume transport, which is inhibited in the current version."

Specific comments:

* *P34093, L7-13: Only some lightning NOx is detrained in the cloud anvil, much is detrained at lower altitudes during the convective updrafts and downdrafts as seen in the Ott et al. (2010) profiles. I would rephrase this sentence to be "Most NOx produced by lightning is detrained into the free and upper troposphere, where ozone production efficiencies (OPE) per unit NOx emitted are 4 to 20 times higher than at the surface (refs), and therefore lightning exerts a disproportionately stronger effect on photochemistry than surface emissions (refs)."*

We agree with the referee suggestion. This has been changed in the revised version of the manuscript.

* *P34093, L21-23: Recommend changing the start of the sentence to "Therefore, lightning NOx production must be parameterized for inclusion..."*

This has been changed in the revised version of the manuscript.

* *P34093, L26-27: LIS and OTD are currently the only options, and OTD was not on the TRMM satellite.*

We agree with the referee comment and we have change the sentence as follows: "Flashes simulated by CTMs are commonly constrained by satellite observations (Sauvage et al., 2007b; Murray et al., 2012) from the space-borne Lightning Imaging Sensor (LIS) on TRMM and the Optical Transient Detector (OTD) (Christian et al., 2003; Tost et al., 2007)."

* *P34094, L1: Many models now use newer vertical distribution profiles from Ott et al. (2010), including GEOS-Chem, which are "reverse-C"-shaped, so please update the text here and elsewhere.*

This has been changed in the revised version of the manuscript.

- *P34094, L6: I would recast as "Despite the necessity of including lightning NOx emissions in global models, ..."*

This has been changed in the revised version of the manuscript.

- *P34094, L15: Please change "realistic" to "more realistic", as the plume scheme is still a parameterization (and similarly in P34118, L18; P34121, L5; P34123, L27).*

This has been changed in the revised version of the manuscript.

- *P34096, L13-14: Heterogeneous reactions occur on all aerosol types in GEOSChem, not just sulfate and mineral dust.*

This has been changed in the revised version of the manuscript.

- *P34096, L18: Suggest replacing "specially estimate for" with "overwrite those for the"*

This has been changed in the revised version of the manuscript.

- *P34096, L20: "Fossil fuel" should be "Biofuel"*

This has been changed in the revised version of the manuscript.

- *P34096, L22: Lobert et al. is not a GFED reference (see doi:10.5194/acp-10-11707-2010)*

We have changed the reference related to the GFED inventory in the text.

- *P34096, L25-P34097, L2 - I recommend rephrasing the GEOS-Chem description to follow the order of the steps taken in the model to calculate NOx from lightning: (1) flash rates are calculated in active deep convection using the Price and Rind scheme, (2) flash rates are adjusted with local scaling factors to match the satellite climatology, (3) total column emissions are determined using NOx yields that differ in tropics and northern extratropics, and (4) total column is distributed vertically using the Ott profiles. I would also mention that the base lightning NOx scheme is described in detail by Murray et al. (2012). Have the authors made any additional modifications to the standard GEOS-Chem implementation for their base case (BC) simulation, or does that simulation use GEOS-Chem as is publicly released?*

We thank the referee#3 for his/her suggestion. In this present study, there is no additional change to the standard GEOS-Chem implementation related to the BC experiment. This has been changed in the revised version of the manuscript, in the section 2.1, as follows:

"In order to calculate the NO_X from lightning, flash rates are first calculated in active deep convection using the Price and Rind Scheme based on the cloud-top-height (Price and Rind, 1992, 1994), then flash rates are adjusted with local scaling factors to match the satellite climatology (Sauvage et al., 2007b; Murray et al., 2012), and the total column emissions are determined using NO_X yields that differ in tropics and northern extratropics. Finally, the total column is distributed vertically using the reverse C-shaped profile from Ott et al. (2010). Note

that the base lightning NO_X scheme is described in detail by Murray et al. (2012)."

* *P34098, L22-23: Please give the mass of the LNOx tracer used, and specify whether or not it varies in space and time (as the mean mass of NOx does due to changes in NO/NO2 ratios).*

The initial LNOx tracer mass corresponds to the NOx mass at the time of the beginning of the simulation within the GEOS-Chem model. However, the LNOx tracer is considered as a passive tracer within the model following the monotonic exponential decade applied by the plume parameterization. We have clarified this point in the manuscript as follows:

"Following Cariolle et al. (2009), a passive tracer (from the perspective of the usual model chemistry) is added to the CTM to represent NO_X emitted by lightning. The LNO_X tracer initial mass corresponds to the NOx mass at the start time of the simulation. Rather than increasing the concentration of NO_X within the CTM, lightning NO_X emissions now increase the concentration of this new passive tracer, which is transported in the standard way by advection and turbulence. Plume chemistry is considered to be significant when the mixing ratio of the lightning NO_X tracer is higher than a critical NO_X content, hereafter denoted r] . Above this value the lightning NO_X tracer is transferred to the normal NO_X tracer at a rate described by a plume lifetime (τ), which is an exponential decay constant. This corresponds to an exchange time scale between the lightning NO_X plume and the background NO_X."

* *P34099, L13: I should be the injection rate of "LNOx", and the units used here should be the same in P34113, L21.*

This has been changed in the revised version of the manuscript.

* *P34100, L17-20 - Equation (4) includes _NOx and EINOx. However, later in the text it is stated that these values are 1, which is non-physical based on what they are supposed to represent. However, the "fuel" tracer in this case is comprised only of NOx, so I believe the authors should just remove _NOx and EINOx everywhere from this work as superfluous (as long as the molecular mass of the LNOx tracer is specified). If they prefer to leave them in, please state what the g (N, NO, NO2, NOx?) and kg (air, LNOx?) are referring to in EINOx.*

We agree with the suggestion of the referee#3. The EI_{NOX} variable has been removed from the equations.

* *P34101, L4-5: Ozone is still an order of magnitude greater.*

We thank the referee for his/her comment and the sentence has been change in the text as follows:

"In the case of large NOx injection by lightning, the NOx content (~40 ppt in unpolluted atmosphere) becomes close (a few ppb, according to in-situ measurements, Dye et al. (2000); Huntrieser et al. (2002)) to the surrounding ozone (60±24 ppb) (Jaéglé et al., 1998)."

* *P34101, L13-14: Recommend replacing "The sums of the concentrations as detailed by the Eqs. (5)-(7)" with "The rate of change of each chemical family are given by Eqs. (5)-(7)".*

This has been changed in the revised version of the manuscript.

* *P34102, L24-P34103, L2: It is given here that Keff is a function of the plume concentrations of NOx and O3, but the C09 derivation uses only in-plume NOx concentrations and background O3 concentrations in its definition of Keff. Please clarify what is used here and correct the integrals as necessary.*

In the Keff equation, r_{NOx}^{P} and r_{O3}^{P} correspond to the mixing ratios of NOx and O3 respectively in the plume and the overlined r_{O3} term is the background ozone mixing ratio averaged in the model grid as described in Cariolle et al., 2009. We have clarified this point in the text.

* *P34103, L17-P34104 L18: Please add "primarily" to the discussion of the day and night reactions, since both reactions occur both at day and night. Please clarify what is meant by "characterized by the coefficient β " (I assume molar fraction of NOx converted to HNO3?).*

We have clarified this point in the text as follows: ''In addition, we consider the conversion of NOx into HNO3 within the plume. This conversion takes place in two different ways depending on the day or night atmospheric conditions. During the day, NO2 reacts primarily with OH to give HNO3 directly and it is characterized by the coefficient β1. While at nighttime the conversion of NOx to HNO3 occurs mainly through N2O5 formation followed by a heterogeneous hydrolysis reaction, which corresponds to β2. In other words, the β coefficients are the molar fractions of NOx converted to HNO3 within the plume. These two fractions are unitless".

* *P34104, L15: It is somewhat misleading to include PAN here. It is true that PAN is forming in the box model used to calculate β1 and β2, therefore reducing the magnitude of those values by preventing some NOx from being converted to HNO3. However, the plume parameterization does not include a d[PAN]/dt equation, nor does d[NOx]/dt include any losses associated with PAN production in the plume, so this PAN remains as NOx as far as GEOS-Chem is concerned.*

We agree with the referee#3 comment. PAN has been removed here.

* *P34106, L23-24: Recommend changing to "related to highly elevated NOx concentrations relative to the background".*

This has been changed in the revised version of the manuscript.

* *Section 3.2.1: Dh was only estimated for outflow from deep convective anvils, but a lot of lightning NOx is released beneath the anvil. Please clarify if a constant Dh was used in all plumes, and didn't vary with altitude or latitude?*

We agree with the referee, that LNOx may be released beneath the anvil. Three different values of Dh [0.1; 15; 100] $m^2.s^{-1}$ were estimated in our study. The first value Dh=0.1 $m^2.s^{-1}$ was obtained from in situ measurements outside the anvil but close to this region and could be related to the plume from beneath the anvil. The second value, Dh=15 $m^2.s^{-1}$ was obtained from

measurements within the anvil region. Finally the last value, Dh=100 $m^2.s^{-1}$ corresponds to the horizontal diffusion in the anvil and was obtained from a convective cell simulation with Meso-NH.

From these estimates, we have a first guess of Dh in the anvil but also outside and close to the anvil from two different approaches. In this study, Dh is constant for each experiment performed with the GEOS-Chem model. Dh is used in the simple dispersion model (new section 2.4) in order to determine the plume lifetime and K_{eff} but this parameter does not appear directly in our parameterization in the GEOS-Chem model. As discussed before in response to the referee#1, although it is very relevant, the global variability of Dh was not studied here because it is not solve at large scale by the GEOS-Chem model. We may expect that Dh varies mainly with altitude and also latitude. Further modeling studies and in situ measurements should be performed in the future to better understand this parameter variability at large scale and improve the characterization of the LNOx plume dispersion.

We have clarified this point in the revised version of the manuscript in section 3.2.1, as follows: "In order to cover all horizontal diffusivity estimates discussed in this section the range of values 0.1, 15 and 100 m2 · s−1 was used. The horizontal coefficient is constant for all lightning NOx plumes considered in the GEOS-Chem model. Hereafter, the results are detailed for the central value Dh = 15 m2 · s−1."

- *P34107, L5-7: "defined" would be better as "determined"? Please clarify what is meant by "mainly from previous in-situ measurement in thunderstorm anvil".*

We agree with the referee comment. By the sentence "*mainly from previous in-situ measurement in thunderstorm anvil*", we would highlight that the Dh estimate from in-situ measurements may be the most accurate. The Dh estimate related to this method is more realistic (in agreement with Cariolle et al., 2009, Dh estimate) than the estimate from the modeling study. This has been removed in this paragraph but it is mentioned after in this section.

This has been change in the revised version of the manuscript in section 3.2.1, as follows: "The diffusion coefficient was determined by two different ways. A first estimate of the horizontal diffusion was performed by running the 3-D mesoscale Meso-NH model. Then, the Dh coefficient was calculated using in-situ measurements in thunderstorm anvil".

- *P34107, L12: "performed" would be better than "made"*

This has been changed in the revised version of the manuscript.

- *P34107, L17: If e is not Euler's constant, please define.*

The "e" is the exponential function here. It has been replaced by "exp" in the revised manuscript.

- *P34109, L17-23: How are the tropics vs. midlatitudes defined when rl is applied in the model?*

The critical content mixing ratio rl, above which the LNOx plume exists, is used in the plume dispersion model in order to estimate the plume lifetime (τ) and K_{eff}. In these dispersion simulations, the tropics and the mid-latitudes conditions are distinguished using initial concentrations for chemical species relative to the two latitude regions (Table 1). From these runs, we got different values for τ (and K_{eff}). Finally, in GEOS-Chen model, the τ values are applied depending on the latitude region.

* P34110, L1: Please clarify what is meant by "an ensemble of spikes"

In our parameterization, each LNOx plume is associated with several electrical discharges at the convective cell scale. We have clarified this point in section 3.2.3, as follows:

"Here we use a width of 500 m to refer to an ensemble of spikes at cloud scale (i.e. each plume is defined from several electrical discharges associated with a convective cell)."

* *P34111, L2: Please replace "defined" with "estimated"*

This has been changed in the revised version of the manuscript.

* *P34111, L4: Is it appropriate to use separate rl for night and day, when some of the lifetimes are much longer than 12 hours? Why wouldn't we just use the smaller of the two values in both day and night?*

There is some plume lifetimes longer than 12 hours but most are shorter (67 %). Also, there is a significant difference in the plume lifetime between day and night (Table 2). For example, for NO_i^{max} there is 3.6 hours and 13.6 hours difference in the mid-latitudes and tropics respectively. We cannot consider only the smallest value of rl because this could imply longer lifetime, which is less realistic than the use of the rl day and night distinguish values.

* *P34111, L24-25: Please clarify the sentence so it is clear whether it is meant that Keff is "very low" relative to the C09 values or the background K values?*

This has been clarified in the revised version of the manuscript in section 3.2.4, as follows: "Our K_{eff} estimates are smaller than those calculated by Cariolle et al. (2009) for the plume chemistry related to aircraft exhausts. In this previous work, K_{eff} varies from 1.0 to 4.2·10−18 molecules−1·s−1· cm3 with a mean value close to 3 · 10−18 molecules−1 · s−1 · cm3 depending on the NOx loading."

* *P34113, L23: I think "undiluted" should be "diluted" here*

The use if the "undiluted" term is the good choice here. In fact, in our plume parameterization, the mixing ratio of the tracer (r_{LNOx}) represents the NOx mixing ratio from lightning emissions. In other words, this is the NOx in the plume form not yet released to the model grid as a background concentration.

* *P34113, L24: Lightning does produce some NO2 (as well as other species). I would change to "lightning produces negligible quantities of NO2 relative to NO and therefore E is effectively 0 in Eq. (15)."*

This has been changed in the revised version of the manuscript.

* *P34116, L5: "produced" (not reproduced). I would refer to the altitudes in Fig. 3c as "middle and upper troposphere" as the tropopause is ~70 mb in the tropics.*

This has been changed in the revised version of the manuscript as follows: "The lightning NOx tracer is produced at altitudes where lightning NOx are calculated and detrained (in the upper troposphere, between ~500 and 300 hPa) as shown in panels (c) in figure 3."

* *P34117 L6: Should be "volatile"*

This has been changed in the revised version of the manuscript.

* *Sections 4.3.1-4.3.2: Here the word "variability" would be better replaced by "sensitivity", and all the various _O3 and _NOx values referred to as "ranges" or "changes" associated with the uncertainty in the different explored parameters examined.*

This has been changed in the revised version of the manuscript.

P34121, L1: "significant" should probably be "large" here.

This has been changed in the revised version of the manuscript.

* *Figure 1: This diagram needs a longer caption to describe what the lines, arrows, boxes, and colors represent. I would recommend removing the boxes from around the "[NOx] < rl" and "[NOx] > rl" to make it clear that those are a conditional statements (also, [NOx] should probably be [LNOx] there), and move the edge of the green "ERR" box to the other side of the conditional.*

This has been changed in the revised version of the manuscript.

