Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2017-153-RC1, 2017 ©
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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 #1

Received and published: 22 March 2017

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

The submitted manuscript presents airborne in-situ measurements and model simulations of O_3 and its precursors during tropical and extratropical field campaigns over South America and Europe aiming to calculate and assess the vertical distribution of net ozone production/destruction tendencies from both observations and model simulations. The manuscript has an added value on the understanding of the chemical control of ozone from the boundary layer to the upper troposphere over continental and marine environments in South America and Europe. I suggest acceptance of the manuscript for publication after taking into consideration the following comments.

Comments 1) page 3, lines 24-27: The authors cite a number of articles that infer net ozone production/destruction rates from in-situ observations (or at least in part) mentioning that the majority of these articles are limited to the boundary layer. I would suggest to distinguish which of these studies refer to the boundary layer and which to the free troposphere.

Answer:

In the revised version of the manuscript we will differentiate between ground-based and air-borne studies. Additionally we will identify those airborne studies that used in-situ observations of radicals (HO_x, RO_x) instead of those that use radical concentrations derived from constrained box model simulations.

2) page 5, lines 27-29: The authors calculate $J(O^1D)$ by scaling the TUV calculated $J(O^1D)$ using the ratio of observed $J(NO_2)$ and TUV calculated $J(NO_2)$. Are there any limitations in this method? If it is possible it would be nice if the authors could provide a reference providing some kind of evaluation of this scaling method.

Answer:

The scaling accounts for the effect of clouds that are not simulated by the TUV model, in particular enhanced up-welling radiation when flying over larger cloud decks. This method is not ideal, since it does not take into account the wavelength dependency of either cloud transmission or reflection. Shetter et al. (Comparison of airborne measured and calculated spectral actinic flux and derived photolysis frequencies during the PEM tropics B mission, JGR, 108, D2, 8234, doi:10.1029/2001JD001320, 2003) indicate that the TUV simulation of $J(NO_2)$ and $J(O^1D)$ compared to observations are accurate to within 6 – 18 % and 6 – 11 %, respectively.

3) Page 6, lines 20, 26 and 27: The authors use the acronym NOP instead of NOPR that use in the rest of the text. I would suggest to keep a consistency in the use of the acronym throughout the manuscript.

Answer:

We will use NOPR throughout the revised manuscript.

4) Page 6, line 32: The authors state that average altitude profiles for CH_3O_2 and H_2O have been calculated for GABRIEL data. Do they mean CO instead of CH_3O_2 since the radical CH_3O_2 is then calculated from Eq.5?

Answer:

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."

5) Page 7, line 4: Could you please specify which exactly species have handled for data gaps in HOOVER I and II campaigns?

Answer:

Data gaps during all three campaigns are mainly due to the low duty cycle of the TRISTAR instrument used to sequentially measure HCHO, CO, and CH_4. Due to a longer time spent on measuring HCHO and regular HCHO background measurements, only 10 min per hour (16 %) were dedicated to the measurement of CO and CH_4. Additional data gaps during GABRIEL arose from a partial failure of the H_2O measurements. During HOOVER II the NO measurement failed on the regular southbound flights. In the revised manuscript we will clarify this.

6) Page 8, lines 18-21: The authors dis-cuss that the measurement-calculated threshold NO concentration increases from the boundary layer towards the free troposphere mainly due to the decrease of observed HO_2 and estimated CH_3O_2 concentrations above the boundary layer. This could be further discussed if the authors consider that the NO threshold depends mainly to $J(O^1D)$, O_3 and H_2O and how these parameters vary from boundary layer to free troposphere. Of course the NO threshold depends also on other variables such as CO and CH_4 concentrations, temperature and pressure.

Answer:

In the revised manuscript we will add vertical profiles of NO_{th}, NO/NO_{th}, $P(O_3)$ and $L(O_3)$ for the individual processes described in R4, R5, R9, R10, and R12 to discuss differences between observations and model simulations in greater detail.

7) Page 8, line 33: The authors mention that this behavior is also found in the data from the other campaigns. Which campaigns do they mean? HOOVER I and II?

Answer:

Yes the other campaigns are HOOVER I and II. As mentioned above we will add vertical profiles for NO_{th} and the NO to NO_{th} ratio for all the campaigns discussed in our study.

8) Page 10, line 24: It is pointed that the analysis has restricted to background conditions by filtering data that have been affected by deep convection but there is no description somewhere in the manuscript how this filtering was done.

Answer:

Actually we did not filter the data for deep convection. Two flights,

one during GABRIEL and a second one during HOOVER II were dedicated to study the outflow of convective clouds. Those flights were discussed separately.

9) Discussion and conclusions: The NOPR values that have been calculated for the background conditions and presented in Sections 3.2, 3.3 and 3.4 should be also discussed in comparison with relevant calculations from other similar studies based on airborne and in-situ observations.

Answer:

In the revised manuscript we will add a paragraph comparing our results to previous studies.

Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2017-153-RC2, 2017 ©

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.

Chemical processes related to net ozone tendencies in the free troposphere

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Abstract. Ozone (O_3) is an important atmospheric oxidant, a greenhouse gas, and a hazard to human health and agriculture. Here we describe airborne in-situ measurements and model simulations of O_3 and its precursors during tropical and extratropical field campaigns over South America and Europe, respectively. Using the measurements, net ozone formation/destruction tendencies are calculated and compared to 3D chemistry-transport model simulations. In general, observation-based net ozone tendencies are positive in the continental boundary layer and the upper troposphere at altitudes above ~ 6 km in both environments. On the other hand, in the marine boundary layer and the middle troposphere, from the top of the boundary layer to about 6-8 km altitude, net O_3 destruction prevails. The ozone tendencies are controlled by ambient concentrations of nitrogen oxides (NO_x). In regions with net ozone destruction the available NO_x is below the threshold value at which production and destruction of O_3 balance. While threshold NO values increase with altitude, in the upper troposphere NO_x concentrations are generally higher due to the integral effect of convective precursor transport from the boundary layer, downward transport from the stratosphere and NO_x produced by lightning. Two case studies indicate that in fresh convective outflow of electrified thunderstorms net ozone production is enhanced by a factor 5 – 6 compared to the undisturbed upper tropospheric background. The chemistry-transport model MATCH-MPIC generally reproduces the pattern of observation-based net ozone tendencies, but mostly underestimates the magnitude of the net tendency (for both net ozone production and destruction).

1 Introduction

Ozone plays a pivotal role in the oxidising capacity of the troposphere. Besides being an oxidising agent itself, photolysis of O_3 at wavelengths less than 340 nm produces $O(^1D)$, whose subsequent reaction with water vapour yields two OH radicals, the dominant oxidant in the troposphere. Based on O_3 profiles in the troposphere, Junge (1963) argued that tropospheric ozone stems from downward transport from the stratosphere and is destroyed at the surface by deposition. But in the 1960s, studies indicated that tropospheric ozone is to a large extent due to in-situ photochemical production, similar to the Los

Angeles smog (Haagen-Smit and Fox, 1956; Leighton, 1961). A chemical mechanism for the photochemical production of tropospheric ozone was proposed by Chameides and Walker (1973) and Crutzen (1973) after the identification of a major tropospheric OH source by Levy (1971). Budget calculations based on atmospheric chemistry-transport modelling (e.g. Wild, 2007; Wu et al., 2007; Stevenson et al., 2006; von Kuhlmann et al., 2003), indicate that approximately 390-850 Tg/yr of tropospheric O_3 are due to stratosphere-troposphere-transport, 670-1180 Tg/yr are destroyed by deposition to the surface and -90 to +670 Tg/yr are due to photochemical net ozone production (NOP) in the troposphere (von Kuhlmann et al., 2003, Lelieveld and Dentener, 2000). The NOP itself is a delicate balance between two very large numbers (Lelieveld and Dentener, 2000; von Kuhlmann et al., 2003): ozone production $P(O_3)$ at ~3000-5000 Tg/yr and O_3 destruction $L(O_3)$ at slightly less, ~2500-4500 Tg/yr. The discussion about the relative strength of stratosphere-troposphere-exchange vs. NOP for tropospheric ozone is not yet resolved in detail. Gross production and destruction of ozone in a global model are based on the applied chemical mechanism, emissions of precursors and their subsequent distribution due to transport. Since stratosphere-troposphere-transport of O_3 depends on the gradient of O_3 between the lower stratosphere and upper troposphere, this process also depends on and influences photochemistry especially in the upper troposphere. Therefore, uncertainties in the models' photochemical ozone production have a strong influence on estimates of the amount of O_3 imported from the stratosphere. Furthermore, in chemical transport models (CTMs) and chemistry general circulation models (CGCMs) 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.

