Answer to Interactive comment on "Influence of corona discharge on the ozone budget in the tropical free troposphere: a case study of deep convection during GABRIEL" by H. Bozem et al.

Anonymous Referee #1

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We thank Referee #1 for all the helpful comments. The suggestions are included in the revised manuscript and specific comments are answered below.

Review of Bozem et al. "Influence of cold corona discharge on the ozone budget in the tropical free troposphere: A case study of deep convection during GABRIEL"

General Comments:
Bozem et al., present a case study of deep convection as measured during the GABRIEL campaign in 2005. They use both in situ measurements and photochemical box modeling analyses in an attempt to partition measured ozone in convective ouflow between that which is: 1) lofted from the surface, 2) entrained from the FT, 3) produced photochemically, and 4) produced by lightning. The conclusions of Bozem et al. are that cold corona discharge has a large effect of ozone concentrations in the outflow of deep convection. The paper is well written and the observations are described in sufficient detail. However, there is limited discussion of the implications of high lightning O_3 production rates on other detailed deep convection studies. Below are a few comments that need to be addressed in the revised manuscript:

1) The selection of data for the lower troposphere, 0.4-2.8 km appears somewhat arbitrary. What was the justification for this altitude range and what are the implications for narrowing this or expanding it to the surface. Expanding the references in this section would be helpful, specifically with respect to the altitude range for which air is entrained into a developing Cb cloud. Further, it was not clear what spatial regions were used. The entire flight? Just the immediate region surrounding the cell?

Answer:
For the selection of the data in the lower troposphere the vertical profiles of different long lived and insoluble tracers as for example CO and acetone were analyzed leading to the altitude range. Below 400 m the data were excluded because these measurements where done over coastal regions at a significant distance to the observed thunderstorm cloud to the north (see Fig.1 in manuscript). In combination with the mean wind direction these data points are most probably not representative for the inflow region of the observed cloud. For the inflow region only the immediate region surrounding the cell was used. The vertical extension of the chosen layer was capped by an inversion layer at 3 km, which was also observed on other flights. The so-called trade wind inversion layer was reported in several studies to be present in these regions and acting as a transport barrier where trace gases can accumulate below this layer (*Schubert et al. (1995)*, *Gouget et al. (1996)*, *Andreae et al. (2001)*). During convection these air masses can be transported to the upper troposphere.
The related section in the manuscript was modified.

2)The authors should address if their method for calculating the O3 production rate per flash is consistent with other field observations. There are many observations of [NO] » 100ppt in convective outflow, some observations well above 1ppb. Much of this has been attributed to LNO_x. If the same methodology as argued here was applied in these studies, the O_3 concentrations in the outflow would be very large. Specifically, is there room for this much lightning generated O_3 in the DeCaria analysis of STERAO-A? Or other modeling studies focused on O_3 and NO_x production that have been constrained by field observations?

REF: DeCaria et al., JGR 2000, A cloud-scale model study of lightning-generated NO_x in an individual thunderstorm during STERAO-A

Answer:

The literature about the observation of enhanced ozone concentrations in the vicinity of thunderstorm clouds, related to direct production from electrical discharge associated with lightning, is very sparse. There is a study by *Minschwaner et al. (2008)* that uses a slightly different method to calculate the ratio of O_3 molecules per flash, but they also refer to corona discharge to explain the observations of enhanced O_3 concentrations in a thunderstorm cloud. Our lower range of the rate of ozone molecules per flash is in the same range as *Minschwaner et al. (2008).* Also *Winterrath et al. (1999)* and *Zahn et al. (2002)* suggest direct ozone production from corona discharge to explain the observed enhanced mixing ratios in a thunderstorm cloud and convectively active areas, respectively. In these studies no detailed number of O_3 per flash is given.
The analysis of the 10 July storm during the STERAO-A project by *Skamarock et al. (2000)* for example also observes enhanced ozone mixing ratios in the upper troposphere which are attributed to a possible intrusion of stratospheric air which is not seen in the model analysis. There might be a contribution from direct production of ozone from corona discharge to the observed mixing ratio.
Also a study by *Stenchikov et al. (1996)* gives some room for speculations since an observed ozone enhancement in a storm from 28 June 1989 is not accounted for in the model simulations that do not calculate direct production of ozone from electrical discharges.
In the analysis of the STERAO-A case study by *De Caria et al. (2000)* no detailed information on the vertical distribution of ozone is given. There is also a difference from storm to storm with respect to the characteristics of lightning and electrical discharges, leading to a wide range of production rates per flash for NO and especially ozone and making it challenging to compare different studies.