* *Figures 3-7: I was originally confused because I interpreted these captions as that Dh and NOi were somehow applied in GEOS-Chem, not that the τ and Keff values were trained from the offline simple plume dispersion model using those Dh and NOi values. I would recommend rephrasing to make that distinction clearer.*

This has been changed in the revised version of the manuscript.

Manuscript prepared for Atmos. Chem. Phys.
with version 2015/04/24 7.83 Copernicus papers of the LaTeX class copernicus.cls.
Date: 29 February 2016

Modeling lightning-NO_x chemistry at sub-grid scale in a global chemical transport model

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Abstract. For the first time, a plume-in-grid approach is implemented in a chemical transport model (CTM) to parameterize the effects of the non-linear reactions occurring within high concentrated NO_x plumes from lightning NO_x emissions (LNO_x) in the upper troposphere. It is characterized by a set of parameters including the plume lifetime, the effective reaction rate constant related to NO_x-O_3 chemical interactions and the fractions of NO_x conversion into HNO_3 within the plume. Parameter estimates were made using the DSMACC chemical box model, simple plume dispersion simulations and the mesoscale 3-D Meso-NH model. In order to assess the impact of the LNO_x plume approach on the NO_x and O_3 distributions at large scale, simulations for the year 2006 were performed using the GEOS-Chem global model with a horizontal resolution of $2^\circ \times 2.5^\circ$. The implementation of the LNO_x parameterization implies NO_x and O_3 decrease at large scale over the region characterized by a strong lightning activity (up to 25 % and 8 %, respectively, over Central Africa in July) and a relative increase downwind of LNO_x emissions (up to 18 % and 2 % for NO_x and O_3, respectively, in July) are derived. The calculated variability of NO_x and O_3 mixing ratios around the mean value according to the known uncertainties on the parameter estimates is maximum over continental tropical regions with ΔNO_x $[-33.1; +29.7]$ ppt and ΔO_3 $[-1.56; +2.16]$ ppb, in January, and ΔNO_x $[-14.3; +21]$ ppt and ΔO_3 $[-1.18; +1.93]$ ppb, in July, mainly depending on the determination of the diffusion properties of the atmosphere and the initial NO mixing ratio injected by lightning. This approach allows (i) to reproduce a more realistic lightning NO_x chemistry leading to better NO_x and O_3 distributions at the large scale and (ii) focus on other improvements to reduce remaining uncertainties from processes related to NO_x chemistry in CTM.

1 Introduction

Lightning emissions are one of the most important sources of nitrogen oxides ($NO_x \equiv NO + NO_2$) in the upper troposphere (WMO, 1999; Hudman et al., 2007). Lightning ~~emitted~~ primarily produce

NO and may also induce a negligible quantity of NO_2 with a ratio NO_2/NO_x of 0.5 to 0.1 (Franzblau, 1991; Stark et al., 1996). NO_x emitted by lightning (LNO_x) impact the tropospheric ozone burden (Stockwell et al., 1999; Hauglustaine et al., 2001; Grewe, 2007), and the hydroxyl-radical (OH) concentrations influencing the oxidizing capacity of the atmosphere (Labrador et al., 2004; Banerjee et al., 2014). ~~Lightning flashes including cloud-to-ground and intra-cloud flashes produce reactive nitrogen species which are detrained in the cloud anvil (Weiss et al., 2012) and released directly in the upper troposphere. Because of an ozone production efficiency~~ Most NO_x produced by lightning is detrained into the free and upper troposphere, where ozone production efficiencies (OPE) per unit NO_x emitted are 4 to 20 ~~times larger in the upper troposphere than in the middle or low troposphere (Sauvage et al., 2007a; Martin et al., 2007), effects of LNO_x on chemistry are expected to be stronger in the upper troposphere~~ higher than at the surface (Sauvage et al., 2007a; Martin et al., 2007), and therefore lightning exerts a disproportionately stronger effect on photochemistry than surface emissions (Pickering et al., 1990; Hauglustaine et al., 1994; Zhang et al., 2003; Choi et al., 2009). The longer NO_x lifetime in the upper troposphere (1-2 weeks) allows the long-range transport of LNO_x through the large circulation patterns (Hemispheric Transport of Air Pollution, HTAP report, 2010: http://www.htap.org/).

Although the importance of the LNO_x emissions on the upper tropospheric chemistry is well known, it remains highly uncertain with a best estimate of 2-8 $TgN{\cdot}yr^{-1}$ (Schumann and Huntrieser, 2007). Lightning NO_x emissions are associated with deep convection (horizontal scale $\sim$ 10 km) and correspond to the "sub-grid" in global chemical transport models (horizontal resolution $\sim 100s$ km). ~~This implies that the impact of the~~ Therefore, lightning NO_x ~~emissions should~~ production must be parameterized for inclusion into a large scale model. Global models commonly used convection proxies such as the cloud-top-height (Price and Rind, 1992) and the updraft intensity to estimate the lightning flashes. Flashes simulated by CTMs are commonly constrained by satellite observations (Sauvage et al., 2007b; Murray et al., 2012) ~~such as measurements~~ from the space-borne Lightning Imaging Sensor (LIS) on TRMM and the Optical Transient Detector (OTD) ~~on TRMM~~ (Christian et al., 2003; Tost et al., 2007). The lightning NO_x emissions are then redistributed according to a vertical profile generally a reverse "C-Shape" profile ~~(Pickering et al., 1998)~~ (Ott et al., 2010) a priori defined depending on season, latitude and continent/ocean location. Also, corrections on the calculations of lightning NO_x emissions using satellite observations (SCIAMACHY, Martin et al. (2007)) and in-situ measurements (INTEX-NA, Hudman et al. (2007)) are usually applied.

Despite the ~~success in simulating the~~ necessity of including lightning NO_x emissions in global models, the small scale nature of the flashes and the non-linear chemistry (Lin et al., 1988) of the atmosphere will lead to biases on the large scale with instantaneous dilution of gases in the large grid box volume. It seems likely that this will lead to an overestimate of the OPE and an underestimate of the nitric acid (HNO_3) production. For instance, by forcing NO_x concentration in GEOS-

Chem grid box over Southeast Asia to represent the measured lightning plumes, Cooper et al. (2014) ~~estimate~~ estimated a ratio for O_3 to HNO_3 produced leading to a 15 mol/mol OPE in lightning plumes, that reinforces the fact that instantaneous dilution in global model implies issues in sub-grid chemistry.

In this work, a more realistic lightning NO_x chemistry as well as a plume parameterization is implemented into a global chemical transport model (CTM) allowing reproducing more accurately the ~~large scale~~ NO_x and O_3 ~~distribution~~distributions at large scale. The plume approach used in this study was previously developed by Cariole et al. (2009) for aircraft NO_x emissions in the LMDz-INCA and MOBIDIC models and also implemented to deal with the ship NO_x emissions (Huszar et al., 2010). This approach avoids the double count in the CTM calculation of the emitted NO_x, first instantaneously diluted into the point grid and ~~second~~ secondly as the plume form. In addition, the plume parameterization is the first that considers the NO_x from lightning as a plume with the transport of the related non-linear chemistry effects. NO_x from lightning emissions are emitted in the upper troposphere characterized by strong winds ~~that allows~~ allowing the large scale transport of trace species. Thus, it is relevant to consider a plume growth from lightning emissions, which could be diluted long time after the initial lightning pulse, downwind of emissions. Consequently, the plume parameterization previously developed for aircraft exhausts has been adjusted to LNO_x emissions and implemented into the GEOS-Chem global chemical transport model.

Section 2 gives a description of the GEOS-Chem model in which the plume-in-grid parameterization is implemented and ~~models~~ the models which are used to evaluate the diffusion properties of the atmosphere and to determine parameters characterizing the physics and chemistry of the lightning NO_x plume. A concise description of the plume approach is then presented in section 3 followed by a detailed explanation of the determination of parameters related to LNO_x emissions. Section 4 summarizes the results of the simulations performed with GEOS-Chem and finally these results and the sensitivity on NO_x and O_3 variations of the parameterization are discussed in section 5.

2 Models

Three different models are used in this evaluation and are described in this section. GEOS-Chem is used to provide a global framework to assess the impact of lightning NO_x. Meso-NH is used to provide estimates of the plume diffusion timescales and DSMACC is a box model used to assess the non-linear chemistry in the plume.

2.1 The GEOS-Chem chemical transport model

The GEOS-Chem chemical transport model (Bey et al., 2001) is a global 3-D model of atmospheric composition driven by assimilated meteorology from the Goddard Earth Observing System (GEOS-5) of the NASA Global Modeling Assimilation Office (GMAO). The 09-01-01 version (http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_v9-01-01) of the CTM has been used in this study. The model transports 43 tracers to describe tropospheric O_3-NO_x-VOC chemistry. The horizontal resolution is $2^\circ \times 2.5^\circ$ and 47 vertical levels are defined from the ground to 80 km altitude. The CTM includes modules for emissions, transport, chemistry, deposition, aerosols and surface.

The large-scale advection of tracers is performed using the TPCORE advection scheme (Lin and Rood, 1996) corresponding to a semi-lagrangian flux method. Shallow and deep moist convection processes are carried out using the Relaxed Arakawa-Schubert scheme (Moorthi and Suarez, 1991). Mixing in the lower atmospheric layers is represented by a non-local scheme of the planetary boundary layer described by Lin and McElroy (2010). The wet deposition for water-soluble aerosols and for gases follows Liu et al. (2001) and Amos et al. (2012). Aerosol scavenging by ice crystals and cold/mixed precipitation is also reproduced in the model (Wang et al., 2011). The dry deposition is associated to a scheme which calculates bulk surface resistance in series (Wesely, 1989). Photolysis rates are calculated with the Fast-JX code (Bian and Prather, 2002). The atmospheric chemistry is resolved using the SMVGEAR solver (Jacobson and Turco, 1994) with more than 300 species and 785 chemical reactions. Heterogeneous chemical reactions are represented on the surface of ~~the sulfate aerosols (Bey et al., 2001) and mineral dust (Martin et al., 2002)~~aerosols (Bey et al., 2001; Martin et al., 2002). Effects of aerosols on the photolysis rates are based on Martin et al. (2003). Primary NO_x and VOCs (Volatile Organic Compounds) emissions are separated depending on sources. Global anthropogenic emissions are given by the GEIA (Wang et al., 1998) and EGDAR (Olivier, 2005) inventories and regional anthropogenic emissions are ~~specially estimate for~~ overwrite those for the US (NEI05), Canada (CAC), Mexico (BRAVO), Europe (EMEP) and East Asia (Streets et al., 2006; Zhang et al., 2009). ~~Fossil fuel~~ Biofuel emissions are provided by EPA and STREETS 2006 inventories (Yevich and Logan, 2003), biomass burning emissions by GFED inventory ~~(Lobert et al., 1999)~~(van der Werf et al., 2010), and biogenic emissions by the MEGAN model calculations (Guenther et al., 2012). In addition, NO_x from soil emissions are calculated by an algorithm depending on temperature and precipitation (Yienger and Levy, 1995).

~~The lightning~~ In order to calculate the NO_x ~~emissions calculation is initially~~ from lightning, flash rates are first calculated in active deep convection using the Price and Rind Scheme based on the cloud-top-height ~~parameterization (Price and Rind, 1992, 1994)with a "~~(Price and Rind, 1992, 1994), then flash rates are adjusted with local scaling factors to match the satellite climatology (Sauvage et al., 2007b; Murray et al., 2012),

and the total column emissions are determined using NO_x yields that differ in tropics and northern extratropics. Finally, the total column is distributed vertically using the reverse C-shaped ~~" profile describing LNO_x vertical distribution (Pickering et al., 1998; Ott et al., 2010). Lightning flashes are constrained using the climatologies from the LIS/OTD observations (Sauvage et al., 2007b; Murray et al., 2012). Global~~ profile from Ott et al. (2010). Note that the base lightning NO_x ~~emissions are also constrained to 6 $TgN \cdot yr^{-1}$ in order to match to satellite observations (Martin et al., 2007).~~ scheme is described in detail by Murray et al. (2012).

2.2 The Meso-NH model

The Meso-NH model is an atmospheric model developed jointly by the Laboratoire d'Aérologie and by CNRM-GAME (http://mesonh.aero.obs-mip.fr/mesonh51). The model includes a non-hydrostatic and anelastic system of equations (Lafore et al., 1998) and has a complete set of parameterizations allowing to reproduce physical processes such as radiation (Gregory et al., 2000), atmospheric turbulence (Cuxart et al., 1999), convection (Bechtold et al., 2000), microphysics related to warm clouds (Cohard and Pinty, 2000), and atmospheric ice (Pinty and Jabouille, 1999; Lascaux et al., 2006). Meso-NH includes also on-line chemistry (Tulet et al., 2003, 2006). The model deals with large (synoptic) to small (large eddy) scales. In this study, the Mesonh-49 version was used in order to compare the horizontal diffusion coefficient (D_h) estimate within the anvil of thunderstorms from in-situ measurements to a modeling ideal case of a convective cell.

2.3 The DSMACC chemical box model

The Dynamical Simple Model of Atmospheric Chemical Complexity (DSMACC) is a simple box model developed for improving our understanding of the tropospheric chemistry (Emmerson and Evans, 2009). The model is composed of the KPP chemical pre-processor (Damian et al., 2002) to solve differential equations representing the chemical system. The TUV (Tropospheric Ultraviolet and Visible Radiation Model) photolysis scheme is used, which calculates the spectral irradiance, the spectral actinic flux, photodissociation coefficients (J-values) (Madronich and Flocke, 1999), and biologically effective irradiance. The chemical scheme used derives from the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/MCM/), (Jenkin et al., 1997; Saunders et al., 2003), which contains 17000 elementary reactions of 6700 primary, secondary and radical species.

In order to study the chemical interactions that could occur in the undiluted plume fraction, a set of short simulations was carried out with the DSMACC chemical box model as explained in the section 3.2.2.

2.4 The simple plume dispersion model

To model the dispersion of lightning NO_x emissions we use a simple dispersion model similar to the plume model used for aircraft NO_x emissions, except that the plume is supposed to be oriented along a vertical axis. The plume is represented as a cylinder that encompass horizontal diffusion with a constant coefficient D_h (section 3.2.1). This simple model is composed of 30 horizontal circles with spacing increasing progressively from the center axis. The discretization of the diffusion equation is mass conservative.

The chemistry scheme and associated reaction rate constants is adapted from the large-scale chemical model MOCAGE (Teyssèdre et al., 2007). It includes the main reactions involved in the $NO_x - HO_x$ system. Simple plume simulations were performed in order to estimate the physical and chemical characteristics of the plumes related to lightning NO_x emissions.

3 Plume parameterization for lightning NO_x emissions

3.1 General description

The LNO_x plume parameterization is based on a method initially developed by Cariolle et al. (2009) for NO_x emissions related to aircraft exhausts later adapted to ship emissions of NO_x (Huszar et al., 2010). In this approach, the plume effects at sub-grid scale are represented via a fuel tracer, to follow the amount of the emitted species in the plume and an effective reaction rate for the ozone production and nitric acid production/destruction during the plume's dilution into the background (Cariolle et al., 2009; Paoli et al., 2011). The parameterization requires a proper estimation of the characteristic plume lifetime during which the non-linear interactions between species are important and simulated via specific rates of conversion. The approach ensures the mass conservation of species in the model. This is the only method which considers a plume evolution related to the local NO_x emissions allowing the transport of the non-linear effects occurring at smaller scale than the model grid.