Tropospheric O_3 production is initiated by the oxidation of CO and volatile organic compounds by the OH radical:

$$CO + OH (+ O_2) \rightarrow HO_2 + CO_2 \qquad (R1)$$

$$CH_4 + OH + (O_2) \rightarrow CH_3O_2 + H_2O \qquad (R2)$$

$$RH + OH + (O_2) \rightarrow RO_2 + H_2O \qquad (R3)$$

The resulting peroxy radicals HO_2, CH_3O_2 and RO_2 subsequently react with NO to produce NO_2:

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (R4)$$

$$CH_3O_2 + NO (+O_2) \rightarrow NO_2 + HO_2 + HCHO \qquad (R5)$$

$$RO_2 + NO + (O_2) \rightarrow NO_2 + HO_2 + \text{carbonyl} \qquad (R6)$$

Subsequently, the NO_2 can be photolysed to recycle NO and produce O_3:

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) + (O_2) \rightarrow NO + O_3 \qquad (R7)$$

In remote regions where VOC concentrations other than CH_4 are low the production of O_3 can be approximated by:

$$P(O_3) = k(4)\,[HO_2]\,[NO] + k(5)\,[CH_3O_2]\,[NO] \qquad (\text{Eq. 1})$$

With k(4) and k(5) being the temperature dependent rate constant of reaction R(4) and R(5). Chemical destruction of O_3 is either due to photolysis or reaction with OH, HO_2 or an alkene:

$$O_3 + h\nu\ (\lambda < 340\ \text{nm}) \rightarrow O(^1D) + O_2 \qquad (R8)$$

$$O_3 + OH \rightarrow HO_2 + O_2 \qquad (R9)$$

$$O_3 + HO_2 \rightarrow OH + 2\ O_2 \qquad (R10)$$

$$O_3 + \text{alkene} \rightarrow \text{products} + O_2 \tag{R11}$$

Whether reaction R8 results in a permanent loss of O_3 depends on the fate of the electronically exited $O(^1D)$ radical. Reaction of $O(^1D)$ with either N_2 or O_2 leads to deactivation and subsequent reformation of O_3, but reaction with water vapour yields two OH radicals, leading to O_3 loss:

$$O(^1D) + H_2O \rightarrow 2\,OH \tag{R12a}$$

$$O(^1D) + O_2\,(+O_2) \rightarrow O_3 + O_2 \tag{R12b}$$

$$O(^1D) + N_2\,(+O_2) \rightarrow O_3 + N_2 \tag{R12c}$$

The branching ratio among the reactions R12a and R12b mainly depends on the water vapour concentrations and is thus altitude dependent.

In remote regions the reaction with alkenes can be neglected and the ozone loss $L(O_3)$ is given by reactions R8 – R10, with reaction R8 weighted by the branching ratio α:

$$L(O_3) = \alpha\, JO(^1D)\,[O_3] + k(9)\,[OH][O_3] + k(10)\,[HO_2][O_3] \tag{Eq. 2}$$

Where $JO(^1D)$ is the O_3 photolysis rate and α is given by Eq. 3:

$$\alpha = \frac{k(12a)[H_2O]}{k(12a)[H_2O]+k(12b)[O_2]+k(12c)[N_2]} \tag{Eq. 3}$$

The branching ratio α is typically of the order of 1 to 15 % for the upper troposphere and the boundary layer, respectively.

The net ozone production rate (NOPR) in ppbv/h is defined as the difference between production and loss:

$$NOPR = P(O_3) - L(O_3) \tag{Eq. 4}$$

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 (e.g. Pusede et al., 2015):

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{R13}$$

$$NO_2 + RO_2 + M \rightarrow NO_2RO_2 + M \tag{R14}$$

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{R15}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{R16}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{R17}$$

Here we neglect the loss of NO_2 due to reaction R13 and R14 in Eq. 4. This is justified by the overall low NO_x concentrations above the continental boundary layer. Reactions R15 to R17 will affect HO_x levels and would have to be taken into account to calculate their concentrations using a box model. In this study we will use in-situ observations of OH and HO_2 instead.

The threshold NO concentration, at which ozone production and loss are equal, can be calculated by setting

$$P(O_3) = L(O_3) \tag{Eq. 5}$$

and re-arranging for NO:

$$NO_{th} = \frac{\alpha\, J(O^1D)[O_3]+k(10)[HO_2][O_3]+k(9)[OH][O_3]}{k(4)[HO_2]+k(5)[CH_3O_2]} \tag{Eq. 6}$$

With reaction R4 being approximately 4000 times faster than R10 a typical range for NO_{th} is 10-20 pptv at an ozone concentration of about 50 ppbv. Below this NO_{th} concentration O_3 destruction prevails, while net production occurs at higher NO concentrations.

Model studies indicate that chemical O_3 destruction is generally found in the lower troposphere over the oceans due to low NO and high H_2O concentrations, while generally higher NO_x concentrations in the continental boundary layer lead to net O_3 production (Klonecki and Levy, 1997). Over the oceans O_3 loss extends to the free troposphere, while enhanced NO_x due to lightning, convective up-lift from anthropogenic or biomass burning sources and downward transport from the stratosphere leads to O_3 production in the free troposphere and tropopause region (Roelofs and Lelieveld, 1997). This difference between oceanic and continental free troposphere vanishes in the upper troposphere, where O_3 production prevails (Klonecki and Levy, 1997; von Kuhlmann et al., 2003). Studies that infer net ozone production at least in part from in-situ measurements are rare and often limited to the boundary layer (Ren et al., 2013; Liu et al., 2012; Sommariva et al., 2011; Kleinman et al., 2005; Fischer et al., 2003; Kanaya et al., 2002; Kleinman, 2000; Zanis et al., 2000; Penkett et al., 1997; Cantrell et al., 1996). A number of studies based on aircraft measurements have been performed, using in-situ O_3, CO, NO_x, volatile organic compounds (VOC) and radiation measurements in combination with a box model to calculate HO_x and RO_x radical levels to study NOPR in the free troposphere (Kuhn et al., 2010; Kondo et al., 2004; Davis et al., 2003; DiNunno et al., 2003; Ko et al., 2003; Reeves et al., 2002; Olson et al., 2001; Schultz et al., 1999; Crawford et al., 1997a; Crawford et al., 1997b; Davis et al., 1996; Jacob et al., 1996). NOPR studies based on in-situ HO_x or RO_x measurements by aircraft have been performed by Olson et al., 2012; Ren et al., 2008; Cantrell et al., 2003a and Cantrell et al., 2003b. Carzola and Brune (2010) described the application of an in-situ instrument to measure ozone production, while estimating the NOPR requires in-situ measurements of radicals (OH, HO_2, RO_2), nitrogen oxide (NO) and photolysis rates (i.e. $J(O^1D)$) in addition to ozone and water vapour. Here we present airborne in-situ measurements of radicals and ozone precursors over the tropical rainforest in South-America during the GABRIEL (Guyanas Atmosphere-Biosphere exchange and Radicals Intensive Experiment with a Learjet) campaign in October 2005, and compare with a series of north-south transects over Europe in the extratropical troposphere as part of the HOOVER (HOx OVer EuRope) campaign in 2006 and 2007. For the first time the NOPR over the tropical rainforest in South America as well as over Europe is evaluated based only on in-situ measurement data (except peroxy radicals) and compared to a 3D chemical transport model.

