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Reply to

Interactive comment on “Chemical processes related to net ozone tendencies in the free troposphere” by Heiko Bozem et al.

Anonymous Referee #2

Received and published: 20 April 2017

We thank the referee for her/his comments, that we will address point by point in our reply

The paper offers an assessment of in situ ozone production rates based on observations from two field campaigns, GABRIEL and HOOVER. Ozone production rates derived from observations are compared to values obtained from a large scale chemical transport model, MATCH-MPIC. The analysis is somewhat limited by shortcomings in the observational dataset and the results confirm what has been well established by previous studies dating back more than two decades. The lack of novelty in the findings and quality of the dataset make it difficult to endorse publication. Specific comments and suggestions are offered below to expand on these points.

Answer:

We regret that the referee feels that our manuscript suffers from a lack of novelty and shortcomings in the observational data set which we believe is not justified:

Novelty:

The referee states that this study only confirms results obtained from studies dating back more than two decades, and she/he points out a number of studies performed during several large airborne campaigns. Among the studies cited by the referee (9 in total) only 3 use in-situ measurements of radicals (Olson et al., 2001; Ren et al., 2008; Olson et al., 2012) to deduce net ozone production rates (NOPR). All other studies cited by her/him and in our manuscript use precursors (peroxides, CO, NMHC) to deduce HO_x and RO_x levels using box models. The studies that use in-situ observations of HO_x radicals found significant differences between observations and constrained box model calculations for HO_x in particular in the upper troposphere (e.g. Ren et al. state a median (mean) deviation between observed and modeled HO_2 at 8-12 km of 2.05 (5.49) (their Table 1) while Olsen et al. (2012) found median ratios (model/observation) for HO_2 of 0.49 for ARCTAS-A (their Table 5) and 0.60 for ARCTAS-B (their Table 6). This underscores that there is uncertainty in the HO_x budget of the troposphere, in particular the UT, which was not detected before measurements of HO_x on airborne platforms were introduced in the early 2000s. HO_x plays a

central role in NOPR (Eq. 4 in our manuscript) and threshold NO levels (Eq. 7), thus it can be expected that all previous studies suffered from this uncertainty. We agree with the referee, that the chemical mechanism for net ozone formation in the troposphere is well established, but in order to calculate NOPR and NO_{th} one has to know the concentrations of all species affecting these calculations in great detail, either by in-situ measurements or modeling. Our study is, to the best of our best knowledge, only the fourth that uses in-situ observations of all relevant species (except peroxy radicals) to evaluate NOPR and the first over Europe and the rain forest in South America, respectively. From this perspective we consider our study to present novel results.

This is also the first study that compares observation based NOPR calculations (at least including HO_x measurements) to simulations from a 3D chemical transport model. All previous studies cited by the referee or in our manuscript used constrained box models for comparison. Box models are obviously ideal tools to study a chemical mechanism and are thus adequate to study NOPR from observational data, but ozone budgets rely on 3D models and we believe that comparing with such a model adds a new dimension, since it provides additional information about how well a CTM or GCM simulates the 4 dimensional distribution of O_3 precursors and how this affects the model's capability to simulate O_3 distributions.

Shortcomings in the observational data:

We are sorry that we obviously did an inadequate job explaining how we dealt with missing data. Missing data arise mainly from different time resolutions and duty cycles. In order to calculate NOPR, simultaneous measurements of all species used in the calculation have to be available. O_3, NO_x, HO_x, water vapor and radiation are measured at 1 Hz resolution with a duty cycle of nearly 100 % (except during calibrations and background measurements). CO and CH_4 are measured together with HCHO by the three laser quantum cascade laser spectrometer TRISTAR in a time multiplexed mode (Schiller et al., 2008). Although this instrument also has a time resolution of 1 sec it measures species sequentially. Due to the low concentrations of HCHO the majority of the measurement cycle is dedicated to this species (60 %) leaving 20% each for CO and CH_4. Additional interruptions of ambient measurements are due to regular HCHO background measurements (20 – 50 s every 3-4 min) and calibrations every 30 – 40 min further reducing the duty cycle for CO and CH_4 to 16%, which we consider not to be a problem considering the relatively constant background concentrations.