3.1.1 Physical plume formulation

Following Cariolle et al. (2009), a passive tracer (from the perspective of the usual model chemistry) is added to the ~~model~~ CTM to represent NO_x emitted by lightning. The LNO_x tracer initial mass corresponds to the NO_x mass at the start time of the simulation. Rather than increasing the concentration of ~~the~~ NO_x ~~tracer in the model~~within the CTM, lightning NO_x emissions now increase the concentration of this new passive tracer which is transported in the standard way by advection and turbulence. Plume chemistry is considered to be significant when the ~~concentration~~ mixing ratio of the lightning NO_x tracer is higher than a critical NO_x content, hereafter denoted r_l. Above this value the lightning NO_x tracer is transferred to the normal NO_x tracer at a rate described by a plume lifetime (τ), which is an exponential decay constant. This corresponds to an exchange time

scale between the lightning NO_x plume and the background NO_x. The continuity equation related to the tracer evolution is detailed by the equation 1.

$$\frac{\partial \overline{r_{LNO_x}}}{\partial t} + < F_{LNO_x} >= I - \frac{1}{\tau} \cdot \overline{r_{LNO_x}} \quad (1)$$

Where $\overline{r_{LNO_x}}$, is the ~~concentration (in $molecules \cdot cm^{-3}$~~ mixing ratio (in ppb) of the NO_x lightning tracer in the model grid (note that all overlined terms referred to grid average quantities in the CTM), $F_{LNO_x} \equiv \nabla \cdot (\overline{r_{LNO_x}} u) + \nabla \cdot (D_t \nabla \overline{r_{LNO_x}})$ and it corresponds to the flux divergence related to the large-scale transport of the tracer (advection and turbulent diffusion, in ~~$molecules \cdot cm^{-3} \cdot s^{-1}$~~ $molecules \cdot cm^{-2} \cdot s^{-1}$), I is the injection rate of ~~NO_x (in $molecules \cdot cm^{-3} s^{-1}$~~ LNO_x (in s^{-1}) and τ is the plume lifetime (in seconds).

The calculation of τ requires evaluating the mass fraction of the lightning NO_x (M(t)) corresponding to the undiluted fraction of the plume and characterized by a NO_x ~~concentration~~ mixing ratio above the r_l critical value. In other words, the plume boundary is defined by the critical value r_l depending on the time of day. The NO_x mass, M(t) decreases monotonically to zero until $t = T_l$ for which the tracer ~~concentration~~ mixing ratio is everywhere below the r_l threshold. The plume lifetime is obtained by an exponential function depending on the mass (equations 2 and 3):

$$M(t) = \int_{V_p} \rho \cdot r_p \cdot \mathrm{d}V \quad (2)$$

$$\tau = \int_{t_0=0}^{+\infty} \exp(-t/\tau) \cdot \mathrm{d}t = \frac{1}{M(t_0)} \int_{t_0=0}^{T_l} M(t) \cdot \mathrm{d}t \quad (3)$$

Where V_p is the volume of the plume, ρ is the density of the air, r_p is the NO_x ~~concentration~~ mixing ratio within the plume (~~$molecules \cdot cm^{-3}$~~ in ppb) and T_l is the time for which the ~~concentration~~ mixing ratio r_p is everywhere below the critical value r_l. The calculation of the plume lifetime, by simple plume dispersion simulations, depends on (i) the initial emissions of NO_x by lightning, (ii) the r_l value, and (iii) the dispersion properties of the atmosphere (related to the horizontal diffusion coefficient, D_h) and is detailed on the section 3.2.3.

Note that the mean dispersion properties of the atmosphere were associated with the horizontal diffusion only. The lightning NO_x emissions occur in the convective part of clouds where the vertical diffusion is ~~less efficient than the horizontal one (Cariolle et al., 2009) and it is not considered in this study. In addition~~strong. Therefore, the vertical diffusion coefficient is a determining parameter for the LNO_x distribution in the cloud. As mentioned in section 2.1, the vertical ~~dispersion of the plume is related to the vertical distribution of~~ distribution of the LNO_x ~~a priori forced in the GEOS-Chem model by the C-shape profile (Ott et al., 2010) and it is beyond the scope of this study~~is a priori calculated from Ott et al. (2010) as a reverse C-shaped profile. The LNO_x plume parameterization

is applied a posteriori after that lightning NO_x are vertically prescribed and concerns convective outflow where the NO_x are detrained in the troposphere. In this region of detrainment, the horizontal dispersion may be more efficient than the vertical one as it is discussed in (Cariolle et al., 2009).

3.1.2 Plume chemistry of NO_x, O_3 and HNO_3

Once the lightning NO_x is emitted, it is transferred to model's background NO_x based on the lifetime of the plume (τ). Thus, the continuity equation for the NO_x species emitted in the plume and released to the large scale can be deduced as described by the equation 4.

$$\frac{\partial \overline{r_{NO_x}}}{\partial t} + < F_{NO_x} >= + \frac{1}{\tau} \cdot \overline{r_{LNO_x}} \cdot \alpha_{NO_x} \cdot EI_{NO_x} + L_{ss} \quad (4)$$

Where, $\overline{r_{NO_x}}$, is the ~~concentration~~ mixing ratio of NO_x (~~$molecules \cdot cm^{-3}$~~in ppb) in the model grid, α_{NO_x} is the molecular mass ratio between the air and NO_x species ~~, EI_{NO_x} is the emission index for NO_x (in g/kg)~~ and L_{ss} are the large-scale sources and sinks (in ~~$molecules \cdot cm^{-3} \cdot s^{-1}$~~$molecules \cdot cm^{-2} \cdot s^{-1}$) such as natural and anthropogenic emissions, photochemical reaction, mixing, and conversion to reservoir species.

We consider a fairly simple chemistry within the plume as described below. The increase of the nitrogen oxides concentration in the upper troposphere leads to ozone production through the reaction of NO with peroxyde (HO_2), CH_3O_2, or RO_2 radicals from the OH oxydation as shown by the reaction $R1$.

$$NO + RO_2 \longrightarrow NO_2 + RO \quad (R1)$$

In the case of large NO_x injection by lightning, the NO_x content (~ 40 ppt in unpolluted atmosphere) becomes ~~of the same order~~ close (a few ppb, according to in-situ measurements, Dye et al. (2000); Huntrieser et al. (2002)) ~~than~~ to the surrounding ozone (60 ± 24 ppb) (Jaéglé et al., 1998). The ozone evolution within the plume is described by the reactions R2-R6.

$$NO_2 + h\nu(\lambda < 400\text{nm}) \longrightarrow NO + O \quad (R2)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (R3)$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (R4)$$

$$O + NO_2 \longrightarrow NO + O_2 \quad (R5)$$

$$O + O_3 \longrightarrow 2O_2 \quad \text{(R6)}$$

From these equations we can define an O_x family (~~$O_x \equiv O + O_2 + NO_2$~~$O_x \equiv O + O_3 + NO_2$) where the only net loss of O_x is by reactions between atomic oxygen and NO_2 or O_3. The ~~sums of the concentrations as detailed~~ rate of change of each chemical family are given by the equations 5, 6 and 7 (Cariolle et al., 2009).

$$\frac{d(O + O_3)}{dt} \frac{d([O] + [O_3])}{dt} = +k_2 \cdot [NO_2] - k_3 \cdot [NO] \cdot [O_3] - k_5 \cdot [O] \cdot [NO_2] - 2 \cdot k_6 \cdot [O_3] \cdot [O] \quad (5)$$

$$\frac{d(O + O_3 + NO_2)}{dt} \frac{d([O] + [O_3] + [NO_2])}{dt} = -2 \cdot k_5 \cdot [O] \cdot [NO_2] - 2 \cdot k_6 \cdot [O_3] \cdot [O] \quad (6)$$

$$\frac{d(NO + NO_2)}{dt} \frac{d([NO] + [NO_2])}{dt} = 0 \quad (7)$$

Where k_i correspond to the rate constants for the R_i reactions.

Thus two processes occur to O_3 in the plume at daytime. On short timescales O_x is conserved. Lightning emissions of NO in the plume are converted into NO_2 but as NO_2 is in O_x family, there is net conservation of O_x. However, on long timescales O_x can be destroyed through the reaction of O with NO_2 and O_3. Both of these processes need to be considered.

The first regime (regime I) occurs at low concentrations of NO_x (relative to O_3). Under these conditions the reaction R5 is slow. There is the rapid equilibrium between NO, NO_2 and O_3 (reactions R2, R3 and R4). As a consequence, O_3 is converted into NO_2 and can be restored later after dilution of the plume depending on the balance between NO and NO_2 at ~~the~~ large scale (Cariolle et al., 2009). Overall O_x is conserved. In this regime NO emitted reacts with the available O_3 until the NO to NO_2 ratio in the plume reaches that in the background. Thus, the impact on the O_3 background concentration is to reduce it by the number of molecules of NO emitted multiplied by the background NO_2 to NO_x ratio. The effect of the first regime on the ozone burden is expressed by the equation 8.

$$\frac{\partial \overline{r_{O_3}}}{\partial t} + < F_{O_3} > = -\frac{1}{\tau} \cdot \overline{r_{LNO_x}} \cdot \alpha_{NO_x} \cdot EI_{NO_x} \cdot (\frac{\overline{NO_2}}{\overline{NO_x}} - E) \cdot \delta + L_{ss} \quad (8)$$

Where, $\overline{r_{O_3}}$, is the ~~concentration~~ mixing ratio of O_3 (~~$molecules \cdot cm^{-3}$~~in ppb) in the model grid, E is the $\frac{NO_2}{NO_x}$ ratio in the initial emissions, δ is equal to 1 during the day and 0 at nighttime, L_{ss} are the sources and sinks of ozone such as photochemical production, transport from the stratosphere,

surface deposition, photolysis reactions, and photochemical destruction.

The second regime (regime II) occurs at high concentrations of NO_x (relative to O_3). Under these conditions the rate of R5 is large. The non-linear chemical interactions between NO_x and O_3 occur with different rates than in the background atmosphere. To account for this, Cariolle et al. (2009) introduced an effective reaction rate constant (K_{eff}), which is related to the production or the destruction of the odd oxygen (O_x) within the plume. K_{eff} is expressed by the equation 9.

$$K_{eff} = \frac{\int_{t_0}^{T_l}(\int_{V_p} K \cdot r_{NO_x}^P \cdot r_{O_3}^P \cdot \mathrm{d}V_p) \cdot \mathrm{d}t}{\overline{r_{O_3}} \cdot \int_{t_0}^{t_l}(\int_{V_p} r_{NO_x}^P) \cdot \mathrm{d}V_p) \cdot \mathrm{d}t} \tag{9}$$

Where $r_{NO_x}^P$ and $r_{O_3}^P$ are the ~~concentration~~ mixing ratios of nitrogen oxides and ozone within the plume, $\overline{r_{O_3}}$ is the background ozone mixing ratio averaged in the model grid and K is the rate of NO_x-O_3 reaction within the plume.

The analysis of the chemical reactions related to the two regimes shows that ~~$O_3 \gg O$ and $k_5 \cdot NO_2$~~ $[O_3] \gg [O]$ and $k_5 \cdot [NO_2]$ is more efficient than ~~$k_6 \cdot O_3$~~ $k_6 \cdot [O_3]$ as a sink for O_x (Cariolle et al., 2009). Thus, the equation 6 is simplified to give the equation 10.

$$\frac{d(O_3 + NO_2)}{dt} \frac{d([O_3] + [NO_2])}{dt} = -2 \cdot k_5 \cdot [O] \cdot [NO_2] \tag{10}$$

Consequently, K_{eff} can be simplified to equation 11.

$$K_{eff} = \frac{2 \cdot (\int^T k_5 \cdot O \cdot NO_2 \cdot \mathrm{d}t)}{(NO_x \cdot \int^T O_x \cdot \mathrm{d}t)} \tag{11}$$

The calculation of K_{eff} is detailed in section 3.2.4. Considering the two regimes related to the sub-grid plume chemistry, the ozone burden is described by the equation 12 at daytime and nighttime. Note that at nighttime there is no direct impact due to the ozone plume chemistry on its burden as $\delta = 0$. Only indirect effects are expected from NO_y chemistry.

$$\frac{\partial \overline{r_{O_3}}}{\partial t} + < F_{O_3} > = -\frac{1}{\tau} \cdot \overline{r_{LNO_x}} \cdot \alpha_{NO_x} \cdot EI_{NO_x} \cdot (\frac{\overline{NO_2}}{\overline{NO_x}} - E) \cdot \delta - K_{eff} \cdot \overline{r_{LNO_x}} \cdot \rho \cdot \alpha_{NO_x} \cdot EI_{NO_x} \cdot \overline{r_{O_3}} \cdot \delta + L_{ss} \tag{12}$$

In addition, we consider the conversion of NO_x into HNO_3 within the plume. This conversion takes place in two different ways depending on the day or night atmospheric conditions. During the day, NO_2 reacts primarily with OH to give HNO_3 directly and it is characterized by the coefficient β_1. While at nighttime the conversion of NO_x to HNO_3 occurs ~~through~~ mainly through the N_2O_5 formation followed by a heterogeneous hydrolysis reaction, which corresponds to β_2. In other words,

the β coefficients are the molar fractions of NO_x converted to HNO_3 within the plume. These two fractions are unitless.

In summary, the equation system solved at large scale by the CTM for lightning NO_x source is detailed by the equations 13, 14 and 15.

$$\frac{\partial \overline{r_{NO_x}}}{\partial t} + < F_{NO_x} >= +\frac{1}{\tau} \cdot \overline{r_{LNO_x}} \cdot (1 - \beta_1 \cdot \delta - \beta_2 \cdot (1 - \delta)) \cdot \alpha_{NO_x} \cdot EI_{NO_x} + L_{ss} \quad (13)$$

$$\frac{\partial \overline{r_{HNO_3}}}{\partial t} + < F_{HNO_3} >= +\frac{1}{\tau} \cdot \overline{r_{LNO_x}} \cdot (\beta_1 \cdot \delta + \beta_2 \cdot (1 - \delta)) \cdot \alpha_{NO_x} \cdot EI_{NO_x} + L_{ss} \quad (14)$$

$$\frac{\partial \overline{r_{O_3}}}{\partial t} + < F_{O_3} >= -(\frac{1}{\tau} \cdot (\frac{\overline{NO_2}}{\overline{NO_x}} - E) + K_{eff} \cdot \overline{r_{O_3}} \cdot \rho) \cdot \overline{r_{LNO_x}} \cdot \alpha_{NO_x} \cdot EI_{NO_x} \cdot \delta + L_{ss} \quad (15)$$

Where, $\overline{r_{NO_x}}$, $\overline{r_{HNO_3}}$ and $\overline{r_{O_3}}$, correspond to the NO_x, HNO_3 and O_3 ~~concentrations~~ mixing ratios averaged over the grid cell of the model, respectively.