2 Methods

2.1 GABRIEL and HOOVER measurements

The GABRIEL campaign took place in October 2005 over the tropical rainforest in French Guyana and Surinam. A total of 10 measurement flights, each between 3 and 3.5 hours long, were performed between 3° and 6°N and 59° to 51°W at altitudes between 300 and 9000 m (Figure 1a). All flights followed a similar pattern, with take-off from Zanderij airport

(Surinam, 5.3°N, 55.1°W), followed by a high altitude stretch east over the Atlantic Ocean, and a descent into the marine boundary layer off the east coast of South America. Turning west the aircraft followed the main wind direction in-land, performing flights in and out of the continental boundary layer over the rainforest. Finally, before landing at the home base a high altitude profile was flown over Surinam. Additionally, similar flight profiles were performed in the N-S direction. Take-off times of the flights were varied over the campaign in order to investigate diurnal variations. Details of the scientific objectives, measurement and model results can be found in Lelieveld et al. (2008) and the GABRIEL special issue in Atmospheric Chemistry and Physics (http://www.atmos-chem-phys.net/special_issue88.html).

HOOVER consisted of a total of two measurement campaigns in October 2006 and July 2007, composed of 4 measurement flights each. The measurements covered Europe from 40° to 75°N between 8° and 15°E and up to a maximum altitude of 12 km (Figure 1b). From the home base Hohn (Germany, 54.2°N, 9.3°E) regular research flights were performed southward with a stop-over at Bastia airport, Corsica (France, 42.2°N, 9.29°E) and northward with a stop-over at Kiruna airport (Sweden, 67.5°N, 20.2°E). The majority of the flights were performed in the upper troposphere, but regular profiles were flown in and out of the home and stop-over bases, as well as approximately half way towards the respective destination in either Southern Germany or Northern Scandinavia. Additional flights in summer 2007 were directed to the Arctic (Svalbard, Norway, 78.1°N, 15.3°E) and two flights over central Germany to study the influence of deep convection. Details about the campaigns can be found in two previous publications (Klippel et al., 2011; Regelin et al., 2013).

2.2 Observations

During both campaigns a Learjet 35A from GFD (Hohn, Germany) was used. This jet aircraft has a range of 4070 km and a maximum flight altitude of approximately 14 km. In the present configuration both the horizontal and vertical range were limited due to the use of two wing-pods housing additional instrumentation. The scientific instrumentation was similar during both campaigns. It consisted of a chemiluminescence detector (ECO Physics CLD 790 SR, Switzerland) for NO, NO_2 and O_3 measurements (Hosaynali Beygi et al., 2011), a set of up- and downward looking 2π-steradian filter radiometers for $J(NO_2)$ measurements (Meteorologie Consult GmbH, Germany), a quantum cascade laser IR-absorption spectrometer for CO, CH_4 and HCHO measurements (Schiller et al., 2008), a dual enzyme fluorescence monitor (model AL2001 CA peroxide monitor, Aero-Laser GmbH, Germany) to measure H_2O_2 and organic hydroperoxides (Klippel et al., 2011), a laser induced fluorescence (LIF) instrument for simultaneous measurements of OH and HO_2 (Martinez et al., 2010; Regelin et al., 2013), a non-dispersive IR-absorption instrument (model LI-6262, Li-COR Inc., USA) for CO_2 and H_2O measurements (Gurk et al., 2008), a proton transfer reaction mass spectrometer (PTR-MS, Ionicon, Austria) for partially oxidized volatile organic compounds measurements and a series of canisters for post flight analysis of non-methane hydrocarbons (Colomb et al., 2006). Here a sub-set (O_3, NO, CO, CH_4, H_2O, OH, HO_2 and $J(NO_2)$) of these measurements will be used to deduce NOPR values. Details about the performance of those measurements with respect to time resolution, precision, detection limits and total uncertainties can be found in Table 1.

2.3 Estimating peroxy radical concentrations and $J(O^1D)$

Most species that are needed for an evaluation of equations 1 – 4 are provided by in-situ observations with the exception of $[CH_3O_2]$ in Eq. 1 and $J(O^1D)$ in Eq. 2, that have to be derived from other measurements.

As mentioned in the introduction, we assume that in remote areas outside of the continental boundary layer, the concentrations of other volatile organic compounds besides methane are low, so that CH_3O_2 is the only organic peroxy radical at significant concentrations in view of O_3 formation. According to R1 and R2 the production rates for HO_2 and CH_3O_2 radicals are proportional to the concentrations of CO and CH_4, respectively. Since the photochemical lifetimes of both radicals with respect to their reaction with NO (R4, R5) or self-reactions leading to peroxides are similar (Hosaynali Beygi et al., 2011; Klippel et al., 2011), we assume that the ratio of HO_2/CH_3O_2 is proportional to their production rates $k_{(CO+OH)}[CO][OH]/k_{(CH4+OH)}[CH_4][OH]$, so that the concentration of CH_3O_2 can be deduced from equation 5:

$$[CH_3O_2] = \frac{k(2)[CH_4]}{k(1)[CO]}\,[HO_2] \qquad \text{(Eq. 7)}$$

Thus using measured mixing ratios for CO, CH_4 and HO_2 and the temperature dependent rate coefficients for R1 and R2, the mixing ratio of CH_3O_2 can be estimated. Hosaynali Beygi et al. (2011) have used this approach in the marine boundary layer and compared it to both box model and 3D chemical transport model simulations in order to demonstrate the applicability of Eq. 7 in remote regions. We expect this to also hold for the free troposphere. In the continental boundary layer and in the outflow of deep convective clouds, R4 will most probably underestimate peroxy radical concentrations and thus O_3 production according to Eq. 1.

The O_3 photolysis rate $J(O^1D)$ and $J(NO_2)$ were calculated with the radiation transfer model TUV (https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model) (Madronich and Flocke, 1999) and scaled to the observed $J(NO_2)$ values. The scaling accounts for the effects of clouds that are not simulated by the TUV model, in particular enhanced up-welling radiation when flying over larger cloud decks. This method is not ideal, since it does not take into account the wavelength dependency of either transmission or reflection by clouds. Shetter et al. (2003) indicate that the TUV simulation of $J(NO_2)$ and $J(O^1D)$ compared to observations are accurate to within 6 – 18 % and 6 – 11 %, respectively.

2.4 MATCH simulations

To compare the experimentally derived NOPR values with model simulations the 3D chemistry transport model MATCH-MPIC (Lawrence et al., 2003; von Kuhlmann et al., 2003) (hereinafter referred to simply as MATCH) has been used. The model is driven by meteorological data from the National Centre for Environmental Prediction (NCEP) Global Forecast System (GFS). The chemical scheme, including details of the non-methane hydrocarbon chemistry, is described in von

Kuhlmann et al. (2003). The model was run with a resolution of approximately 2.8° x 2.8° in the horizontal direction and includes 42 vertical σ-levels up to 2 hPa. Emissions from anthropogenic and natural sources are based on the Emission Database for Global Atmospheric Research EDGAR v3.2 (Olivier et al., 2002). The model has been used for chemical weather forecasting to guide the day-to-day flight planning during GABRIEL and HOOVER. Here we used post-campaign analysis simulations to produce virtual flights through the model along the actual aircraft trajectories, as done in Fischer et al. (2006). From the model results NOPR values derived from a full chemistry scheme including also higher order peroxy radicals have been calculated for every point along the flight tracks.