Restricting calculations to only those times when all species are available would thus pose a significant limitation, in particular since CO and CH_4 are only used in Eq. 5 to calculate CH_3O_2. Additional

data gaps are due to instrument failures of TRISTAR and the H_2O instrument on parts of the GABRIEL flights due to an overheated cabin. Instead of interpolation we used campaign averaged profiles (we will address the use of median instead of mean values later in our reply) for CO, CH_4 and H_2O to fill in missing data during GABRIEL and HOOVER. This procedure was used since all species exhibited only small horizontal but large vertical variations. Together with measured HO_2 these average profiles were used to calculate CH_3O_2 radical concentrations.

To substantiate our hypothesis that this approximation (through average profiles) is sufficiently accurate we compared the reduced data set (only points when all species have been measured simultaneous) to an extended data set (factor 4 for GABRIEL) with added CO and CH_4 values and found that no significant difference for the calculated NOPR in a given bin. If our hypothesis would have been wrong (e.g. due to strong latitudinal gradients in CO, CH_4 or H_2O) one would expect to see some deviations. Since data gaps mainly affect the CH_3O_2 concentrations and our studies and those e.g. of Ren et al. (2008) indicate that ozone production due to the reaction of NO with CH_3O_2 is rather small at higher altitudes (less than 10% of the production due to NO + HO_2 above 6 km) it is not to be expected that our procedure to add missing data affects the results for NOPR at all.

Missing NO values are much more critical and our discussion in connection with HOOVER 2 clearly demonstrates that simple measures to infer NO concentrations from other flights or campaigns will most likely fail. Nevertheless, we would like to keep this discussion, since it nicely illustrates the sensitivity of NOPR to an accurate measurement of NO.

Comments on the Introduction:

This section of the paper fails to adequately recognize previous work and contains information that is both incorrect and incomplete that requires clarification and correction.

In trying to provide for some historical perspective, the authors provide a rather lean description of the relevant events and debate surrounding tropospheric ozone. Indeed, the reference to Junge regarding transport from the stratosphere and the 1960s references to LA are appropriate. However, it is key to note that a chemical explanation for tropospheric ozone was not available until Levy (1971) posited a source for OH in the troposphere and the development of a photochemical theory for tropospheric ozone was developed by Chameides and Walker (1973) and Crutzen (1973). It is also important to note that scientific debate on the relative importance of photochemistry versus downwelling from the stratosphere continued to be contentious for at least two more decades.

Answer:

We will follow the recommendation of the referee and will add a discussion of the critical role the studies of Levy, Chameides and Walker and Crutzen had on the development of the photochemical mechanism for ozone production in the troposphere. We will also

indicate that the discussion on the role and strength of STE for the tropospheric Ozone budget is still not resolved.

The capability for detailed ozone budget calculations by chemical transport models is indeed important, but this discussion is also unnecessarily limited. The major reference is to von Kuhlmann et al. (2003), but several more relevant and up-to-date assessments have occurred since then and should be recognized, e.g., Stevenson et al. (2006), Wu et al. (2007), and Wild et al. (2007). The range of values for budget terms provided from Kuhlmann et al. are based on a more limited sampling of models than from these other studies. It is also fails to recognize a couple of important aspects regarding the factors influencing ozone budget calculations in global models:

Answer:

We will add these references. Originally we restricted our discussion to the von Kuhlmann paper since it describes results from the same model that we later use for the intercomparison.

1) When discussing Net Ozone Production (NOP), the authors state that “The NOP itself is a delicate balance between two very large numbers. . .” referring to ozone production and destruction. This statement fails to recognize is that NOP has nothing to do with these larger terms in global model calculations. Instead, it is governed by the balance between ST exchange and surface deposition. Thus, when sampling across models, NOP is highly correlated to ST exchange (which tends to have the highest uncertainty) and is moderately correlated to surface deposition. By contrast, there is little correspondence between NOP and gross production and destruction terms across models.