In this study, the tropospheric chemistry and especially the LNO_x plume chemistry is considered both at daytime and nighttime since all reactions are not initiated during the day. The chemical interactions during the night correspond mainly to the reactions of O_3 and O with NO and NO_2 as well as the NO_x deactivation and the chemistry of the nitrogen reservoir species (here HNO_3 ~~, N_2O_5 and PAN~~ and N_2O_5) and the nitrate radical (NO_3). NO_3 is the main oxidant in night conditions and ~~it~~ is produced from the slow oxidation of NO_2 by O_3 (reaction $R7$).

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (R7)$$

The other dominant source of NO_3 is the destruction of N_2O_5 (reaction $R8$), but as N_2O_5 is formed from NO_3 (reaction $R9$), the two species act in a coupled manner.

$$N_2O_5 + M \longrightarrow NO_3 + NO_2 + M \quad (R8)$$

$$NO_3 + NO_2 + M \longrightarrow N_2O_5 + M \quad (R9)$$

As mentioned previously, N_2O_5 is a ~~determinant~~ determining species for the tropospheric chemistry at nighttime allowing the HNO_3 formation by the heterogeneous reaction on the particle surface (aerosols and ice crystals). During the day, NO_3 rapidly ~~undergo~~ undergoes photolysis to produce NO or NO_2. In addition, NO_3 reacts very quickly with NO which is more concentrated at daytime than at nighttime (reaction $R10$) but NO_3 is very low at daytime. However, this reaction can take

place during the night especially for a plume characterized by high NO ~~concentrations (~~mixing ratios (like a plume from lightning emissions) which is transported both during the day and night.

$$NO_3 + NO \longrightarrow NO_2 + NO_2 \quad \text{(R10)}$$

Furthermore, the nitrate radical can potentially reacts with VOCs. The reaction of the unsaturated hydrocarbons such as, isoprene, butenes, and monoterpenes, with NO_3 leads to the HNO_3 formation (Monks, 2005) (reaction $R11$).

$$NO_3 + RH \longrightarrow HNO_3 + R \quad \text{(R11)}$$

Considering NO_3 reaction with alkenes, an additional mechanism is found initiating a complex chemistry allowing to form NO_2 or organic nitrates (Monks, 2005). Finally, NO_3 can initiate the VOCs oxidation via peroxy radical production (reaction $R12$). That way, it can involve as a chain propagator (reactions R13 to R17).

$$NO_3 + \text{Organic Compound} \longrightarrow R + \text{Products} \quad \text{(R12)}$$

$$R + O_2 + M \longrightarrow RO_2 + M \quad \text{(R13)}$$

$$RO_2 + NO_3 \longrightarrow RO + NO_2 + O_2 \quad \text{(R14)}$$

$$RO + O_2 \longrightarrow R^{'}R^{''}CO + HO_2 \quad \text{(R15)}$$

$$HO_2 + O_3 \longrightarrow OH + 2O_2 \quad \text{(R16)}$$

$$HO_2 + NO_3 \longrightarrow OH + NO + O_2 \quad \text{(R17)}$$

The reactions of HO_2 with ozone ($R16$) or NO_3 ($R17$) imply OH production. Also, the reaction of ozone with alkenes ~~allows to form~~ allowing formation of OH during the night (reaction $R18$) (Aumont, 2005).

$$\text{Alkene} + O_3 \longrightarrow v_1OH + v_2HO_2 + v_3RO_2 \quad \text{(R18)}$$

The reaction $R18$ occurs when ozone concentrations remain sufficiently high in night conditions, in other words for polluted atmosphere.

In this context, we consider different values at daytime and nighttime for the plume lifetime, the effective reaction rate constant and for the fraction of NO_x conversion into HNO_3 within the plume. Distinguishing day and night chemistry is linked with the fluctuation of the critical r_l value (below which the sub-grid plume chemistry is negligible) depending on atmospheric conditions. Therefore, if r_l changes with sunlight, the plume lifetime changes also. Note that except the β_2 fraction, this night chemistry is not considered by the initial plume approach developed by Cariolle et al. (2009), which considers NO_x plumes from aircraft exhausts only at daytime.

Figure 1 summarizes all elements which define the plume approach and how it has been adapted and implemented into the model.

3.2 Parameter calculations for lightning NO_x emissions

In order to reproduce more accurately the lightning NO_x sub-grid chemistry, some points should be considered: (i) the latitude (NO_x emissions by lightning are higher in tropics than in mid-latitudes); (ii) the sunlight conditions (day and night) which impacts photochemistry and heterogeneous chemistry; (iii) the plume evolution with its own physical characteristics (the lifetime and the dispersion properties); and finally (iv) chemical interactions within the plume related to ~~high concentrated fraction of~~ highly elevated NO_x ~~considerably higher than background concentrations~~ concentrations relative to the background. In the following section, physical and chemical characteristics of the plume associated with lightning NO_x source have been defined.

3.2.1 Dynamical conditions

The horizontal diffusion coefficient (D_h) is a key parameter of the atmospheric dynamical conditions in determining the dispersion of the lightning NO_x plume. D_h is used as the dispersion constraint for the simple plume dispersion simulations carried out in order to estimate the plume lifetime and the effective reaction rate constant. The diffusion coefficient was ~~defined by~~ determined by two different ways. A first estimate of the horizontal diffusion was performed by running the 3-D mesoscale Meso-NH model~~but mainly from previous~~. Then, the D_h coefficient was calculated using in-situ ~~measurement~~ measurements in thunderstorm anvil.

The Meso-NH mesoscale model was used (see section 2.2) to investigate D_h. A simple convective cell forced by warm bubble and initialized by a radiosounding at the ~~beginning of the simulation~~ simulation start was run as an ideal case. Simulations were realized for a domain of 24 km in the two horizontal directions and the grid horizontal resolution is $\Delta x = \Delta y = 1$ km and $\Delta z = 500$ m. The convective cell is located at $43.29° N$ latitude and $0°$ longitude (Klemp and Wilhelmson, 1978). Simulations of 6 hours were ~~made~~ performed allowing the complete development and the dissipation of the convective cell. D_h has been calculated within the anvil using the mixing length diagnostic

variable, hereafter denoted L, as described by the equation 16 (Cuxart et al., 1999).

$$D_h = \frac{2}{3} \times \frac{L}{4} \times e^{\frac{1}{2}} \exp(\frac{1}{2}) \quad (16)$$

At the mature stage of the cell, D_h was calculated as 100 $m^2 \cdot s^{-1}$ within the upper levels of the convective cell (i.e. in the anvil, defined empirically).

In addition to modeling estimate, we used in-situ measurements to calculate D_h. Turbulence measurements were performed by a B-757 commercial aircraft along a ~~fight~~ flight from the west of Kansas to the north of Missouri and corresponding to a trajectory of more than 500 km (Trier and Sharman, 2008). These in-situ measurements were accomplished from 0700 to 1000 UTC the 17 June, 2005, during the development of a mesoscale convective system (MCS). This MCS is associated with a turbulence event characterized by the measurement of the atmospheric eddy dissipation rate (ϵ) and the turbulence kinetic energy (TKE) above and within the cloud anvil. The higher values of ϵ ($\epsilon^{1/3} \sim 0,4\ m^{2/3} \cdot s^{-1}$) were recorded between 11.3 and 11.6 km altitude corresponding to the cloud anvil levels. In addition, for this MCS, the TKE was about 1 $m^2 \cdot s^{-2}$ at the locations of the highest ϵ values.

According to these observations, the turbulent diffusivity (equation 17) was estimated above the anvil of the MCS (http://www.ral.ucar.edu/projects/turb_char/) such as: $D_h > 0.1\ m^2 \cdot s^{-2}$. Then, D_h was calculated within the anvil such as: $D_h = 15\ m^2 \cdot s^{-1}$ using the same formulation (equation 17). This last estimate seems to be the most common value compared to the diffusion coefficient value of 20 $m^2 \cdot s^{-1}$ used by Cariolle et al. (2009), close to the tropopause level and the D_h value calculated for contrails (15 $m^2 \cdot s^{-1}$) in the upper troposphere (Knollenberg, 1972).

$$D_h = \frac{(TKE)^2}{\epsilon} \quad (17)$$

The D_h estimate using Meso-NH model is high compared to the results from measurements and corresponds to the upper limit of the calculated diffusion coefficients and could be associated with the turbulence in the convective cloud. However, it is important to note that usually most numerical simulations are performed with 1-D turbulence models. What is interesting in the use of Meso-NH in this study is that the 3-D turbulence is solved. This simulation provides an additional estimate of D_h allowing comparison with the calculation from in-situ measurements. Moreover, studies on the diffusivity in cloud anvils are uncommon. It is necessary to conduct additional work in the future on that issue again constrained with new in-situ measurements of the atmospheric turbulence in the anvil.

It is important to note that the 3-D turbulence is not solved online in the GEOS-Chem model because of the fine scale characterizing this process but prescribed by the GEOS-5 met fields.

Therefore, the global variability of D_h is not calculated by the CTM and it is beyond the scope of this study.

In order to cover all ~~of~~ horizontal diffusivity estimates discussed in this section the range of values 0.1, 15 and 100 $m^2 \cdot s^{-1}$ was used. The horizontal coefficient is constant for all lightning NO_x plumes which are considered in the GEOS-Chem model. Hereafter, the results are detailed for the central value $D_h = 15\ m^2 \cdot s^{-1}$. Sensitivity tests depending on the uncertainty associated with the parameter estimate are performed and presented later in section 4.3.

3.2.2 The NO_x critical plume content (r_l)

The r_l critical value is the NO_x ~~concentration~~ mixing ratio within the undiluted phase of the plume below which the non-linear chemistry can be neglected (section 3.1). It has been estimated using the 0-D DSMACC chemical box model (section 2.2). Initial conditions for simulations carried out with the DSMACC box model are from outputs of the GEOS-Chem model. Especially, initial atmospheric parameters and atmospheric background concentrations of species correspond to the average of the GEOS-Chem outputs (i) from 8 km to 11 km, (ii) for two latitude regions (tropics and mid-latitudes), and (iii) for the year 2006 (table 1). The altitude range refers to the detrainment region estimated by GEOS-Chem using the GEOS-5 met fields (section 2.1) both in the tropics and in the mid-latitudes. Note that this range could vary depending on the met fields and the convection parameterization. In addition, the LNO_x plume parameterization should have an impact outside of this altitude range mainly between 6 km and 12 km but in a lesser extent.

In order to focus on chemistry interactions only between chemical species of interest and removing the mixing influence and sunlight fluctuations, short simulations (i.e. one hour each) were run with the DSMACC model. The effects of the day or night conditions were carefully considered carrying out separate simulations at daytime and nighttime. Simulations were run for a large range of initial NO ~~concentrations~~ mixing ratios from 0.01 ppb to 1 ppm. The r_l value is defined from the NO value for which the $\frac{\partial O_x}{dt}$ trend is perturbed. In other words, r_l is associated to the second derivative of O_x, i.e. the curve optimums on figure 2. The r_l threshold was defined as to be 0.1 and 0.25 ppb during the day and night for mid-latitudes and 0.1 and 0.75 ppb during the day and night in the tropics (figure 2).

Note that the mid-latitudes and the tropics were separated because of the large differences in $LNOx$ emissions between the two regions in terms of the number of flashes in a particular convective cell which is higher in the tropics according to the LIS/OTD climatologies (Christian et al., 2003). This last point is important for the plume lifetime estimate detailed in the following section.

3.2.3 The plume lifetime τ

The plume lifetime (τ) depends directly on (i) the initial NO pulse from lightning emissions, (ii) the r_l critical value, and (iii) the diffusion properties of the atmosphere. The plume lifetime also depends on the initial size of the plume. Here we use a width of 500 m to refer to an ensemble of spikes at the cloud scale ~~.~~(i.e. each plume is defined from several electrical discharges at a convective cell scale). τ is crucial for the physical description of the NO_x plumes and it has been computed in carrying out dispersion simulations of a simple plume assumed to be cylindrical. ~~The simple model is composed of 30 levels of dispersion. In the~~ In this model, the standard atmospheric conditions are represented by temperature, pressure and species concentrations of the background atmosphere, which are similar to the initial conditions used for the DSMACC simulations. As a reminder, initial conditions are from GEOS-Chem outputs averaged (i) from 8 km to 11 km, (ii) for two latitude regions (tropics and mid-latitudes), and (iii) for the year 2006 (table 1). Simulations are initialized by a NO pulse from lightning emissions (hereafter denoted NO_i) and the plume dispersion depends on the D_h value estimated in section 3.2.1.

The initial tracer concentrations NO_i related to lightning NO emissions at the scale of a convective cell (gathering several flashes together) in mid-latitudes were defined according to previous aircraft measurement campaigns. Especially, the STERAO campaign recorded NO spikes of magnitude from 1-10 ppb related to lightning activity in thunderstorms occurring 9-10 July 1996 over ~~the~~ northern Colorado (Dye et al., 2000; Stith et al., 1999). Lange et al. (2001) measured NO spikes of 3.5 ppb during the STREAM campaign associated with a matured storm over ~~the~~ Ontario. Several peaks of NO mixing ratios from 0.7-6 ppb were also observed during EULINOX (Huntrieser et al., 2002) over Germany in July 1998. The LINOX aircraft campaign recorded NO spikes from 0.75-1.25 ppb (Huntrieser et al., 1998) related to thunderstorm over Europe, the 30 July 1996. From these studies, the NO concentration associated with the electrical activity in thunderstorms occurring over the mid-latitudes was determined as $NO_i^{mean,Midlats}$ = 3.4 ppb ($NO_i^{min,Midlats}$ = 0.7 ppb and $NO_i^{max,Midlats}$ = 10 ppb). Because there are much fewer LNO_x measurements in the tropics and in order to be consistent with the LNO_x emissions defined in the GEOS-Chem model, the ratio $R_{LNO_x} = \frac{LNO_x^{Midlatitudes}}{LNO_x^{Tropics}}$ was defined as in the CTM. During the year 2006, the relative mid-latitudes and tropics LNO_x contribution was about $R_{LNO_x} = 0.33$. This result is in agreement with higher LNO_x emissions in these regions rather than in the mid-latitudes. The value of NO mixing ratio injected by lightning in ~~tropics was defined~~ the tropics was estimated as $NO_i^{mean,Tropics}$ = 10.2 ppb ($NO_i^{min,Tropics}$ = 2.8 ppb and $NO_i^{max,Tropics}$ = 29.7 ppb).

Once NO_i estimate was completed, the calculation of the plume lifetime was achieved using the detailed formulation given in section 3.1.1. The results for τ are summarized in table 2. Hereafter, the results are detailed for NO_i^{mean} in section 4 and sensitivity tests are carried out using all NO_i values

for ~~midlatitudes and~~ the mid-latitudes and the tropics (section 5). Model calculations for NO_i^{mean} and $D_h = 15\ m^2 \cdot s^{-1}$ provide a minimum plume lifetime of 3 (6) hours for the mid-latitudes and maximum plume lifetime of 9 (21.3) hours for the tropics at daytime (nighttime).