3 Results

3.1 Data Processing

In the following, net ozone production rates in ppbv/h are calculated from in-situ data according to Eq. 4, with ozone production $P(O_3)$ calculated from Eq. 1, including Eq. 7 for $[CH_3O_2]$ and ozone loss $L(O_3)$ from Eq. 2 with Eq. 3 for α. A filter ($O_3 < 100$ ppbv) was applied to the data to exclude direct stratospheric influence. Data from two flights dedicated to the investigation of deep convection (GABRIEL flight GAB 08 on 12 October 2005 (Bozem et al., 2014) and HOOVER II flight 07 on 19 July 2007) were not included, and will be discussed separately. For the remaining data tropospheric NOPR rates were calculated along the flight tracks using merged data sets with a time resolution of 30 s. Instead of presenting the NOPR data as a time series for individual flights, we make use of the sampling strategy followed in the two campaigns. As can be seen in Figure 1, flights during GABRIEL were mostly oriented from east to west (in Fig. 1a), while flights during HOOVER had a north south orientation (Fig. 1b). Therefore, all NOPR data from the individual flights have been binned into altitude-longitude (GABRIEL) and altitude-latitude (HOOVER) bins. The bin size is 1 km in altitude, 0.5° in longitude (GABRIEL) and 2.5° in latitude (HOOVER). NOPR values are presented as median values for a given altitude/longitude (GABRIEL) or altitude/latitude (HOOVER) bin. Additionally, the 1σ-standard deviation of the individual NOPR values in the respective bin is given as a measure of the atmospheric variability. Please note, that median values are used throughout the manuscript for NOPR calculations instead of mean values, in order 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 terms of NO enhancement, we do not filter the data, but instead use median values that are not affected by occasional peak values. The same applies to values below the detection limit (e.g. for radicals) that might otherwise bias the calculations. 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 I as shown in the respective figures.

Since NOPR values can only be calculated for those bins that have at least one data point for each trace gas species needed in Eq. 1 – 7 (O_3, NO, CO, CH_4, H_2O, OH, HO_2 and $J(NO_2)$), missing data strongly limit data coverage. Data gaps during all three campaigns are mainly due to the low duty cycle of the TRISTAR instrument used to sequentially measure HCHO, CO, and CH_4. Due to a longer time spent on measuring HCHO and regular HCHO background measurements, only 10 min per hour (16 %) were dedicated to the measurement of CO and CH_4. Additional data gaps during GABRIEL arose from a partial lack of H_2O measurements. To overcome this, altitude profiles (median and standard deviation) for CO, CH_4 and H_2O have been calculated for the GABRIEL data set to substitute missing values by median values from the profiles for a particular altitude bin. This way the available number of NOPR calculations could be increased by a factor of 4, without changing trends in NOPR for different regions. Similar data gaps for CO and CH_4 during HOOVER I and II have been handled accordingly. These data gaps mainly affect the calculation of CH_3O_2 radicals in Eq. 7.

Further, for HOOVER II, nitrogen oxide (NO) data are not available from the flights to and from Corsica, thus in particular south of the Alps NOPR calculations cannot be based on in-situ data. Based on an additional flight between the home base in Northern Germany and Northern Italy (HOOVER II flight 06 from Hohn to Baaden Airport (Germany) on 19 July 2007), an average NO profile has been calculated for the southern part of Europe and used as a proxy for missing NO values. Note that data from HOOVER II flight 07 on the same day have not been used, since they were affected by strong convection over south-eastern Germany. Uncertainties due to the missing NO data during HOOVER II will be discussed further below. 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.

Simulation results for $P(O_3)$, $L(O_3)$ and NOPR along the flight trajectories obtained from MATCH have been filtered for stratospheric influence, processed and binned in a similar way as the in-situ data and will be presented together with the in-situ data.

3.2 NOPR for GABRIEL

Figure 2 shows results for NOPR calculations based on in-situ measurements (Fig. 2a) and MATCH simulations (Fig. 2c) for the GABRIEL campaign in October 2005. As mentioned above NOPR values have been calculated along the flight tracks and sampled into bins of 1 km height and 0.5° longitude. The median values of NOPR per bin are presented with different colours, ranging from blue (negative NOPR indicating net O_3 destruction) to red (positive NOPR indicating net O_3 production). The number of data points within a bin is given as a number in the lower left corner. The circle inside the bin is a measure of the variability, with a box filling circle indicating a variability of more than 50 % relative to the median. Note that a variability value is presented even if only 2 data points are available for an individual bin. Both figures are oriented from west to east, so that data over the Atlantic Ocean are on the right hand side of the figure. With the South American coastline located between 53.5°W and 53.0°W, bins east of this longitude are representative for marine air masses and bins towards the west represent continental air masses.

In the lowest bins (0 – 1 km altitude) representing the boundary layer, NOPR values indicate a change from O_3 destruction in the marine boundary layer (-0.2 to -0.4 ppbv/h between 51°W and 54°W) towards a highly variable O_3 production (0 – 0.6

ppbv/h) regime in the continental boundary layer over the tropical rainforest (54°W to 57.5°W) (Fig. 2a). Highest NOPR values are observed at the coast at 52.5°W – 53°W, due to local pollution enhancing NO (see the discussion of Fig. 3a further below) most probably in the vicinity of Cayenne, the capital of French Guyana. Note that the absolute values for NOPR in the boundary layer, in particular over land, are less reliable, since we do not consider the contributions of higher organic peroxy radicals to ozone production and also neglect an additional O_3 sink due to reaction with alkenes, in particular isoprene. In the free troposphere, above 1 km and below 6 km altitude, NOPR values are generally negative, with strongest O_3 destruction in the first 2 km above the boundary layer. Above 6 km there is again a region with slightly positive NOPR, hence net O_3 production. In general, above the boundary layer NOPR values exhibit no difference between marine and continental regions. Note that similar results are obtained from calculations based only on the sub-set of data points for which simultaneous in-situ measurements of all species necessary to calculate NOPR are available. Thus, replacing the missing values by median values from average profiles does not change the results significantly. This statement holds also for results from the other campaigns, with the exception of missing NO measurements south of 55°N during HOOVER II. This will be addressed in section 2.4.

The MATCH simulations (Fig. 2c) exhibit similar NOPR tendencies for the different altitude regimes, though the absolute values are generally smaller (-0.2 ppbv/h and 0.1 ppbv/h, respectively). Also, MATCH simulates net O_3 destruction in the continental boundary layer over the tropical rainforest, in contrast to the calculation derived from the in-situ observations (Fig. 2a).

To illustrate the differences in NOPR between observations and model simulations, average (median, mean, 1σ-standard deviation) altitude profiles for the individual production and destruction terms are given in Fig. 2b and d for the observations and the simulations, respectively. Production throughout the troposphere is dominated by the reaction of NO with HO_2 (red dots in Fig. 2b and d), while the reaction of NO with CH_3O_2 (red squares) is much smaller by about a factor of 2. This behaviour is seen in both the observations (Fig. 2b) and the model simulations (Fig. 2d), but the absolute values for the production rates differ by a factor of two, with the observations being higher than the simulations. The concentration of HO_2 (and thus according to Eq. 7 the concentration of CH_3O_2) decreases with altitude throughout the troposphere by roughly a factor of 10 (Kubistin et al., 2010) so that the increase in the production rates is mainly due to an increase in NO concentrations, partly due to the shift in the NO_x partitioning at low temperatures (Brunner et al., 2001; Ziereis et al., 2000). Ozone destruction is dominated by photolysis up to an altitude of 6 km (blue dots in Fig. 2b and d) with much higher (up to a factor of 4) destruction rates deduced from the observations (Fig. 2b). The reactions between ozone and either HO_2 or CH_3O_2 (triangles) are rather constant throughout the troposphere with larger rates (factor of 2) derived from observations compared to the model simulations. It is worth mentioning that the destruction rates are proportional to the ozone concentration. Increasing mixing ratios with altitude thus compensate for the pressure drop leading to almost constant O_3 concentrations.