Answer:

The referee argues for a perspective of dominant processes which is not certain to apply to atmospheric models. Gross production and destruction in a global model is a summation over simulated O_3 production and destruction based on the model’s chemical mechanism, emissions of precursors and their subsequent distribution due to transport. Stratosphere-troposphere transport of O_3 depends on the gradient of O_3 between the lower stratosphere and upper troposphere, which in turn both depends on and influences the photochemistry especially in the upper troposphere. So one can claim that either is the dominant process, and in this sense it can be claimed that ST exchange is adapted to NOP, and not necessarily vice versa, indicating that uncertainties in the models NOP force ST. Furthermore, in CTMs and GCMs the stratospheric source of O_3 is often highly parameterized, e.g. with prescribed O_3 concentrations in the lower stratosphere to reproduce measured ozone profiles. So we think it is fair to address the question whether the NOP in a model is accurately reflecting the processes in the atmosphere.

2) There are VERY few models that infer net destruction of ozone globally, and these are the models with very high estimates for ST exchange; thus, it is not incorrect to state that the vast majority of models calculate net ozone production. For example, in Stevenson et al. (2006) 20 of 21 models have positive NOP, in Wild et al. the few models with negative values are pre-2000 studies, and all models in Wu et al. exhibit positive NOP.

Discussion of net ozone production on page 3 (lines 12-17) is overly simplistic. Describing net ozone production as a “non-linear function of the concentration of peroxy radicals. . .as well as the concentration of NO" glosses over the subject in a way that does not provide any insight, especially given that there is no reference provided for a deeper discussion of this nonlinearity. More importantly, net production is not "non-linear" over much of the remote atmosphere since non-linearity is only present when there is enough NO_x to influence the HO_x budget to limit radical availability. As noted only a few lines above, you neglect the loss of NO_2 due to reaction with OH, but it is precisely this reaction that often drives nonlinearity in ozone production. The discussion of threshold NO is also too simplified. A well-defined equation for this quantity is introduced later in the text, so why try to reduce it to competition between reactions R4 and R10? The rate constants for these two reactions have opposite temperature dependencies and R4 may be 4000 times faster than R10 near the surface, but this difference more than doubles at the colder temperature of the upper troposphere. Additionally, there are many environments where reaction R12a is the dominant ozone loss term rather than R4.

Answer:

We agree with the referee that our discussion of the nonlinearity of NOP is overly simplistic. We will replace this paragraph by:

"NOPR is nonlinear with respect to NO and peroxy radicals. This nonlinearity arises because RO_x and NO_x drive ozone production (R4-R6) but also terminate free radical chemistry (Puesede et al., 2015 doi: 10.1021/cr5006815):

$NO_2 + OH + M \rightarrow HNO_3 + M$ **(R13)**

$NO_2 + RO_2 + M \rightarrow NO_2RO_2 + M$ **(R14)**

$OH + HO_2 \rightarrow H_2O + O_2$ **(R15)**

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ **(R16)**

$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ **(R17)**

Note that we neglect loss of NO_2 due to reaction R13 and R14 in Eq. 4. This is justified by the overall low NO_x concentrations outside the continental boundary layer. Reactions R15 to R17 are also excluded since they affect HO_x levels and would have to be taken into account to calculate their concentrations using a box model. Here we use observations of OH and HO_2 instead."

To address threshold NO we will move the presentation and discussion of Eq. 7 to the introduction and skip the discussion of competition between R4 and R10.

3) On page 3 (line 24) the authors state that "Studies that infer net ozone production at least in part from in-situ measurements are rare and often limited to the boundary layer. . ." I couldn't disagree more. The statement is followed by an extensive list of references (17 in all, with 11 focused only on the boundary layer), but this list of references overlooks a wealth of previous work that refutes this statement. The literature on ozone production assessed from in situ airborne measurements through the depth of the troposphere is prolific and covers many parts of the globe. I point the author to literature on North America in summer (Ren et al., 2008), the western North Pacific in different seasons (Davis et al., 1996 & 2003; Crawford et al., 1997a & 1997b), the South Atlantic (Jacob et al. 1996), the South Pacific in different seasons (Schultz et al., 1999; Olson et al. 2001), and the Arctic in different seasons (Olson et al., 2012). All of these references provide findings that corroborate the NOPR results shared in this paper, establishing that these features of ozone photochemistry have been well documented and understood for decades.