3.2.4 The effective reaction rate constant (K_{eff})

The non-linear chemistry within the plume has been considered in calculating the effective reaction rate constant (K_{eff}), which is used to compute the formation of the secondary species (O_x and HNO_3) within the plume. That corresponds to the evolution of odd oxygen depending on the O and O_3 reactions with NO_2 and NO, and also on the NO_x activation (day) or deactivation (night) with the HNO_3, N_2O_5 and PAN chemistry. Note that in the case of lightning emissions other species like VOCs, HO_x and H_2O may be uplifted in the convective region. However, we assumed that the OPE is mainly controlled by NO_x in the upper troposphere as previously showed by Sauvage et al. (2007b). Therefore, K_{eff} calculation is here mainly dependent on NO_x content. Future studies should try to investigate this issue for lightning emissions mixed with strong surface emissions in order to sharpen our parameterization.

K_{eff} is calculated according to the equation 11 of the section 3.1.2 using the same simple plume dispersion simulations than those carried out to define the plume lifetime (section 3.2.3).

Results for K_{eff} are summarized in table 3. Model calculations using NO_i^{mean} and $D_h = 15\ m^2 \cdot s^{-1}$ give a K_{eff} value of $5.49 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$ ($4.55 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$) in the mid-latitudes and $3.64 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$ ($2.98 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$) in the tropics, at daytime (at nighttime).

Our K_{eff} ~~estimations obtained in this study are very low as well as~~ estimates are smaller than those calculated by Cariolle et al. (2009) ~~,~~ for the plume chemistry related to aircraft exhausts. In this previous work, K_{eff} varies from 1.0 to $4.2 \cdot 10^{-18}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$ with a mean value close to $3 \cdot 10^{-18}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$ depending on the NO_x loading. The very low value for K_{eff} point out that the plume parameterization implies a delay of the production of ozone at the large scale rather than its destruction within the plume.

3.2.5 The fractions of NO_x conversion to HNO_3 (β_1 and β_2)

The fractions β_1 and β_2 represent the NO_x conversion into HNO_3 within the plume at daytime and nighttime respectively. They were computed using the DSMACC chemical box model.

The β_1 coefficient was calculated for day conditions depending mainly on the OH concentration. The conversion of NO_x into HNO_3 at nighttime (β_2 coefficient) is related to the heterogeneous

reaction of N_2O_5 and so depends on particles (aerosols and ice crystals) concentration and their lifetime. This is directly linked with the surface density and the radius of particles in the anvil region of thunderstorms, which is highly uncertain. We defined these values using in situ measurements. The surface area (S_T) and the radius (R) for aerosols are defined such as: $S_T = 0.28\ m^{-1}$ and $R = 1\ \mu m^{-1}$ (Huntrieser et al., 2002) and for ice, $S_T = 0.03\ m^{-1}$ and $R = 30\ \mu m^{-1}$ (Knollenberg et al., 1993). In addition, the reaction probabilities of NO_x on aerosols and ice crystals $\gamma^{aerosols}_{N_2O_5} = 0.02$ (Evans and Jacob, 2005) and $\gamma^{ice}_{N_2O_5} = 0.03$ (Sander et al., 2006), respectively, were used for our box model simulations. These values correspond to the probability that a N_2O_5 molecule impacting an aerosol or an ice crystal surface was subjected to react. The results for β_1 and β_2 coefficients are summarized in table 4.

The estimate of β_1 fraction does not show significant variation neither between latitudes regions nor depending on NO_i. The minimum β_1 value is $1.34 \cdot 10^{-4}$ for the tropical regions and NO_i^{min}, and the maximum β_1 value is $1.88 \cdot 10^{-4}$ for the mid-latitudes and NO_i^{max}. The study of production and destruction rates for day conditions taking into account all reactions pathways (not shown here) demonstrates that production of HNO_3 during the day is mainly determined by reaction of NO_3 with formaldehyde ($HCHO$) and acetaldehyde (CH_3CHO). Surprisingly, the HNO_3 formation via the $NO_2 + OH$ reaction seems to be less efficient. This result could be explained by the low initial concentrations of OH used for the DSMACC simulations and it is in agreement with the small β_1 values. Then, the averaged β_2 coefficient is higher by a factor 10 compared to β_1 with a minimum value of $0.24 \cdot 10^{-3}$ in the tropics for NO_i^{max} and a maximum estimate of $14.4 \cdot 10^{-3}$ in the mid-latitudes for NO_i^{min}. The analysis of the production and the destruction rates for night conditions taking into account all reactions pathway shows that the predominant reaction in the HNO_3 evolution is $N_2O_5 + H_2O$ (or the heterogeneous reaction on the aerosols and ice crystals surface).

4 Results: CTM simulations

In this section, the effects of the lightning NO_x plume parameterization, i.e. the influence of the sub-grid processes related to lightning emissions, on the NO_x and O_3 tropospheric distributions at large scale are evaluated. Then, the parameterization sensitivity to initial NO mixing ratio injected by lightning (NO_i), D_h, β_1 and β_2 coefficients is analyzed to quantify the variability of the results regarding the plume-in-grid parameter calculations.

4.1 Implementation of the LNO_x plume parameterization

The implementation of the lightning NO_x plume parameterization into the GEOS-Chem model requires specifying the system of continuity equations related to the plume chemistry solved at large

scale by the model (section 3.1.2, equations 13, 14 and 15). Lightning NO_x emissions calculated in each grid box (in $molecules \cdot cm^{-2} \cdot s^{-1}$) by the model are directly used to compute the injection rate I (s^{-1}) of NO at each chemical time step of the simulation. Then, we consider ~~the following setup:~~ that $\alpha_{NO_x} = 1$ ~~and $EI_{NO_x} = 1,$~~ in order to represent the mixing ratio of the undiluted fraction of NO_x by the tracer (r_{LNO_x}). Furthermore, lightning produce ~~only~~ negligible quantities of NO_2 relative to NO ~~among NO_x species thus $E = 0$~~ and therefore E is 0 in the equation 15. Finally, the ratio $\frac{\overline{NO_2}}{\overline{NO_x}}$ is the relative balance between NO and NO_2 in the diluted phase at large scale reproduced by the model.

4.2 Impact of LNO_x emissions on the NO_x and O_3 distributions

We perform a spin-up of six months (from July 2005 to January 2006) in order to obtain a steady state in the model after activation of the plume parameterization. Then, simulations were run for the entire year 2006. The transport and the convection time steps are 15 minutes and the emissions and the chemical time steps are 30 minutes.

In the following, standard simulation refers to simulation with standard lightning NO_x emissions i.e. instantaneously diluted in a grid cell, while modified simulation refers to simulation considering the plume parameterization and then sub-grid chemistry. Note that the modified simulation was run using mean values for the initial NO mixing ratio ($NO_i^{mean,Midlats} = 3.4\ ppb$ et $NO_i^{mean,Tropics} = 10.2\ ppb$) and $D_h = 15\ m^2 \cdot s^{-1}$. The Base Case (BC) experiment corresponds to the standard simulation minus the standard simulation without lightning NO_x emissions. The $P1$ experiment corresponds to the modified simulation minus the standard simulation without lightning NO_x emissions. The $P2$ experiment is the same as the $P1$ experiment but without considering the nitrification mechanism in the modified simulation (i.e. $\beta_1 = \beta_2 = 0$). In addition, sensitivity tests were performed for $P1$ defined by the modified simulation using the minimum and the maximum values for D_h, NO_i, β_1 and β_2 coefficients. All experiments are summarized in table 5.

Lightning emissions rates and the associated LNO_x tracer distributions are first discussed, then the effects of the implementation of the plume parameterization ($P1$) compared to the experiment without the plume-in-grid development (BC case) is presented.

4.2.1 Lightning emissions and LNO_x tracer distributions

Figure 3 displays the geographical distributions of the 9 km lightning NO_x emissions (a), the related LNO_x tracer distributions (b) and the LNO_x tracer zonal averaged (c) in January (top panels) and in July (bottom panels) reproduced by the CTM from the $P1$ experiment. These results are shown for an approximate detrainment level (9 km altitude) where the detrainment of LNO_x ~~are the most concentrated~~is the largest. In January, the highest emissions of NO_x from

lightning ($4-6\cdot10^9\ molecules\cdot cm^{-2}\cdot s^{-1}$) are located in the southern hemisphere around the tropics over West Australia and Central-South Africa. Also, the model gives low LNO_x emissions ($<3\cdot10^9\ molecules\cdot cm^{-2}\cdot s^{-1}$) over South America and North America especially over the Gulf of Mexico. In July, the highest LNO_x emissions ($4-6\cdot10^9\ molecules\cdot cm^{-2}\cdot s^{-1}$) are calculated in the northern hemisphere over North America, North of India, Central Africa and Sahel. In addition, LNO_x emissions are modeled over Europe and over East Asia but to a lesser extent ($<2\cdot10^9\ molecules\cdot cm^{-2}\cdot s^{-1}$).

The lightning NO_x tracer introduced into the model represents the lightning NO_x emissions affected by the transport and the exponential decay depending on the plume lifetime. Figure 3 shows that the tracer distribution is consistent with the lightning NO_x emissions. However, it is important to note that the plume lifetime is a key factor in the evolution of the LNO_x tracer mixing ratio. A long plume lifetime (several hours to several days) allows the intercontinental transport of LNO_x plumes. The representation of the sub-grid chemistry and the transport of the non-linear chemistry effects related to the plume consideration becomes important for the chemistry of the regions located far downwind from source regions. The plume lifetime depends on the latitude because of the different background chemical concentrations and the different amount of NO_x emitted from lightning in the tropics and in the mid-latitudes. In addition, as mentioned before, we consider the influence of day and night conditions on the plume lifetime estimate. According to its preliminary calculation (section 3.2.3), the plume lifetime is longer in the tropics (9 and 21.3 hours for day and night conditions, respectively) than in the mid-latitudes (3 and 6 hours, for day and night conditions, respectively). So, the LNO_x tracer is characterized by a shorter lifetime as a plume over North America than over Central Africa and around the Sahel while the model simulated ~~less important~~ fewer emissions over these regions especially in summer. In boreal winter, the mixing ratio of the lightning NO_x tracer calculated by the model is about 0.21 ppb over Central and South Africa, 0.18 ppb over West Australia and 0.11 ppb over South America. In summer, the tracer mixing ratio is simulated as 0.21 ppb, 0.32 ppb and 0.16 ppb over Central Africa, North India and North America, respectively. The lightning NO_x tracer is ~~mainly reproduced~~ produced at altitudes where lightning NO_x are ~~produced~~ calculated and detrained (in the upper troposphere between $\sim$ 500 and 300 hPa) as shown in panels (c) in figure 3.

4.2.2 Impact of lightning on NO_x and O_3 distributions with the plume parameterization

The difference between $P1$ and BC experiments ~~($P1-BC$)~~ ($P3$) was calculated in order to quantify the changes on NO_x and O_3 mixing ratios at large scale implied by the implementation of the plume-in-grid parameterization into GEOS-Chem. Figures 4 and 5 display the geographical distributions of the NO_x, HNO_3, PAN and O_3 absolute changes (in ppb) in January and in July, respectively. The 9 km altitude level was chosen because of the most significant variations at this

altitude compared to the rest of the troposphere.

In boreal winter, LNO_x plume chemistry leads to a maximum decrease at large scale over regions of emissions of 120 ppt for NO_x and a decrease of 68 ppt for HNO_3 and 16 ppt for PAN over Central and South Africa. These variations are associated with a maximum O_3 decrease of 2.8 ppb over regions of emissions. A similar NO_x, HNO_3, PAN and O_3 reduction is obtained in other areas of high LNO_x emissions (i.e. over West Australia and South America). Downwind of LNO_x emissions, the opposite effect is observed for NO_x and HNO_3 species with maximum increase of 40 ppt for NO_x and 13.5 ppt for HNO_3 observed over South Atlantic and Indian Ocean. Generally, PAN still decreases over oceans but in a lesser extent compared to regions of LNO_x emissions, with a maximum reduction of 9 ppt. O_3 response is a maximum increase of 1.13 ppb around area where the transport is effective and especially over the oceans. In summer, maximum decreases of 140 ppt for NO_x and 60 ppt for HNO_3 and 24 ppt for PAN are calculated by the CTM leading to a maximum O_3 decrease of 2.4 ppb over Central Africa (reduction also observed over North America and North India). Downwind of lightning emissions, increase of NO_x and HNO_3 is observed with a maximum value of 30 ppt and 38 ppt, respectively. PAN reservoir species also still decreases slightly downwind with 2 ppt changes. Finally, that leads to maximum O_3 increase of 0.7 ppb.

Note that the production of PAN is limited by the supply of NO_x or non-methane ~~volatil~~ volatile organic compounds (NMVOCs). Above continental lightning sources regions, NMVOCs are uplifted by deep convection but with lower NO_x due to the activation of the plume parameterization. That implies a less efficient PAN production in these regions. Downwind of lightning sources regions (oceanic regions), NO_x increases because of the LNO_x transport in the plume form but there is less NMVOCs available to produce PAN. Therefore, ~~the~~ both in regions of LNO_x emissions and downwind, the PAN production is limited leading to ~~an~~ overall lower PAN ~~production~~ mixing ratios at large scale in P1 ~~.~~experiment. However, this may be nuanced by considering the PAN chemistry in future studies using similar LNO_x plume parameterization by introducing the PAN and CH3C(O)OO continuity equations and a new term to consider the fraction of NO_x converted to PAN within the plume. This should allow the PAN production during the plume transport, which is inhibited in the current version.

In order to provide a full overview of the effects of the plume parameterization, the relative difference between the $P1$ and BC experiments (i.e. ~~$(P1 - BC)/BC$~~ $P3/BC$) was calculated integrated throughout the troposphere. Figures 6 and 7 show zonal averaged of NO_x (upper panels) and O_3 (bottom panels) relative changes (in %) integrated throughout the troposphere for regions of interest for January and July, respectively. During boreal winter, the highest NO_x (O_3) decreases of 10 % (5 %) in West Australia, then 20 % (6 %) in Central Africa are calculated. These negative variations

are mainly calculated between 400 hPa and the tropopause level for NO_x and ozone. South America is characterized by a decrease of 20 % of the nitrogen oxides and 1 % of ozone. Over this region, variations are significant in the entire troposphere for both species. In contrast to the continent decrease, NO_x increase is observed over the major part of South Atlantic and Indian Ocean with 14 % and 20 % maximum, respectively. The O_3 response in an increase of 1 % near the tropopause and it becomes higher close to the surface of about 4 %. In summer, there is a NO_x (O_3) decrease of 25 % (8 %) over Central Africa, 20 % (2 %) over North India, and 5 % (0.5 %) over North America. Also, South Atlantic and Indian Ocean (located downwind of lightning NO_x emissions) are characterized by a maximum increase of 18 % for NO_x and 2 % for O_3.