In Figure 3 the ratio between NO and NO_{th} calculated from Eq. 7 is plotted for in-situ data (Fig. 3a) and MATCH simulations (Fig. 3d). According to Eq. 7 the measurement-calculated threshold NO concentration in the boundary layer is 9 pptv, while it increases to about 20 pptv above the boundary layer (Fig. 3b). This is mainly due to the decrease of observed

HO_2 and estimated CH_3O_2 concentrations above the boundary layer, which leads to an increase of the threshold NO value. Measured NO mixing ratios are higher than the threshold values in the continental boundary layer (approx. 2 times larger), and at altitudes above 6 km (up to 3 times larger) (Fig. 3a), indicating net ozone production regimes as shown by Fig. 2a.

The evaluation of MATCH shows a slightly different altitude-dependent behaviour of NO_{th}, with highest values (21 pptv) in the boundary layer, decreasing almost linearly with altitude to lowest values of 10 pptv at 8 km (Fig. 3d). This behaviour is due to the underestimation of the reaction of O^1D with H_2O, most likely due to an underestimation of lower tropospheric H_2O concentrations. Figure 3b shows that simulated NO concentrations in MATCH are almost always lower than the threshold values (NO/NO_{th} ratio between 0 and 1), except at the highest altitudes (NO about 50% higher than NO_{th}), thus explaining the overall negative NOPR values in Fig 2b. Therefore, the deviations between model simulations and in-situ data for NOPR are due to differences in the threshold NO levels (NO_{th}) and generally lower NO concentrations in the model simulations. Discrepancies in NO_{th} by the MATCH model are possibly related to the non-methane hydrocarbon chemistry scheme, which may underestimate radical recycling under low NO_x conditions and high isoprene (Kubistin et al., 2010; Taraborrelli et al., 2012).

In general, the charts of the NO to NO_{th} ratio resemble the NOPR charts, with ratios larger than unity corresponding to net ozone production and ratios less than unity to ozone destruction. The values also scale quantitatively, illustrating the strong dependency of NOPR on NO mixing ratios. At the rather moderate NO levels in the free troposphere this relationship seems to be linear. This behaviour is also found in the data from the HOOVER campaigns.

3.3 NOPR for HOOVER I

Figure 4 shows results for NOPR calculations based on in-situ (Fig. 4a) and MATCH simulations (Fig. 4d) for the HOOVER I campaign in October 2006 over Europe. For this campaign the data for NOPR have been combined into 1 km altitude and 2.5° latitude bins. The majority of the data is obtained in the upper troposphere, while vertical profiles are restricted to take-offs and landings in airports on Corsica (40° - 42.5° N), Hohn (52.5° - 55°N) and Kiruna (67.5° – 70°N). Additional profiles were flown north and south of the Alps (45° - 50°N) and over Sweden (60° - 62.5°N). Overall, the in-situ data indicate net ozone production (0.1 – 0.3 ppbv/h) throughout the troposphere, except at the most northern (0 ppbv/h) and southern (~ -0.1 ppbv/h) parts of the flights. Threshold NO values are between 15 and 20 pptv below 2 km altitude and approximately 10 pptv between 2 and 10 km. Above that altitude they linearly increase to approx. 35 pptv at 12 km (Fig. 5b). In regions with net ozone production (NOPR > 0 ppbv/h), measured NO concentrations are up to a factor of 4 higher than NO_{th}. In the regions with NOPR ≤ 0 ppbv/h the measured NO concentration is smaller than NO_{th} (Fig. 5a).

MATCH simulations of NOPR (Fig. 4c) exhibit slightly lower values (0 – 0.1 ppbv/h) compared to those derived from in-situ data, but the general tendencies are reproduced well. Figure 4b and d indicate that this difference between observations and model simulations is mainly due to an underestimation of the NO plus HO_2 reaction (red dots) by the model (~ factor of 2). The other production term ($NO + CH_3O_2$) is similar for observations and model simulations (red squares). As has been observed for GABRIEL the almost constant production terms are due to an increase of NO with altitude, while HO_2 and thus CH_3O_2 concentrations drop by approximately a factor of 6 (Regelin et al., 2013). Contrary to GABRIEL, ozone photolysis is not the dominant sink (blue squares in Fig. 4b and d), but is similar to the other destruction rates ($HO_2 + O_3$ and $OH + O_3$). The absolute destruction rates are comparable between observations and model simulations. This similarity of the destruction rates in observations and model simulations is most probably responsible for the similarity of the NO_{th} values. The altitude profile of NO_{th} derived from observations and MATCH are very similar, with the absolute values below 10 km being only slightly different (8 pptv from MATCH compared to 10 pptv from the observations) (Fig. 5b and c). As indicated in Fig. 5a and c NO/NO_{th} values are also comparable. The only exception is the vertical profile over Sweden, were the observations indicate strong ozone production due to high NO concentrations, which are not reproduced by MATCH. Overall, MATCH tends to underestimate NO concentrations throughout the troposphere, possibly related to underestimated vertical mixing of pollution from the boundary layer or missing NO_x reservoir species such as alkyl nitrates in the chemistry scheme.

3.4 NOPR for HOOVER II

As mentioned above, NOPR calculations for HOOVER II are strongly affected by the failure of the CLD instrument used for NO measurements on the flights to the south, from Hohn to Corsica and back. Figure 6a shows results for NOPR calculations based on this limited data set. The NOPR calculations based on in-situ data are limited to latitudes north of 50°N. At higher latitudes a similar pattern to that during HOOVER I is observed, with net ozone production in the boundary layer, negligible to negative NOPR in the middle troposphere and a tendency for moderate net ozone production in the upper troposphere. This general pattern is reproduced by MATCH simulations north of 50°N as shown in Fig. 6d.

In order to improve the data coverage, in particular south of 50°N, we used an average NO profile measured on 19 July 2007. On this day, two measurement flights were performed (HOOVER II flights 06 and 07), to study deep convection over Southern Germany out of Baaden airport (48.4°N, 8.4°E). Since no nitric oxide measurements were obtained on the regular flights south, the transfer flight to Baaden airport was extended southward to Northern Italy. Thus a limited data set of NO could be obtained south of 50°N. Profile information is available from a descent north of the Alps close to Oberpfaffenhofen (48.4°N, 11.1°E) and the landing at Baaden airport. From this data set an average profile was deduced and median values have been used in the calculation of NOPR south of 55°N (Fig. 6b). This led to overall negative ozone tendencies throughout the troposphere at latitudes south of 50°N in contrast to the MATCH simulations that predict net ozone production (Fig. 6d). Both the model and NO_{th} calculations based on in-situ data indicate a threshold NO concentration of 15 – 20 pptv between the boundary layer and approx. 9 km altitude (with strongly increasing NO_{th} above this altitude), with the model calculating slightly smaller values. The MATCH model simulates NO concentrations south of 55°N that are a factor of 2 to 3 higher than the simulated NO_{th}. The NO values from the HOOVER II flight 06 profile used to fill in data gaps south of 50°N are more than 50 % lower than the deduced NO_{th} based on in-situ observations. Thus the negative ozone tendencies in Fig. 5b are mainly due to an underestimation of NO mixing ratios. Therefore, a sensitivity study was performed by doubling the NO concentrations obtained from the HOOVER II flight 06 profile. The results for NOPR are shown in Figure 6c. The doubling of NO mixing ratios leads to a shift to positive NOPRs south of 55°N and to a much better agreement with the model simulations shown in Fig. 5d. It should be mentioned that the enhanced NO mixing ratios are in rather good agreement with NO measurements obtained over southern Germany and northern Italy in the summer of 2003 as part of the UTOPHIAN-ACT campaign (Stickler et al., 2006). Thus it seems that the NO mixing ratios from the HOOVER II flight 06 profile may not be representative of background NO south of 50°N. This sensitivity study clearly showed the dominant role of NO for the NOPR calculations for HOOVER II. Taking into account the uncertainty in the measured NO data south of 55°N it does not make sense to discuss and compare production and destruction terms as in GABRIEL and HOOVER I.