Answer:

We will add the above cited references to the paper and discuss ground-based and airborne studies separately. Here we will also emphasize that only a few airborne studies have been performed using in-situ observations of HO_x and this is the first study performed for Europe and South America.

Comments on Data Processing:

While I appreciate the caveats presented by the authors, I have some concerns about the degree of inference used in the analysis of the observations.

Twice it is mentioned that median values are taken from average altitude profiles (bottom of page 6 and top of page 7). This does not make sense to me and needs to be clarified.

Answer:

Median values are used throughout the manuscript instead of mean values to limit the influence of extreme events. Such events mainly influence NOPR calculations at the highest and lowest altitudes and are predominantly due to NO spikes associated with aircraft emissions in the proximity of the airports or in flight corridors. Since these events are rare and vary strongly in the NO enhancement, we choose not to filter the data, but instead use median values that are not affected by a few high values. The same accounts for values below the detection limit (e.g. for radicals) that otherwise might bias the data. Differences between mean and median NOPR values are insignificant during GABRIEL and up to a factor of two in the continental boundary layer during HOOVER 1.

For consistency, we choose to use median instead of mean values for average CO and CH_4 profiles. Since these two species are hardly affected by extreme events (the only exception is a local fire in the boundary layer over Suriname during GABRIEL that was sampled on one flight yielding enhanced CO and CH_4 mixing ratios) the differences between profiles based on median and mean values is negligible.

There is no discussion of filtering for time of day. What is the range of solar zenith angles for these measurements? Rather than calculate an average altitude profile for CH_3O_2 (page 6, line 32), wouldn't it be better to calculate an average CH_3O_2/HO_2 ratio and scale CH_3O_2 to HO_2? This would better capture variability in the photochemical environment which should affect CH_3O_2 and HO_2 similarly.

Answer:

We did not filter the data for the time of the day. All flights were performed during daylight hours between approx. 10:00 and 17:00 local time.

Average profiles based on median mixing ratios for a given altitude bin were used to fill in data gaps in CO and CH_4 during all campaigns (and H_2O in GABRIEL). Calculations of CH_3O_2 are based on Eq. 5 using actual measurements of HO_2 and the production rates. Page 6, line 32 should read:

“To overcome this, average altitude profiles for CO, CH_4 and H_2O have been calculated for the GABRIEL data set.”

When taking care of all data gaps, the authors increase the number of calculations for GABRIEL by a factor of 4 (page 7, line 3), but how can the reader be convinced that this leads to a more robust result? The number of calculations is increased “without changing trends in NOPR for different regions.” This seems like a circular statement, since the expanded calculations rely heavily on inferences from the more limited dataset. If the trends don’t change, then all of this extra effort seems of little value.

Answer:

We explained the motivation for our procedure to fill in missing CO, CH_4 and H_2O data above. Using this procedure we ignore potential longitudinal (GABRIEL) or latitudinal (HOOVER) gradients in those species. To test the influence of this simplification by using only one average altitude profile we compared NOPR values calculated with and without the data gaps at various longitudes and latitudes. Since no differences were observed, we conclude that our hypothesis of a weak lateral dependency is correct. We cannot follow the referee in his statement that this method is circular. In the case of CO and CH_4 this might be fortuitous due to the small contribution of CH_3O_2 to NOP in the free troposphere as has been shown by Ren et al. (2008). To illustrate this, we will add vertical profiles of individual rates of ozone production and loss for all campaigns (observations and model results) to Fig. 2, 4 and 5.

The use of an average NO profile for HOOVER calculations is even more disturbing given the critical role of NO in determining the strength of the ozone production rate. I am not comfortable with this approach. Anyone experienced in airborne measurements will corroborate that NO is one of the most variable quantities in the atmosphere and that measurements from one day cannot be reasonably used to infer conditions on another day.