As a result, the sub-grid chemistry associated to the LNO_x emissions implies (i) a decrease of the nitrogen oxides and ozone mixing ratios at large scale over regions characterized by intense lightning emissions and (ii) an increase of these species downwind of emissions. Especially the plume parameterization related to the lightning NO_x leads to:

1. Significant effects on NO_x mixing ratio (± 20 %): these effects on nitrogen oxides are important because NO_x is the first criterion which is constrained in a CTM in order to determine the global LNO_x production ($6\ TgN \cdot yr^{-1}$ in the GEOS-Chem model);

2. Lower effects on O_3 mixing ratio (± 5 %): these limited impacts on ozone could be explained by compensatory effect of the NO_y species (mainly conversion of NO_x into ~~(i)~~ HNO_3 within the plume~~or (ii)PAN)~~).

The effects of the plume parameterization are simulated over the entire troposphere mainly for ozone. Indeed, the spreading of effects on ozone to the lower free troposphere is related to the subsidence areas of the Walker circulation. These regions are characterized by the accumulation and creation of ozone for low altitude levels. Nevertheless, the maximum NO_x and O_3 variations are calculated for altitude levels associated with a mean detrainment level. The more realistic representation of the sub-grid processes ($P1$ experiment) related to the LNO_x plume is in contrast with the simplified instantaneous dilution in the grid cell of the lightning NO_x emissions (BC experiment).

The plume approach allows the conversion of NO_x into HNO_3 during the plume lifetime. In addition, the high NO_x concentration within the plume (much higher than the background content) leads to the O_3 titration and more generally to the O_x destruction within the plume. The most important impact of the plume parameterization is the transport of the LNO_x emissions as a plume and the transport of the associated non-linear chemistry effects leading to a delay of the O_3 production at large scale. In other words, O_3 is less produced over the regions with intense lightning NO_x emissions than downwind of LNO_x emissions by photochemical reactions from NO_x.

4.3 Plume sensitivity to the estimated uncertainties of parameter calculations

4.3.1 The Atmospheric dynamical conditions and the initial NO mixing ratio injected by lightning

The impact of (i) the diffusion properties of the atmosphere (D_h) and (ii) the initial NO mixing ratio injected by lightning (NO_i) are analyzed. D_h and NO_i are the two key parameters in the determination of the physical and chemical characteristics of the plume. The modified simulation characterizing the $P1$ experiment was run for the ranges of the horizontal diffusion coefficients and the initial NO mixing ratio injected by lightning. It is important to note that for these sensitivity tests, β_1 and β_2 coefficients remain constant using their mean values. τ and K_{eff} values related to these simulations are those previously calculated (section 3) and summarized in tables 2 and 3. Figure 8 displays τ (upper panels) and K_{eff} (bottom panels) variations depending on D_h and NO_i. As expected, the strongest the horizontal diffusion is the most efficient the dispersion of the plume is. In both, the mid-latitudes and the tropics, τ decreases when D_h becomes larger. In addition, τ increases with the initial NO mixing ratio injected by lightning. In contrary, K_{eff} increases with D_h coefficient in the two regions of the globe.

The ~~variability of~~ sensitivity of the NO_x and O_3 mixing ratios around the mean value for regions and seasons depending on the known uncertainties associated with parameter calculations have been quantified. Figure 9 shows the ~~intervals of variability~~ ranges of sensitivity of NO_x and O_3 (ΔNO_x and ΔO_3, respectively) at 9 km altitude reproduced by GEOS-Chem depending on D_h and on the initial NO mixing ratio (NO_i). Note that for the sake of readability, the scale of NO_x and O_3 changes differs by region. Results are also summarized in table 6.

We chose representative continental areas such as Florida and Congo, which correspond to regions characterized by intense electrical activity for the mid-latitudes and the tropics, respectively. North and South Atlantic were selected to represent regions downwind of NO_x emissions, for ~~mid-latitude and tropic~~ the mid-latitudes and the tropics variations, respectively. The highest ~~ranges of~~ NO_x and O_3 ~~changes~~ ranges are obtained for continental tropical regions with ΔNO_x $[-33.1; +29.7]$ ppt and ΔO_3 $[-1.56; +2.16]$ ppb, in January, and ΔNO_x $[-14.3; +21]$ ppt and ΔO_3 $[-1.18; +1.93]$ ppb, in July. The largest ~~variation~~ range associated with the tropical continents could be explained by the largest difference on parameter values defining the plume in this region (especially NO_i). The smallest ~~intervals~~ changes are observed over continental mid-latitude regions for winter with ΔNO_x $[-1.7; +1.8]$ ppt and ΔO_3 $[-0.16; +0.72]$ ppb and over oceanic tropical regions in summer such as ΔNO_x $[-11.5; +2.6]$ ppt and ΔO_3 $[-0.14; +0.92]$ ppb. As a result, the ~~variability~~ sensitivity of NO_x and O_3 species to the parameter uncertainties is a few ppt for NO_x and less than 2 ppb for O_3.

4.3.2 Coefficients related to the nitrification mechanism (β_1 and β_2)

In order to estimate the ~~variability~~ sensitivity of the NO_x and O_3 mixing ratios related to the uncertainties on β_1 and β_2 fractions (table 7), the difference between $P1$ experiment using β_1 and β_2 mean values and $P1$ experiment using minimum and maximum β_1 and β_2 coefficients has been calculated. This implies that τ and K_{eff} are constant.

In January, the highest ~~variability~~ sensitivity on NO_x mixing ratio is ΔNO_x $[-2.3; +0.9]\cdot10^{-2}$ ppt over the continental tropical regions and ΔO_3 $[-10; +11]\cdot10^{-4}$ ppb over the tropical ocean on O_3, while ~~mid-latitude~~ the mid-latitudes oceanic areas show minimum ranges on NO_x and O_3 with $\Delta NO_x \pm 2.3 \cdot 10^{-2}$ ppt associated with ΔO_3 $[-9; +4]\cdot10^{-4}$ ppb. In July, the maximum ranges are calculated over oceans in the mid-latitudes for NO_x such as ΔNO_x $[-21.1; +6.6]\cdot10^{-2}$ ppt and in the tropics for O_3 with ΔO_3 $[-30; -2]\cdot10^{-4}$ ppb. Finally, the smallest ~~intervals~~changes, ΔNO_x $[-0.9; -0.4]\cdot10^{-2}$ ppt and ΔO_3 $[-24; -6]\cdot10^{-4}$ ppb, are simulated for the tropical ocean and ~~mid-latitude~~ the mid-latitudes continent, respectively.

In addition, the impact of the nitrification mechanism was assessed comparing the $P1$ experiment using mean β_1 and β_2 values and $P2$ experiment for which $\beta_1 = \beta_2 = 0$. As a result, taking into account NO_x conversion into HNO_3 using the mean β fractions calculated in this study does not imply strong changes in NO_x and O_3 distributions ($\Delta NO_x < 10^{-4}$ ppb and $\Delta O_3 < 10^{-2}$ ppb).

In the case of significant values of β fractions, the rate of the nitrification mechanism should imply a delay of the O_3 formation from the NO_x in the plume because of the NO_x storage ~~into~~ in HNO_3. On the other hand, HNO_3 is considered as a one of the main sink for NO_x species undergoing wet deposition and seemingly limiting their affect on global ozone.

The sensitivity tests point out the limited effect of the NO_x conversion to HNO_3 within the plume using our β_1 and β_2 ~~estimates. The variability~~ calculations. The sensitivity on NO_x and O_3 mixing ratios related to β coefficients is about a few ppt. ~~That could be explained by small β values resulting from our estimate unlike Cariolle et al. (2009) highlighted the significant influence of these fractions~~ Indeed, our β_1 and β_2 estimates are smaller than those calculated by Cariolle et al., 2009 ($\beta_1 = 0.06$ and $\beta_2 = 0.2$), which showed a large impact of this mechanism in the case of aircraft NO_x emissions. ~~In our~~ In the present study, we can easily suppose that the increase of the β_1 and β_2 coefficients should be in agreement with the work of Cooper et al. (2014) in reducing the ~~underestimation of~~ underestimate of the HNO_3 production induced by NO_x emissions from lightning. Further estimates of β should be realized using future observations in cloud anvil of primary species, aerosols and particules needed for NO_x conversion at daytime and nighttime to improve the determination of these parameters. The β_1 coefficient is particularly dependent on the HO_x radicals,

which could vary significantly within the cloud anvil in part because of the transport of peroxides from the lower troposphere by convective uplift (Wennberg et al., 1998). Then, the determination of β_2, corresponding to the NO_x conversion fraction into HNO_3 via N_2O_5 formation during nighttime is considerably dependent on (i) the estimate of aerosols and the ice crystal concentration and their lifetime within the cloud anvil which is highly uncertain according to measurement campaigns and (ii) on the reaction probability on aerosols $\gamma_{N_2O_5}^{aerosol}$ and ice crystals $\gamma_{N_2O_5}^{ice}$ from laboratory studies extrapolations.

According to results presented in this section, the sensitivity tests show the predominance of the initial NO mixing ratio injected by lightning (NO_i) and the diffusion properties of the atmosphere (D_h) in the variability of the NO_x and O_3 mixing ratios around the mean value in response to the plume-in-grid parameterization in the CTM. In winter, the NO_x and O_3 ~~variability~~ sensitivity is the highest for continental regions in the tropics and the smallest ~~variability~~ sensitivity is calculated for the mid-latitudes. In summer, the most important ~~variability~~ sensitivity of NO_x and O_3 is simulated in the tropics over regions characterized by intense LNO_x emissions while the least significant sensitivity is obtained still in the tropics but downwind of emissions (mainly over oceans).

5 Conclusions

For the first time, a more realistic lightning NO_x chemistry is implemented as a plume parameterization into a global chemical transport model. The key parameters characterizing the lightning-related plume were estimated depending on two main criteria, i.e. the NO mixing ratio injected by lightning (NO_i) and the atmospheric diffusion coefficient (D_h).

According to the NO_i and D_h ranges, the plume lifetime (τ) and the effective reaction rate constant (K_{eff}) for NO_x-O_3 chemical interactions were estimated as follow:

- $\tau = [0.01; 68.5]$ hours;
- $K_{eff} = [0.77; 23] \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$.

Also, for the conditions defined by NO_i^{mean} and $D_h = 15\ m^2 \cdot s^{-1}$:

- τ is 3 (6) hours in the mid-latitudes and 9 (21.3) hours in the tropics at daytime (nighttime);
- K_{eff} is $5.49 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$ ($4.55 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$) in mid-latitudes and $3.64 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$ ($2.98 \cdot 10^{-19}\ molecules^{-1} \cdot s^{-1} \cdot cm^3$) in the tropics at daytime (nighttime).

Finally, the fractions of NO_x conversion into HNO_3 within the plume are $\beta_1 = [1.34; 1.88] \cdot 10^{-4}$, and $\beta_2 = [0.24; 14.4] \cdot 10^{-3}$ for day and night conditions respectively.

GEOS-Chem simulations performed using mean value for NO_i and $D_h = 15\ m^2 \cdot s^{-1}$ reveal nitrogen species and ozone changes compared to the instantaneous dilution. A decrease of NO_x and O_3 mixing ratios at large scale over the regions of strong LNO_x emissions is observed mainly in the northern hemisphere in summer and in the southern hemisphere in winter. In the troposphere, maximum decrease of 20 % (6 %) in January and 25 % (8 %) in July for NO_x (O_3), are found over Central Africa. In contrast, an increase of NO_x (O_3) downwind of emissions is simulated of 20 % (4 %) in January and 18 % (2 %) in July. The LNO_x plume parameterization allows the transport of the effects on the non-linear chemistry occurring within the plume and the conversion of NO_x to the nitrogen reservoir species (mainly HNO_3). However, the most significant impact is the transport of the LNO_x as a plume. That implies a delay of (i) the NO_x release into the point grid and (ii) ozone production from NO_x emitted by lightning flashes corresponding to the decrease of the NO_x and O_3 mixing ratios at large scale over regions of emissions and their increase over transport pathway.

The ~~variability~~ sensitivity of the NO_x and O_3 mixing ratios around the mean value depending on the known uncertainties on the plume physics and chemistry key parameters has been estimated. The highest sensitivity is obtained for the continental tropical regions with ΔNO_x $[-33.1; +29.7]$ ppt and ΔO_3 $[-1.56; +2.16]$ ppb, in January, and ΔNO_x $[-14.3; +21]$ ppt and ΔO_3 $[-1.18; +1.93]$ ppb, in July. Concerning the β_1 and β_2 fractions, the highest ~~variability~~ sensitivity depending on the fraction uncertainties for NO_x is $\Delta NO_x[-2.3; +0.9] \cdot 10^{-2}$ ppt over the continental tropical regions, and ΔO_3 $[-10; +11] \cdot 10^{-4}$ ppb for O_3 over the tropical ocean in January. In summer, the maximum ranges are calculated over oceans in the mid-latitudes for NO_x such as $\Delta NO_x[-21.1; +6.6] \cdot 10^{-2}$ ppt and in the tropics for O_3 with ΔO_3 $[-30; -2] \cdot 10^{-4}$ ppb. Accordingly, parameters leading to the highest uncertainties on results and which drive the plume-in-grid parameterization are NO_i and D_h.

This study demonstrates the importance to consider the plume-in-grid chemistry related to the lightning NO_x emissions occurring at smaller scale for global calculations. Taking into account the plume dilution into the background atmosphere in time and space with the transport of the NO_x and O_3 non-linear chemistry effects and the conversion of NO_x into HNO_3 reservoir species, implies more realistic NO_x and O_3 concentrations in CTM. The plume-in-grid approach, by allowing a more realistic sub-grid chemistry will allow improving the different steps in the lightning NO_x emissions modeling such as the convection process, the calculation of the NO molecules produced by lightning discharges depending on regions according to recent and future satellite observations, and also processes like the HNO_3 scavenging and the HNO_3 uptake by ice crystals.

Acknowledgements. The GEOS-Chem community (Harvard University) and the Laboratoire d'Aérologie (UPS / CNRS) supported this work. The authors acknowledge for the help of Lee T. Murray (NASA, NY, USA) for

his expertise on the lightning NO_x emissions module in the GEOS-Chem model. We thank the University Paul Sabatier III of Toulouse for giving the ATUPS grant allowing the collaboration with the Wolfson Atmospheric Chemistry Laboratories of York in the research group of Mathew J. Evans.