Overall, a general feature of the three missions is a tendency of net ozone production at the highest altitudes, although we calculate strong increases of NO_{th} with altitude. For HOOVER II both model simulations and observation-based calculations indicate a doubling of NO_{th} between 9 and 11 km altitude from approx. 20 pptv to more than 40 pptv. As mentioned in the previous sections, similar tendencies for NO_{th} were also deduced for HOOVER I and GABRIEL. In order to maintain positive NOPR at high altitudes a strong enhancement of NO above 10 km is required. In the next section we will discuss the influence of deep convection on NOPR based on two case studies during GABRIEL and HOOVER II, respectively.

3.5 The influence of deep convection on NOPR

As outlined in section 2.1 the analysis thus far has been restricted to “background conditions” by filtering data that have been affected by deep convection. Research flights to study the outflow of deep convection have been performed during both GABRIEL (Bozem et al., 2014) and HOOVER II (Regelin et al., 2013). Details about the convective systems, the flight tracks and trace gas measurements can be found in these articles.

During GABRIEL the outflow of a single convective cell at 9 to 11 km showed enhancements relative to background mixing ratios for CO, NO, OH and HO_2 of 40%, 130%, 70% and 20%, respectively. The CO increase with altitude suggests a strong contribution of boundary layer air. Transport of HO_x precursors from lower layers of the troposphere led to enhanced OH and HO_2 concentrations in the outflow. The strong enhancement in NO is most likely due to additional NO production from lightning. Ozone mixing ratios were also enhanced (38%), which may contradict the expectation that transport of boundary layer air in convective systems should lead to a decrease of O_3 mixing ratios in the outflow relative to the undisturbed middle and upper troposphere. A detailed discussion of the trace gas budgets, in particular for O_3, can be found in Bozem et al. (2014). Figure 7a shows mean and median values for NOPR in the outflow at the 10.5 km bin relative to campaign background median and mean altitude profiles for non-convective air masses. The median value of 0.2 ppbv/h (mean: 0.27 ± 0.13 ppbv/h) is roughly a factor of 3 higher than the background value (median: 0.06 ppbv/h; mean: 0.06 ± 0.04 ppbv/h). This is mainly due to the enhancement of NO, in addition to the increase of peroxy radical concentrations.

In order to compare the GABRIEL results for NOPR with literature data for the tropics we estimate daily O_3 production by multiplying the hourly value with a typical day length of 12 h, yielding a value of 2.4 ppbv/d (range: 1.62 – 4.77 ppbv/d). This is in good agreement with observations over the Brazilian rain forest during ABLE 2B (1.5 – 1.7 ppbv/d) for conditions with an inflow from rural areas (Pickering et al., 1992a). For storms with an inflow characterized by urban environments generally higher values were deduced during ABLE 2B (16.5 – 17.2 ppbv/d) (Pickering et al., 1992a). Higher values were also observed for convective transport from biomass burning plumes during ABLE 2A over South America (7.4 – 8.5 ppbv/d) (Pickering et al., 1992b), while smaller values of the order of 1 – 1.5 ppbv/d have been observed over tropical oceans (Pickering et al., 1993; Schulz et al., 1999; Kita et al., 2003; Koike et al., 2007).

During HOOVER II an eastward moving mesoscale convective system developed over the southern part of Germany on July 19, 2007. During a research flight out of Baaden airport, in- and outflow of a strong convective cell were probed close to Dresden, the capital of the State of Saxony. The outflow at 10.5 km altitude showed enhancements relative to background mixing ratios for CO, NO, OH and HO_2 by 85%, 600%, 350% and 150%, respectively, due to almost undiluted transport of boundary layer air to the upper troposphere and strong lightning activity. Ozone in the outflow was 20% lower than in background air (Bozem et al., 2017). As shown in Figure 7b this leads to a median NOPR of 1.89 ppbv/h (mean: 1.9 ± 0.28 ppbv/h), a factor of 6 higher than the upper tropospheric background for HOOVER II (median: 0.29 ppbv/h; mean: 0.31 ± 0.07 ppbv/h). The NOPR in the case study over Europe is an order of magnitude larger than over South America during GABRIEL. Median mixing ratios for NO during HOOVER and GABRIEL were 0.96 ppbv and 0.1 ppbv, respectively. Thus the difference in NOPR for the two case studies is mainly due to different NO concentrations. The median daily net ozone production for the HOOVER case is 22.67 ppbv/d (range: 19.47 – 26.11 ppbv/d) and about a factor of 2 – 4 larger than values reported in the literature for NH mid-latitudes, e.g. ~ 15 ppbv/d during PRESTORM, Oklahoma (Pickering et al., 1990; Pickering et al., 1992a), 10 – 13 ppbv/d during STERAO-A over North America (DeCaria et al., 2005), up to 5 ppbv during EULINOX over Europe (Ott et al., 2007), and 5 – 7 ppbv/d during DC3 over North America (Apel et al., 2015).

4. Discussion and conclusions

As mentioned in the introduction, observation based calculations of NOPR using airborne data are rare. The majority of these studies were made over the central and eastern Pacific (Cantrell et al., 2003a; Olson et al., 2001; Kondo et al., 2004; DiNunno et al., 2003; Davis et al., 2003; Schultz et al., 1999; Crawford et al., 1997a; Crawford et al., 1997b; Davis et al., 1996) or the Atlantic Ocean (Ren et al., 2008; Reeves et al., 2002; Jacob et al., 1996). Continental studies thus far are restricted to Australia (Ko et al., 2003), the east coast of North America (Ren et al., 2008), and high latitudes over north America (Olson et al., 2012; Cantrell et al., 2003b). This study is the first performed over the rain forest in South America (GABRIEL) and over continental Europe (HOOVER). It is also the first study that compares observation based NOPR to a 3D model simulation. Previous publications have used constrained box models, which are optimal tools to test the ozone production mechanism.

The net O_3 tendencies derived from both in-situ observations and 3D-model simulations confirm earlier studies with net O_3 formation (NOPR > 0) taking place in the continental boundary layer and the upper troposphere (above approx. 7 km in the tropics and mid-latitudes), and net O_3 destruction (NOPR < 0) in the marine boundary layer and the lower free troposphere (between 1 and 6 km altitude). The main reason that explains this distinction is shown to be the NO concentration. Both observations and model simulations indicate that the fate of ozone depends on the amount of NO relative to the threshold NO concentration, derived from Eq. 7. In our study, the observed NO concentrations are always close to NO_{th} (between 10% and several 100%). The NOPR values are therefore almost linearly dependent on NO, being typical for NO_x limited O_3 production regimes (Seinfeld and Pandis, 1998).

This strong NO dependency also affects the comparison between in-situ observations and model simulations. Although NOPR values show similar tendencies, absolute values are often slightly different, with the modelled absolute NOPR values typically being smaller in magnitude than observed (both for production and destruction regimes). This is partly due to differences in measured and simulated NO concentrations, as has been discussed for HOOVER II. An additional factor influencing the comparison is the calculated threshold NO value, which often differs for the observations and model simulations. This indicates that the reasons for the model-observation differences are complex and depend on more than one parameter.

Absolute values for NOPR are comparable to earlier observations. During INTEX-A, which was performed over the east coast of North America and the western Atlantic Ocean, mean NOPR values of 8.4 ppbv/day, -0.8 ppbv/day and 11.4 ppbv/day were observed for the boundary layer (BL), the middle troposphere (MT) and the upper troposphere (UT), respectively (Ren et al., 2008). Observed daily means of NOPR during HOOVER I (fall season) are ~ 2 ppbv/day (BL), zero (MT) and ~ 1 ppbv/day (UT) increasing to ~ 4 ppbv/day (BL), -1 ppbv/day (MT) and ~ 1 ppbv/day (UT) during the summer measurements (HOOVER II). These values are close to observation based estimates by Olson et al. (2012) over North America during summer 2008 as part of the ARCTAS campaign (BL: 2 ppbv/day, MT: -1 ppbv/day, UT: 1 ppbv/day). Since no data have been reported previously for the troposphere over the tropical rainforest, absolute NOPR values for GABRIEL cannot be compared.