Answer:

As mentioned above we would like to keep this analysis in the paper to demonstrate exactly the point that the referee made: NO is most critical for NOPR and this is kind of a sensitivity study to demonstrate that even small errors or missing data for this central species have large consequences.

Comments on NOPR for GABRIEL:

Page 7, line29: The authors note that high NOPR at the coast is “probably due to local pollution in the vicinity of Cayenne.” Looking at figure 2, this is one of the statistically weakest bins at the lowest altitude. So is this from a single flight through that box? Maybe twice? How representative then is this data point? You also have the data to back up the statement regarding pollution. Instead of guessing, you should corroborate the statement with some indication of the NO and CO levels seen in that box relative to the rest of the data set.

Answer:

The data in this bin is indeed obtained from a limited number of data points (6), indicating that not on all flights the crossing of the coastline has been made on the lowest level as can be seen from the

data points at higher altitudes. The high NOPR in the bin is due to enhanced NO values as documented in Fig. 3a, with NO/NO$_{th}$ being enhanced by a factor 1.5, indicating that NO is at least a factor of 2 higher than in adjacent bins. This points to a local NO source (which is documented in Fig. 3a). So the "guessing" is only for Cayenne as the source of this local pollution. Therefore we reformulate this statement to:
"…due to local pollution enhancing NO (see the discussion of Fig. 3a further below) most probably in the vicinity of Cayenne,…"

Page 7, lines 30-33: The reader is reminded that in the continental boundary layer, NOPR values are less reliable due to the inadequacy of equation 1. Ozone loss to reaction with isoprene is also mentioned, but should be much less important. Without any attempt to quantify this underestimation, it is difficult to place much value on these data. Why are you not taking advantage of the PTR-MS and canister data to at least put a semi-quantitative estimate on the likely influence of isoprene and other VOCs in the continental BL?

Answer:

We do not think that this can be easily done. Although it would be possible to estimate the amount of higher peroxy radicals from canister based NMHC measurements, one should keep in mind that this data set is rather limited since only 24 canisters were sampled per flight, so that the data coverage in the boundary layer is rather poor. Data coverage for isoprene is higher due to the PTRMS measurements but an estimation of its influence of NOPR is even more complex due to its dual role as a potential source of organic peroxides and as a sink for ozone due to the ozonolysis of isoprene. So we would like to maintain our caution about the limitations of our analysis in the boundary layer instead of speculating about the role of other peroxy radicals with the limited amount of data available.

Page 8, lines 4-5: The authors state "Thus, replacing the missing values by median values from average profiles does not change the results significantly." This statement again indicates that the data filling process is somewhat circular, giving the illusion of a more robust result. There is no expectation of additional variance when using these median values to fill gaps. I also am still confused by "median values from average profiles".

Answer:

See our comments above.

Page 8, lines 7-10: The discussion of MATCH data in Figure 2a is inadequate. Which terms in equations 1 and 2 are responsible for these differences? Without deeper discussion of the difference in precursors between the real atmosphere versus MATCH, it is hard to see why the effort was spent do the simulations.

Answer:

We agree with the referee that we could provide more details on the differences between observations and MATCH simulations with respect to NOPR, in particular since such a comparison has never been made before as mentioned above. To do so, we will extend

figures 2, 4 and 5 by adding average profiles of individual ozone production and destruction rates as well as the NOPR (similar to Figure 6) for observations and model result. Additionally, we will add profiles for NO_{th} and the NO/NO_{th} ratios for all campaigns, again for both observations and model data. This will allow us to address differences in precursor levels and their influence on NOPR.

Page 8, lines 16-18: The discussion of threshold NO should be expanded and related to earlier work. This quantity has been previously referred to as the "NO compensation point" or "critical NO" (see Reeves et al., 2002; Davis et al., 1996; Crawford et al., 1997; DiNunno et al., 2003; Kondo et al., 2004 and others). You will also notice that many of these references also refer to a critical NO_x value that tends to have more predictable behavior. By comparing photochemistry at different altitudes for a given abundance of NO_x, you eliminate the need to account for the large changes in partitioning between NO and NO_2 that occur with altitude (and temperature).