3)Some discussion of the near zero isoprene concentrations in the convective outflow is warranted. What does this imply about the vertical velocity within the storm or other sources of entrainment/detrainment that are not considered in this analysis.

Answer:

There are at least two possible reasons for the zero isoprene observed in the convective outflow. Firstly, the concentrations could have been so low that they are below the detection limit of the instrument. Secondly, the vertical profile of isoprene shows very low mixing ratios between 1.5 and 3 km. The budget analysis, especially for CO, suggests that this may be the main inflow region in the lower troposphere. Therefore, no significant amounts of isoprene are to be expected in the convective outflow. The isoprene concentrations might give a hint on the inflow region in the lower troposphere. A link to the vertical velocity within the storm is questionable. With a lifetime of isoprene in the order of hours, this would suggest transport times on the same time scales in the convective updraft. Since no isoprene reaches the upper troposphere, it must have been destroyed during the ascent. Such long upward transport times seem rather unlikely in an active thunderstorm.

Specific Comments:
1) Page 5236 lines 10-15: It would be reasonable to think that mechanistically, the per flash NO production rate would be related to the per flash O_3 production rates as both involve the formation of atomic oxygen. If $O+N_2$ and $O+O_2$ are the production channels for O_3 and NO formation, wouldn't we expect there to be a limit imposed by N_2/O_2 and the kinetics of these processes? Is this consistent with LO_3 / LNO » 1? More extensive references in this section would be helpful
REF: Navarro-Gonzalez et al., GRL 2001 The physical mechanism of nitric oxide formation in simulated lightning.

Answer:

In general, the production of NO and ozone per flash associated with lightning occur in different parts of the lightning flash. Whereas the hot flash channel is known to produce significant amounts of NO but no ozone there are several studies that point out that the cold corona around the flashes or corona discharge on droplets are able to produce significant amounts of ozone but less amounts of NO (*Donohoe et al. (1977)*; *Peyrous and Lapeyre (1982)*; *Hill et al. (1988)*). Mechanistically, the formation processes are slightly distinct thus there

should not be a limit with respect to N_2 and O_2. As the dissociation energy of O_2 is lower than that of N_2, molecular nitrogen only dissociates as a result of lightning flashes, whereas oxygen may also be dissociated by non-lightning discharge processes. In our study we have to assume that corona discharge occurs in the vicinity of a lightning flash to scale the produced ozone with the produced lightning NO_x,since detailed information on the electrification of the cloud is missing. Discharge processes on droplets can-not be considered. This adds uncertainty to the derived rate of O_3 molecules per flash.
We have modified the section in the manuscript related to this comment, and the text has been changed as follows:
"It is well known that electrical corona discharges produce O_3. However, experimental evidence from field studies is very sparse in the literature. It was first postulated by *Shlanta and Moore (1972)* that discharges might occur on cloud water droplets or ice particles in highly electrified environments. *Griffing et al. (1977)* also linked corona discharges to streamer filaments or the surrounding area of lightning channels. Laboratory studies confirm that the production of ozone in hot lightning channels is negligible (*Wang et al (1998)*). In contrast corona discharge effectively produces ozone, as quantified by *Peyrous and Lapeyre (1982)* or *Simek and Clupek (2002)*. *Hill et al. (1988)* compared the production of NO and ozone as a function of energy dissipation by corona discharge, yielding a rate of $(1.4 \pm 0.7) \times 10^{16}$ molecules per Joule and $(4 \pm 2) \times 10^{17}$ molecules per Joule, respectively. *Minschwaner et al. (2008)* suggested a production rate of $1(0.35 – 1.6) \times 10^{27}$ O_3 molecules per flash from balloon measurements in an electrically active thunderstorm in New Mexico, USA. Corona discharge in the vicinity of a lightning flash can be an additional regional source of ozone in convectively active areas. The NO yield in the colder discharge processes (temperatures < 3000 K) in association with lightning or on cloud droplets in general is lower compared to hot channel lightning which was already postulated by Donohoe et al. (1977). In the hot flash channel, the NO yield maximizes at 4000 K (*Bethanabhotla et al. (1985)*; *Martinez and Brandvold (1995)* and *Navarro-Gonzáles et al. (2001)*).
As shown by many theoretical and experimental studies, hot lightning strokes are a significant global source for NO_x with a production rate of 15 (2-40) $\times 10^{25}$ NO molecules per flash (*Huntrieser et al. 2007*, *and references therein*). "

2) Page 5241 lines 16-18: What is the enhancement in NO that is attributed to lightning? From Figure 2, it looks like 50 ppt? Yet the ozone enhancement that will be attributed to lightning in is _20 ppb (page 5242, line 4)? This would imply a LO_3 / LNO is ca. 400? Is this reasonable?