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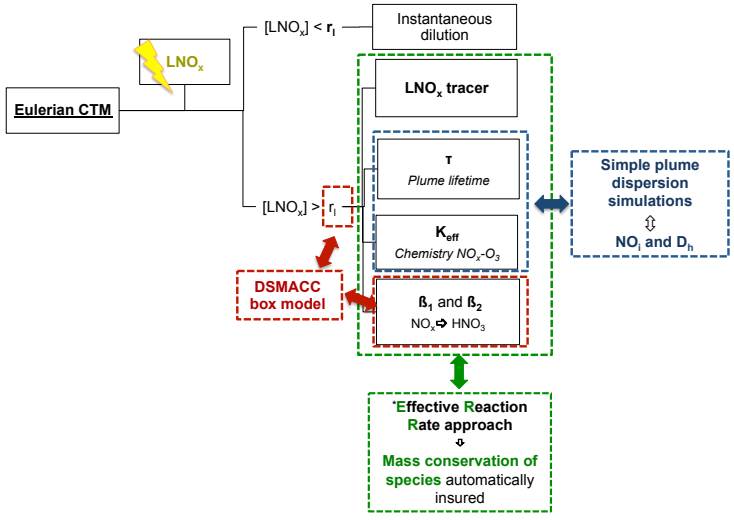

Figure 1. ~~The~~ Diagram of the lightning NO_x plume parameterization based on the Effective Reaction Rate approach. The arrows link the parameters to their estimate approach. The red boxes are for the parameters estimated with the DSMACC model and the blue boxes are related to the parameters calculated with the simple plume dispersion model. Finally the green boxes show the Effective Reaction Rate approach in the GEOS-Chem CTM.

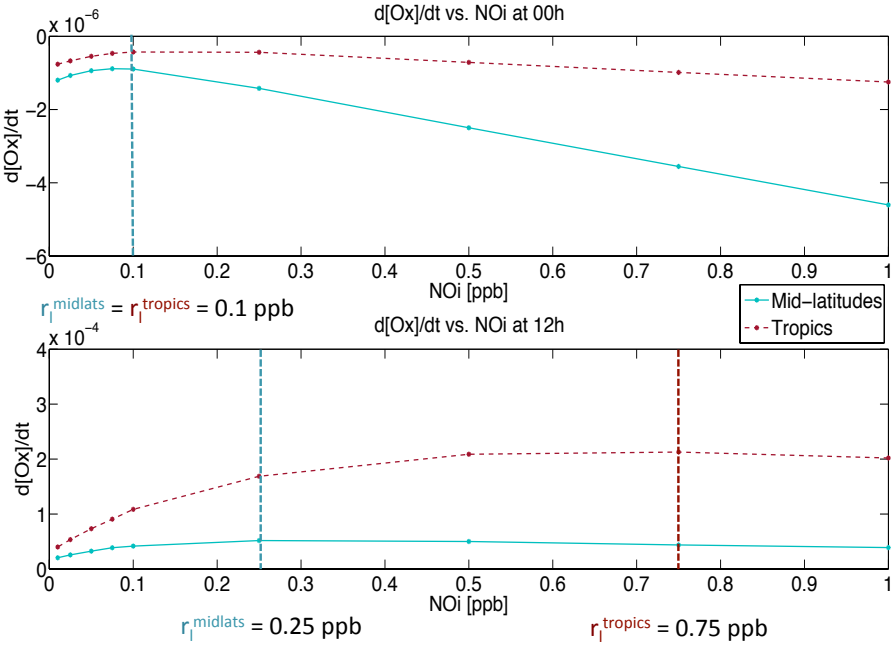

Figure 2. r_l critical value and odd oxygen trends from DSMACC chemistry box model simulations for mid-latitudes (solid line) and tropics (dotted line) (a) at midnight (upper panel) and (b) at midday (bottom panel).

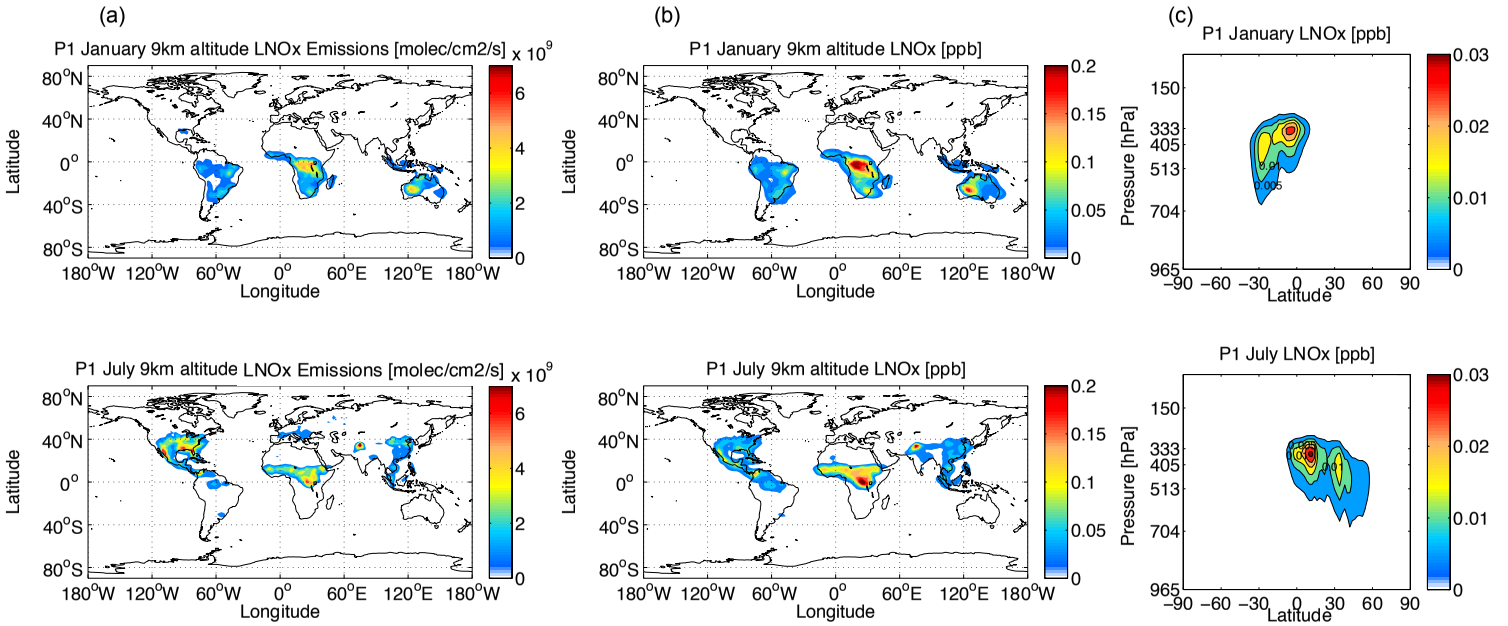

Figure 3. (left panels, a) Geographical distributions at 9 km altitude of lightning NO_x emissions, (middle panels, b) the geographical distributions of the related LNO_x tracer (in ppb) and (right panels, c) the zonal averaged of the LNO_x tracer (in ppb), for January (top) and July (bottom). Experiment $P1$, using τ and K_{eff} determined with $D_h = 15\ m^2 \cdot s^{-1}$ and NO_i^{mean}, performed with the GEOS-Chem model.

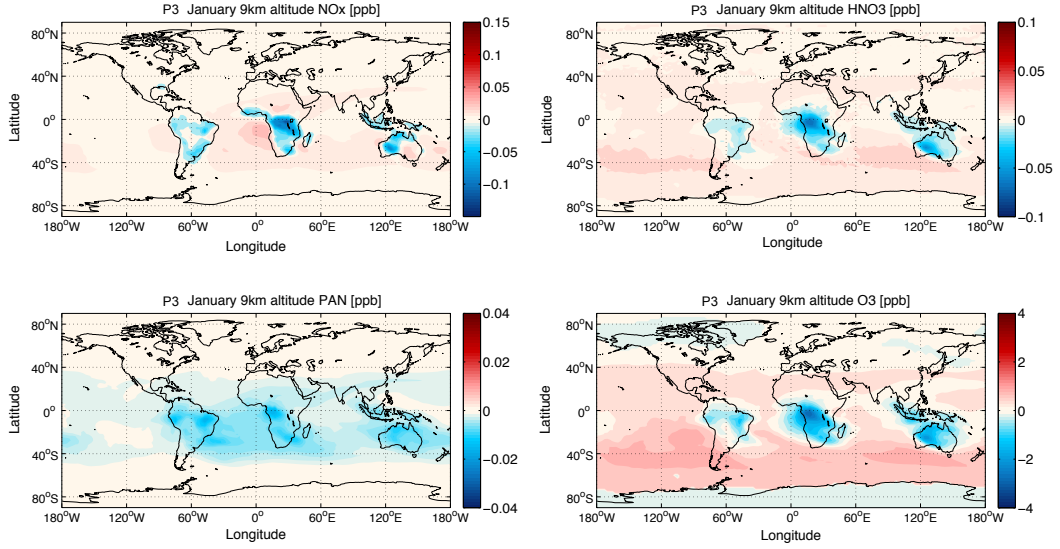

Figure 4. Geographical distributions of NO_x, HNO_3, PAN, and O_3 variations (in ppb) at 9 km altitude for January from the absolute difference (P3) between $P1$ and BC experiments. $P1$ was performed using τ and K_{eff} determined with $D_h = 15\ m^2 \cdot s^{-1}$ and NO_i^{mean} with GEOS-Chem.

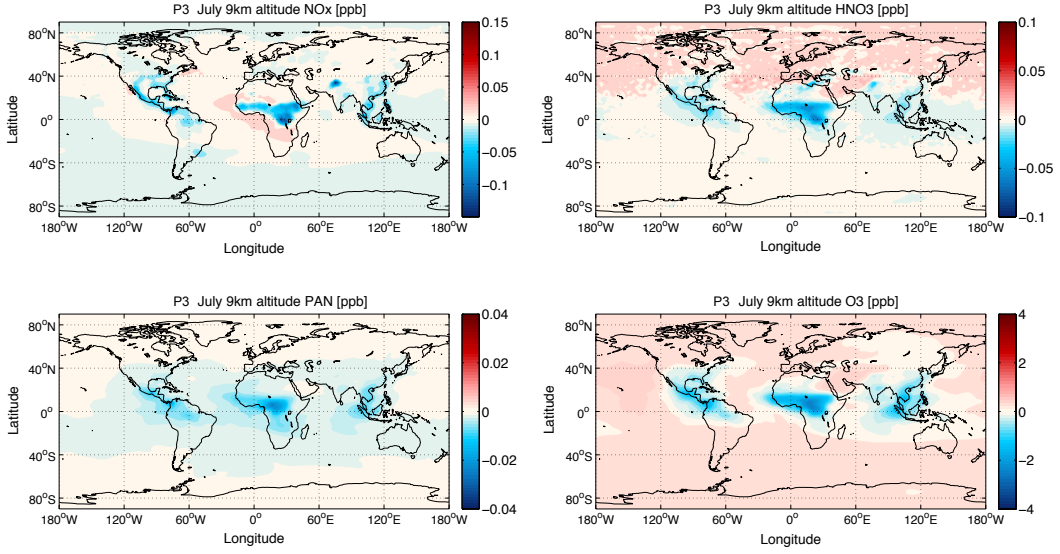

Figure 5. Geographical distributions of NO_x, HNO_3, PAN, and O_3 variations (in ppb) at 9 km altitude for July from the absolute difference (P3) between $P1$ and BC experiments. $P1$ was performed using τ and K_{eff} determined with $D_h = 15\ m^2 \cdot s^{-1}$ and NO_i^{mean} with GEOS-Chem.

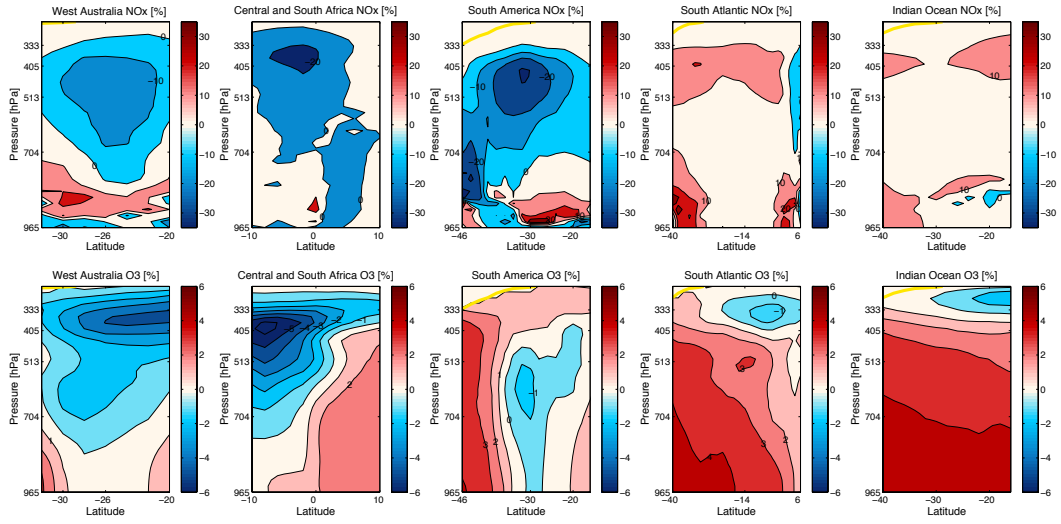

Figure 6. Zonal averaged NO_x (upper panels) and O_3 (bottom panels) variations (in %) over the regions characterized by strong NO_x emissions for January (the yellow solid line represents the tropopause level), from the relative difference between $P1$ and BC experiments (~~$(P1-BC)/BC$~~ $P3/BC$). $P1$ was performed using τ and K_{eff} determined with $D_h = 15\ m^2 \cdot s^{-1}$ and NO_i^{mean} with GEOS-Chem.

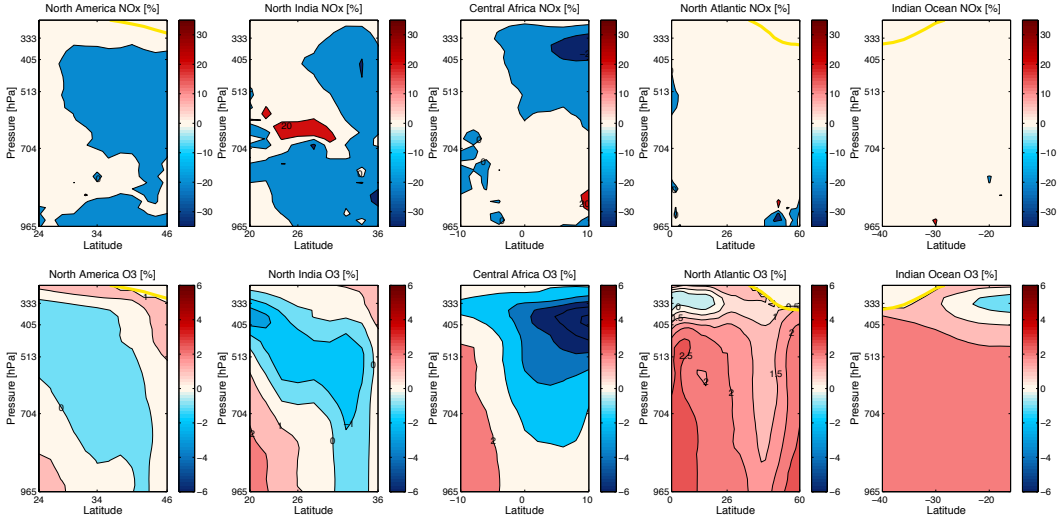

Figure 7. Zonal averaged NO_x (upper panels) and O_3 (bottom panels) variations (in %) over the regions characterized by strong NO_x emissions for July (the yellow solid line represents the tropopause level), from the relative difference between $P1$ and BC experiments (~~$(P1-BC)/BC$~~ $P3/BC$). $P1$ was performed using τ and K_{eff} determined with $D_h = 15\ m^2 \cdot s^{-1}$ and NO_i^{mean} with GEOS-Chem.