Answer:

We will follow the referee's suggestion and compare our results to earlier studies. We are also aware that this quantity has been referred to as "NO compensation point" or "critical NO" in other studies. Nevertheless, we deliberately decided to call the quantity calculated in Eq. 7 a threshold value since it marks the change in a chemical regime, from ozone destruction to production. We don't believe that NO_x (instead of NO) is a good indicator for this threshold, since it is NO that drives ozone production and our results indicate that there is some altitude dependency that might be masked by using NO_x instead of NO.

Comments on NOPR for HOOVER I and HOOVER II:

Discussion of results for HOOVER I are cursory at best. A deeper discussion of the difference between the observations and MATCH is warranted.

The discussion for HOOVER II is slightly longer, but is dominated by treatment of the missing NO measurements for a portion of the flights. It is my opinion that these data should not be included as the attempt to salvage these runs comes with too much uncertainty.

Answer:

The discussions of results for HOOVER I and II will be extended in a similar way as discussed above for GABRIEL, in particular with respect to differences between observations and model results.

Comments on Discussion and Conclusions:

As noted in the opening sentence, these results "confirm earlier studies". In that regard I struggle to find anything novel in the work and am dismayed by the level to which data gaps have had to be filled to get these results as compared to previous studies.

Answer:

We have addressed these points above, early in our general reply to the referee.

I continue to be concerned about the findings for threshold NO which is stated to have a "tendency to increase at the highest altitudes" (page 12, line 13). This is different than all previous studies and I am not convinced by the explanations offered. I have to take particular issue with the statement that “Overall this leads to a rather invariable O_3 loss rate throughout the troposphere.” It is well established that the ozone lifetime increases with altitude by as much as an order of magnitude. This is mainly due to the dramatic decrease in water vapor which is both directly and indirectly responsible for ozone destruction. This also means that ozone destruction falls off more rapidly than production, which is only indirectly related to water vapor through radical availability. The amount of NO needed to overcome this disparity should decrease at the highest altitudes and is shown to do that in numerous studies (e.g., Reeves et al., 2002; Davis et al., 1996; Crawford et al., 1997; DiNunno et al., 2003; Kondo et al., 2004 and others).

Answer:

We agree with the referee that the ozone lifetime increases with altitude by almost an order of magnitude due to decreases in water vapor and slower reaction rates at lower temperatures. But this does not necessarily mean that the ozone destruction rate falls off faster than the production terms. The destruction term is proportional to the ozone concentration and increasing ozone mixing ratios (from approx. 20 ppbv close to the ground to around 100 ppbv close to the tropopause) will almost compensate the pressure drop by a factor of 5 (1000 hPa to 200 hPa). So in total the rate of ozone loss will probably decrease by an order of magnitude driven by the longer lifetime. This has to be compared to the change of HO_2 (and CH_3O_2) concentrations with altitude. Actually, if the drop in HO_2 concentrations with altitude is larger than the change in the total O_3 loss rate, Eq 7 predicts an increase in the NO_{th} as observed in this study. Please note that such an increase might not be observed if one considers a threshold for NO_x due to the change in partitioning.

In summary, the analysis presented is not sufficiently novel, lacks depth, and exhibits some behaviors that deviate from previous findings that do not seem plausible. Given the condition of the data set, I do not expect that these shortcomings can be overcome to generate findings worthy of publication.

Answer:

We hope that we have convinced the referee and editor that this paper holds enough novelty and sufficient data quality to revise this judgement of the manuscript.

Minor points:

Page 1, line 27: the use of “whose” inappropriately personifies $O(^1D)$. It would be better to rephrase as “. . .$O(^1D)$, which can subsequently react with water vapour to yield two OH radicals.”

Page 2, line 2: The reference to von Kuhlmann et al., 2003 is for the wrong paper. These budget numbers come from the ozone manuscript, not the one on ozone-related species.

Answer:

We will address these points in the revised manuscript.

Reference list

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We would like to thank the referee for pointing out these additional references that we will include in our discussion.