Answer:
Taking into account the mean values for the calculation, the enhancement in NO is 58 pptv which indeed gives a LO_3/LNO ratio of 341, which does not seem very reasonable. The sensitivity study for this calculation is taking into account that the species in the different layers considered have an atmospheric variability (see answer to specific comments 4-6). Using now the maximum contributions from dynamic transport (50 ppbv) and photochemical ozone production (3.1 ppbv) and the NO peak values in the outflow region (231 ppt) we get a "missing ozone" of only 2 ppbv and an enhancement in NO due to lightning of 200 ppt. The resulting LO_3 /LNO ratio then decreases to only 7, which is more reasonable (see end of section 5).

3) Section 2.3 Observations of the convectively influenced layer are made during an ascent. As such, the background air, from which the enhancement is derived, is not from the same altitude, but above or below the detrainment region. Given the strong vertical heterogeneity in ozone even in the absence of deep convection, what is the expected impact that this may have on the derived "enhanced O3"?

Answer:
For our specific study the impact of the background air not sampled at the same altitude as the convective outflow is expected to be rather low. As can be seen from the vertical profiles of the different species (see Fig.3 in manuscript) and especially the ozone profile, the variability of ozone in the measurement region below and above the convective outflow is low. Also the ozone sonde profile from 13 October 2005, one day after the measurement flight (see Fig. 4 in manuscript), shows no strong variability in the layers around the outflow giving confidence in our calculations for the "enhanced O_3". The comparison of the background values used for the calculation of the enhancements with values sampled on a later part of the flight at the same altitude of

the convective outflow, but not influenced by the thunderstorm cloud, showed no significant differences within the measurement error.

4) Page 5247: This section needs a more complete error analysis. At the end of the section we have a statement that there is "~" 35% ozone missing from the budget. This needs to be a number x ± y ppb based on a proper representation of the uncertainty in this analysis. Then, section 5 can discuss the potential mechanisms that this is met.

5) Section 5: This section should then piece apart the unaccounted for ozone. For example, upwards of x ± y ppb could be attributed to missing chemistry; x ± y ppb could be attributed to missing dynamics. At the end of this analysis, a missing ozone number could be evaluated and perhaps assigned to lightning production.

6) Page 5249, line 29: Please remove "~". This should be a number with an associated uncertainty. The subsequent discussion of the calculation of the limits for the O_3 lightning flash rate should carry the uncertainty that is derived from section 3 and 4.

Answer:

We comment on the specific points 4 to 6 together, since the three points address the error analysis of this study. We implicitly have the complete error analysis included in the calculations. We take into account the atmospheric variability of the different species in the different observed layers and the measurement uncertainty which is significantly lower than the variability of the species in the atmosphere. For every calculated parameter we state a range which can be translated into a x ± y value. But this is not an error in the common sense. It has to be interpreted as the atmospheric variability of the species, e.g. for the inflow region or the background air. This variability then leads to a range for our calculations as for example for the enhancement of NO and ozone or the fraction of air "a" that is transported from the boundary layer and entrained into the convective outflow in the upper troposphere, respectively. For clarification we have modified the manuscript to explicitly include that range when giving the numbers for the different parameters. Since this study is based only on measurement data, we are not able to piece apart the unaccounted sources for ozone that are mentioned in the beginning of section 5 of the manuscript. There is no additional contribution to the observed outflow value from chemistry due to too slow production rates. We can only speculate on the contribution from entrainment from above due to a lack of measurements. The choice of the layers for the inflow and the entrainment region is the result of sensitivity studies, which are not explicitly shown in the paper but which lead to the most reasonable choice of layers based on the information that was available from the measurements and typical characteristics known from literature. These sensitivity studies are included in the range that is given for different parameters.

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