One remarkable feature is the shift to positive NOPR values above approx. 7 km altitude that is found in both observations and simulations. This shift occurs, although NO_{th} shows a tendency to increase at the highest altitudes. In previous publications NO_{th} has been designated as either $NO_{critical}$ (e.g. Cantrell et al., 2003a) or as NO compensation point (NO_{comp}) (Reeves et al., 2002). Cantrell et al. (2003a) point out that for a number of campaigns critical NO levels generally encompass a “triangular” envelop bounded by about 5 pptv and a line between 25 pptv at the surface and 5 pptv at 12 km altitude (Figure 10e in Cantrell et al., 2003a). Both observation-derived and model calculated NO_{th} values from this study fit into the triangle defined by Cantrell et al. (2003a), but differ at the highest altitudes. While the campaigns listed by Cantrell et al. (2003a) show either constant values throughout the troposphere, or decreasing values with altitude, we find an increase in NO_{th} at the highest flight levels during both HOOVER campaigns. According to Eq. 6 this increase in NO_{th} can be either due to an increase in the O_3 sinks (photolysis and subsequent reaction with H_2O or reaction with OH or HO_2), which are directly and positively correlated to the ozone concentration, or a decrease in the O_3 source (concentrations of HO_2 and CH_3O_2). Due to the pressure decrease by a factor of 4 from the surface to 10 km altitude the concentrations of the radical precursors (CO, CH_4) also decrease by a factor of 4 which strongly reduces the concentrations of HO_2 and CH_3O_2 radicals and thus the denominator of Eq. 6. Ozone exhibits strongly increasing mixing ratios with altitude that compensate the pressure reduction effect, leading to an almost constant concentration throughout the troposphere. Overall this leads to a rather invariable O_3 loss rate throughout the troposphere even at the strongly decreasing H_2O concentrations in the upper troposphere. Most likely the observed increase of NO_{th} in the tropopause region during the HOOVER campaigns is due to a combination of strongly increasing ozone concentrations and decreasing radical (HO_2, CH_3O_2) concentrations. Reeves et al. (2002) report a similar increase in NO_{comp} observed in the middle troposphere over the Atlantic (Fig. 5b of Reeves et al., 2002). Here NO_{comp} increases at an altitude of 3 km due to a strong increase in ozone. To obtain net O_3 production above 7 km altitude, a strong increase in NO concentrations with altitude is required. This NO increase with altitude is partly due to a shift in the partitioning in NO_x, yielding higher NO concentrations at high altitude due to the temperature dependency of the NO + O_3 reaction, whose rate constant decreases with decreasing temperature (Ehhalt et al., 1992; Ziereis et al., 2000). Additional sources of NO associated with convection, lightning and downward transport from the stratosphere further enhance NO at high altitudes (Schumann and Huntrieser, 2007), resulting in the positive NOPR values above 7 km altitude obtained for all three campaigns. The case studies of enhanced NOPR values associated with convection and lightning produced NO_x in section 3.5 thus indicate that the general increase of NOPR above 7 km altitude is most likely due to the integral effect of convection on the upper troposphere.

Acknowledgements. The authors would like to thank Uwe Parchatka, Rainer Königstedt, and Corinne Schiller for their help with the measurements. Also we would like to acknowledge the support from the GABRIEL and HOOVER teams, envisvcope GmbH (Frankfurt), and GFD (Gesellschaft für Zielflugdarstellung, Hohn).

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Table 1: Precision, accuracy and detection limit of the in-situ measurements used to deduce NOPR.

	Precision (1σ)	*Accuracy*	*Detection limit*
$J(NO_2)$	1%	10%	
CO	< 1 %	1 %	
CH_4	< 1 %	1 %	
H_2O		5 %	200 ppmv
O_3	4 %	2 %	2 ppbv
NO	7 %	12 %	5 pptv
OH	7 %	18 %	0.02 pptv
HO_2	1 %	18 %	0.07 pptv

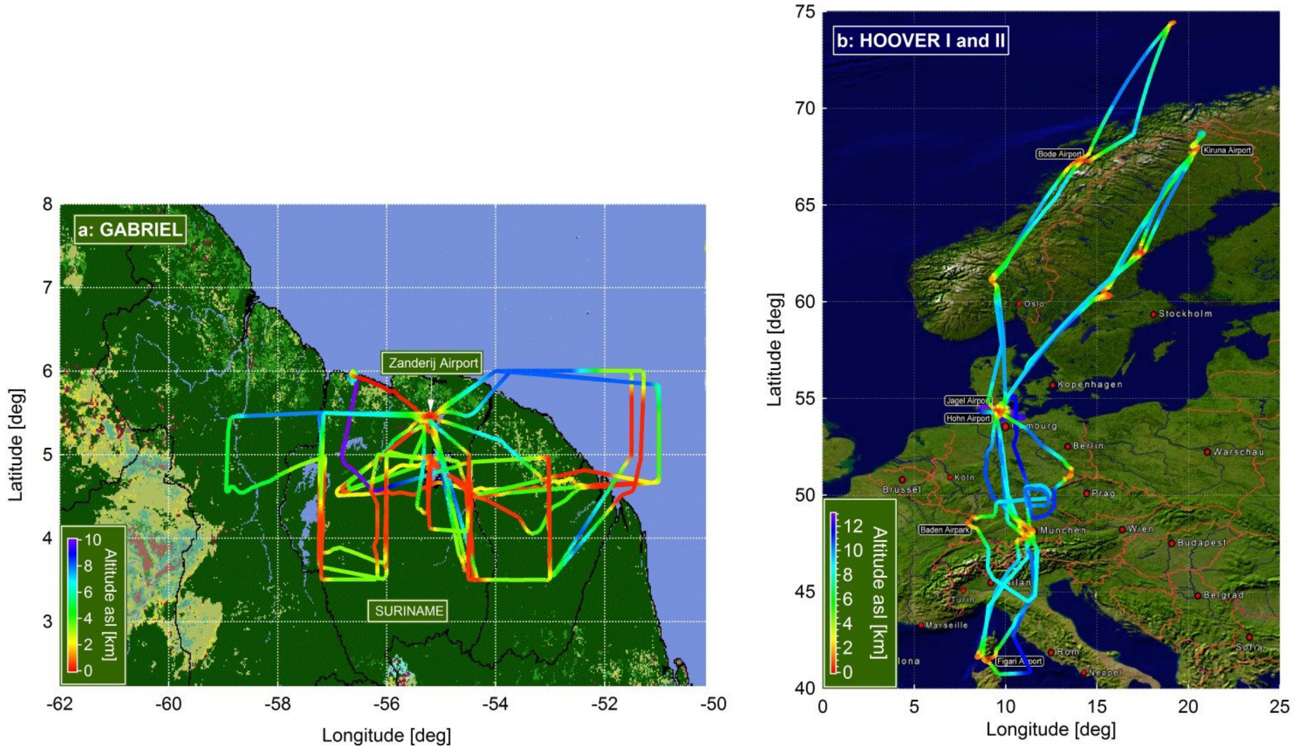


Figure 1: Flight tracks during GABRIEL (a: left panel) and HOOVER I and II (b: right panel).