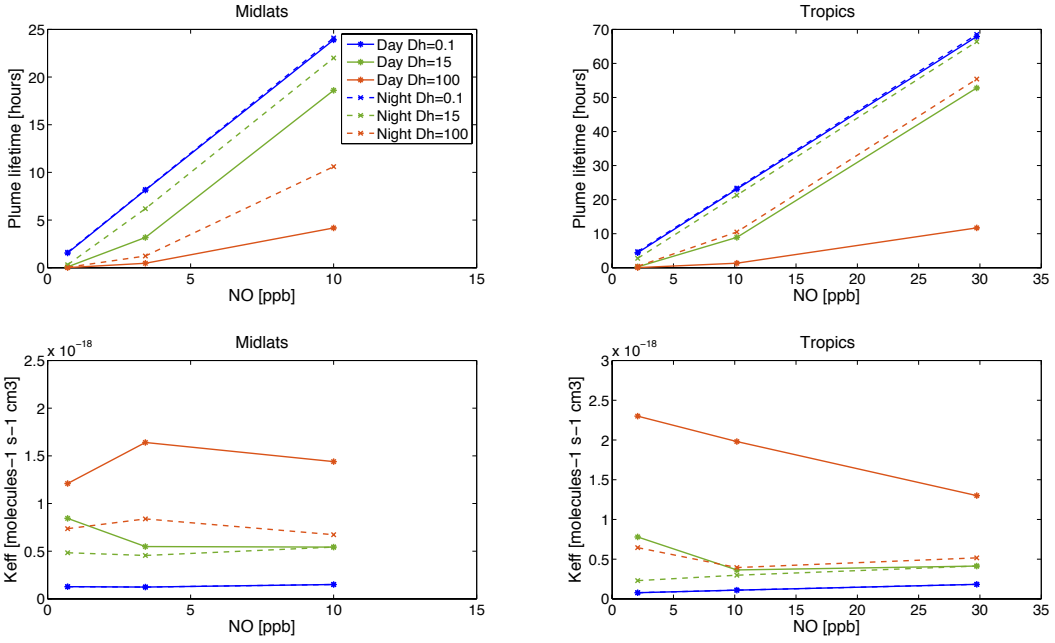

Figure 8. The plume lifetime (τ, upper panels) and the effective reaction rate constant (K_{eff}, bottom panels) depending (i) on the horizontal coefficient diffusion (D_h, $m^2 \cdot s^{-1}$) for the mid-latitudes (left panels) and the tropics (right panels) and (ii) on the NO mixing ratio injected by lightning (NO_i, in ppb).

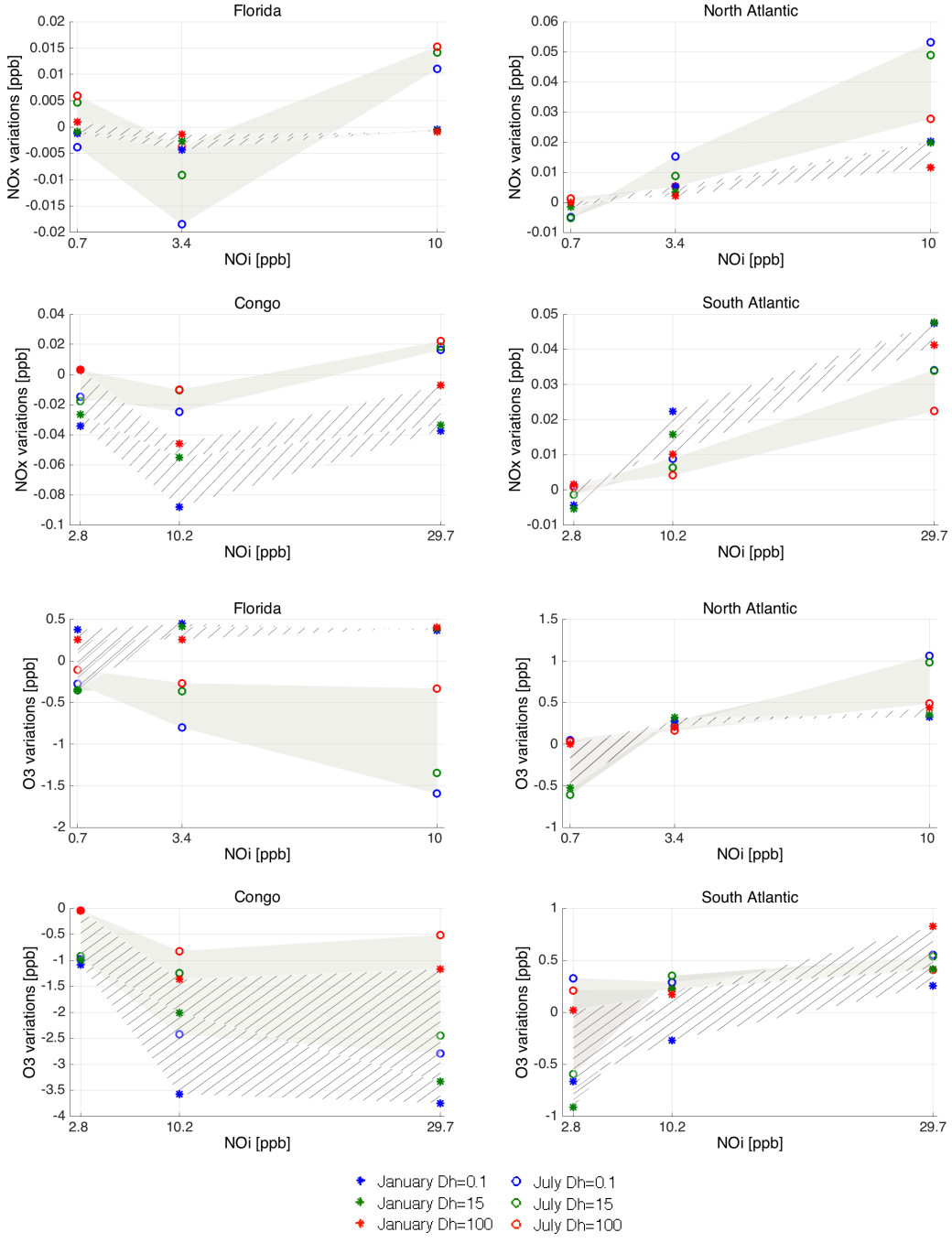

Figure 9. The NO_x (a) and O_3 (b) ~~variability~~ sensitivity at 9 km altitude depending on the horizontal coefficient diffusion (D_h, $m^2 \cdot s^{-1}$) and on the NO mixing ratio injected by lightning (NO_i, ppb) for the mid-latitudes (Florida and North Atlantic) and the tropics (Congo and South Atlantic). Intervals are hatched in January and ~~non-hatched~~ filled in grey in July. Markers correspond to the NO_x variations simulated for $D_h = 0.1\ m^2 \cdot s^{-1}$ (red ones), $D_h = 15\ m^2 \cdot s^{-1}$ (blue ones) and $D_h = 100\ m^2 \cdot s^{-1}$ (green ones).

	TEMP	PRESS	O_3	NO	NO_2	HNO_3	HNO_4	PAN	N_2O_5	CO
Units	(K)	(hPa)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppt)	(ppb)
Mid-latitudes	228	313	67	0.04	0.01	0.15	0.02	0.1	2	94
Tropics	240	313	26	0.03	0.003	0.02	0.006	0.03	2.3	93

	OH	HO_2	H_2O_2	CH_2O	CH_4O_2	C_3H_8	C_5H_8	C_2H_4O	C_3H_6O
Units	(ppb)	(ppt)	(ppt)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Mid-latitudes	0.2	4	0.4	0.06	0.1	0.47	0	7.5	4
Tropics	0.06	6	0.34	0.03	0.17	0.13	7.5	7.5	4

Table 1. The initial atmospheric parameters and background concentrations of chemical species from GEOS-Chem outputs for the DSMACC chemical box model simulations.

Day						
τ (hours)	**Mid-latitudes**			**Tropics**		
NO_i (ppb)	0.7	3.4	10	2.8	10	29.7
$D_h = 0.1$ $(m^2 \cdot s^{-1})$	1.55	8.14	23.9	4.40	23.1	67.9
$D_h = 15$ $(m^2 \cdot s^{-1})$	0.1	3.17	18.6	0.27	8.90	52.8
$D_h = 100$ $(m^2 \cdot s^{-1})$	0.01	0.47	4.17	0.04	1.32	11.7

Night						
τ (hours)	**Mid-latitudes**			**Tropics**		
NO_i (ppb)	0.7	3.4	10	2.8	10	29.7
$D_h = 0.1$ $(m^2 \cdot s^{-1})$	1.62	8.19	24.1	4.74	23.4	68.5
$D_h = 15$ $(m^2 \cdot s^{-1})$	0.31	6.19	22	2.77	21.3	66.4
$D_h = 100$ $(m^2 \cdot s^{-1})$	0.05	1.23	10.6	0.43	10.5	55.4

Table 2. The plume lifetime τ (hours) calculated for mid-latitudes and tropics depending on the initial NO mixing ratio injected by lightning emissions (NO_i, ppb) and the horizontal diffusion coefficient (D_h, $m^2 \cdot s^{-1}$) for day (upper table) and night conditions (bottom table).

Day						
$K_{eff}(10^{-19}\ molecules^{-1}\cdot s^{-1}\cdot cm^3)$	**Mid-latitudes**			**Tropics**		
$NO_i\ (ppb)$	0.7	3.4	10	2.8	10	29.7
$D_h = 0.1\ (m^2\cdot s^{-1})$	1.28	1.24	1.51	0.77	1.2	1.83
$D_h = 15\ (m^2\cdot s^{-1})$	8.44	5.49	5.43	7.79	3.64	4.13
$D_h = 100\ (m^2\cdot s^{-1})$	12.1	16.4	14.4	23	19.8	13

Night						
$K_{eff}(10^{-19}\ molecules^{-1}\cdot s^{-1}\cdot cm^3)$	**Mid-latitudes**			**Tropics**		
$NO_i\ (ppb)$	0.7	3.4	10	2.8	10	29.7
$D_h = 0.1\ (m^2\cdot s^{-1})$	1.28	1.24	1.51	0.77	1.10	1.83
$D_h = 15\ (m^2\cdot s^{-1})$	4.84	4.55	5.43	2.3	2.98	4.13
$D_h = 100\ (m^2\cdot s^{-1})$	7.36	8.39	6.73	6.45	3.94	5.16

Table 3. The effective reaction rate constant K_{eff} ($10^{-19}\ molecules^{-1}\cdot s^{-1}\cdot cm^3$) in mid-latitudes and tropics depending on the initial NO mixing ratio injected by lightning emissions (NO_i, ppb) and the horizontal diffusion coefficient (D_h, $m^2\cdot s^{-1}$) for day (upper table) and night conditions (bottom table).

Day						
β_1 (10^{-4})	**Mid-latitudes**			**Tropics**		
NO_i (ppb)	0.7	3.4	10	2.8	10	29.7
Aerosols	2.53	3.34	3.45	2.51	2.95	2.6
Ice	0.23	0.3	0.3	0.2	0.23	0.3
Mean	1.38	1.8	1.88	1.34	1.59	1.47

Night						
β_2 (10^{-3})	**Mid-latitudes**			**Tropics**		
NO_i (ppb)	0.7	3.4	10	2.8	10	29.7
Aerosols	14.3	9.89	8	4.9	1.69	0.24
Ice	14.4	9.96	8.06	4.89	1.70	0.24
Mean	14.4	9.92	8.03	4.88	1.7	0.24

Table 4. The fractions of NO_x conversion into HNO_3 within the plume (β_1 and β_2) in mid-latitudes and tropics depending on the initial NO mixing ratio injected by lightning emissions (NO_i, ppb) and on particles for day (upper table) and night conditions (bottom table).

Parameters	**Experiments**											
	P1									**P2**		
D_h $(m^2 \cdot s^{-1})$	0.1			15			100			15		
NO_i (ppb)	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Mean		
Mid-latitudes	0.7	3.4	10	0.7	3.4	10	0.7	3.4	10	3.4		
Tropics	2.8	10.2	29.7	2.8	10.2	29.7	2.8	10.2	29.7	10.2		
β_1	Mean									0	Min	$Mean$ Max
β_2	Mean									0	Min	$Mean$ Max

Table 5. Values of the parameters for the plume parameterization corresponding to the experiments $P1$ and $P2$.

	JANUARY				JULY			
	Mid-latitudes		**Tropics**		**Mid-latitudes**		**Tropics**	
	Florida	North Atlantic	Congo	South Atlantic	Florida	North Atlantic	Congo	South Atlantic
$\Delta NO_x \pm$	$[-1.7; +1.8]$	$[-8.2; +1.7]$	$[-33.1; +29.7]$	$[-6.5; +6.9]$	$[-9.3; +5.4]$	$[-21.1; +6.6]$	$[-14.3; +21]$	$[-11.5; +2.6]$
$\Delta O_3 \pm$	$[-0.16; +0.72]$	$[-0.12; +0.53]$	$[-1.56; +2.16]$	$[-0.49; +0.94]$	$[-0.44; +1.01]$	$[-0.49; +0.66]$	$[-1.18; +1.93]$	$[-0.14; +0.92]$

Table 6. The ~~variability~~ sensitivity of NO_x (in ppt) and O_3 (in ppb) depending on the horizontal diffusion coefficient (D_h, $m^2 \cdot s^{-1}$) and on the NO_i mixing ratio (ppb) injected by lightning for mid-latitudes (Florida and North Atlantic) and tropics (Congo and South Atlantic) in January and July.

	JANUARY				JULY			
	Mid-latitudes		**Tropics**		**Mid-latitudes**		**Tropics**	
	Florida	North Atlantic	Congo	South Atlantic	Florida	North Atlantic	Congo	South Atlantic
$\Delta NO_x \pm \cdot 10^{-2}$	$[-1.6; -0.06]$	$[-2.3; -2.3]$	$[-2.3; +0.9]$	$[+0.3; +0.6]$	$[-3.3; +1.4]$	$[-21.1; +6.6]$	$[+0.4; +2.1]$	$[-0.9; -0.4]$
$\Delta O_3 \pm \cdot 10^{-4}$	$[-9; +5]$	$[-9; +4]$	$[-3; +22]$	$[-10; +11]$	$[-24; -6]$	$[-6; +19]$	$[-8; +17]$	$[-30; -2]$

Table 7. The ~~variability~~ sensitivity of NO_x (in ppt) and O_3 (in ppb) depending on β_1 and β_2 values for mid-latitudes (Florida and North Atlantic) and tropics (Congo and South Atlantic) in January and July. Experiment $P1$, using $D_h = 15\ m^2 \cdot s^{-1}$ and NO_i^{mean}, performed with the GEOS-Chem model.