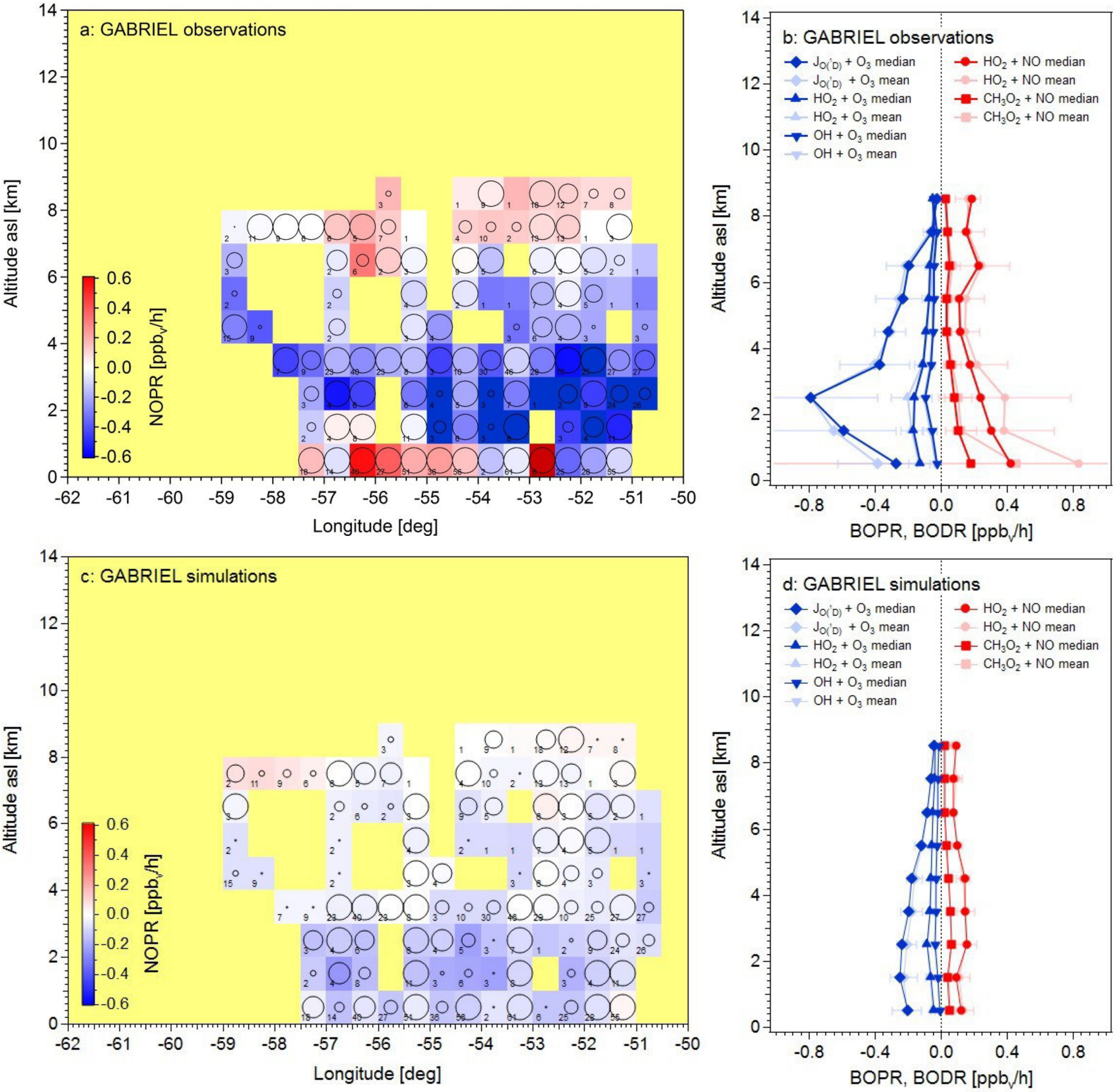


Figure 2: Net ozone production rates (NOPR) in ppbv/h calculated from in-situ data (a: upper panel) and from MATCH simulations (c: lower panel) for GABRIEL. Altitude profiles of individual production and destruction rates are shown in b (observations) and d (model simulations).

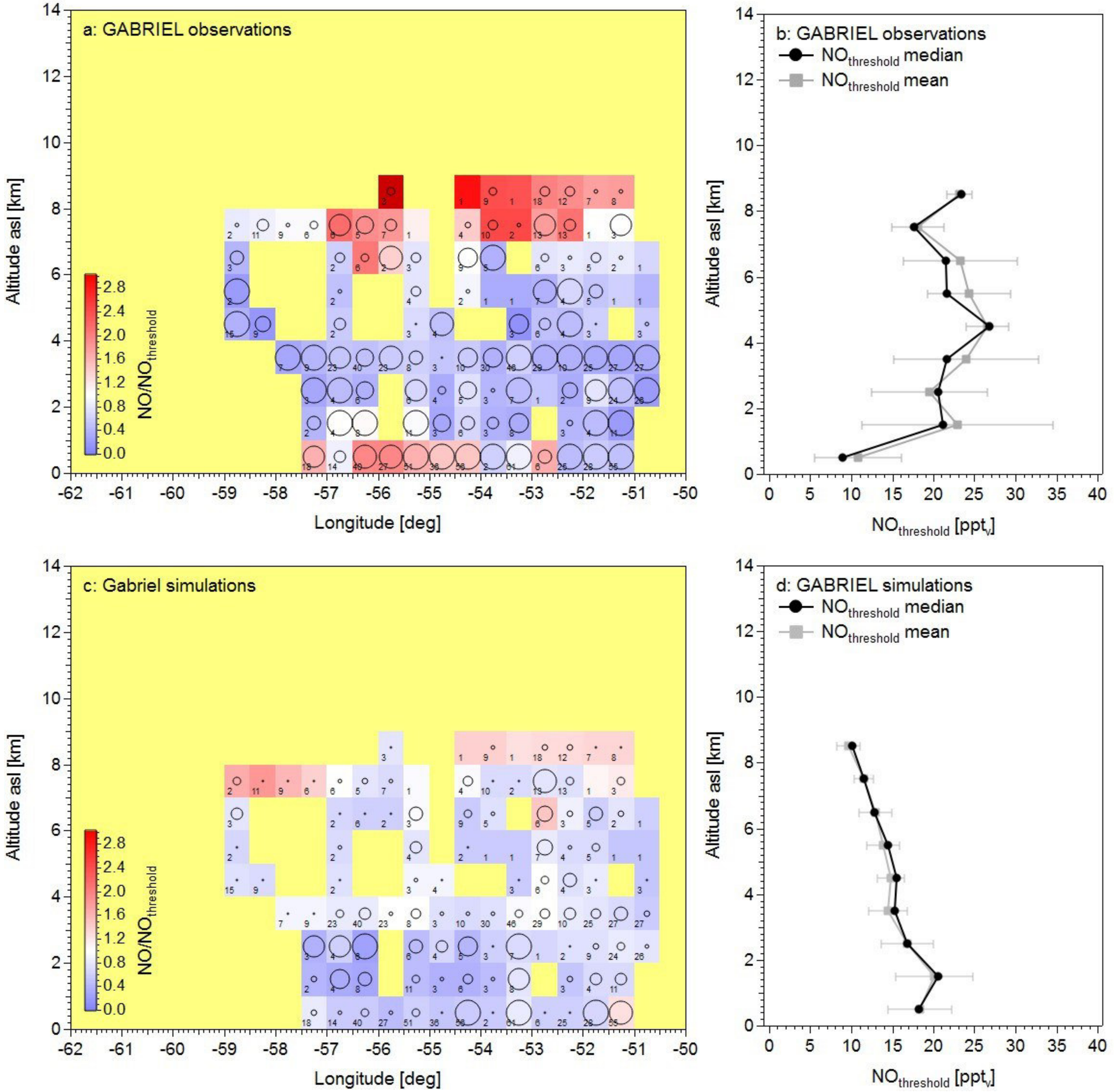


Figure 3: Ratio of NO to NO_{th} deduced from in-situ data (a: upper panel) and MATCH simulations (c: lower panel) for GABRIEL. Altitude profiles for NO_{th} are given in panel b for the observations and in panel d for model simulations.

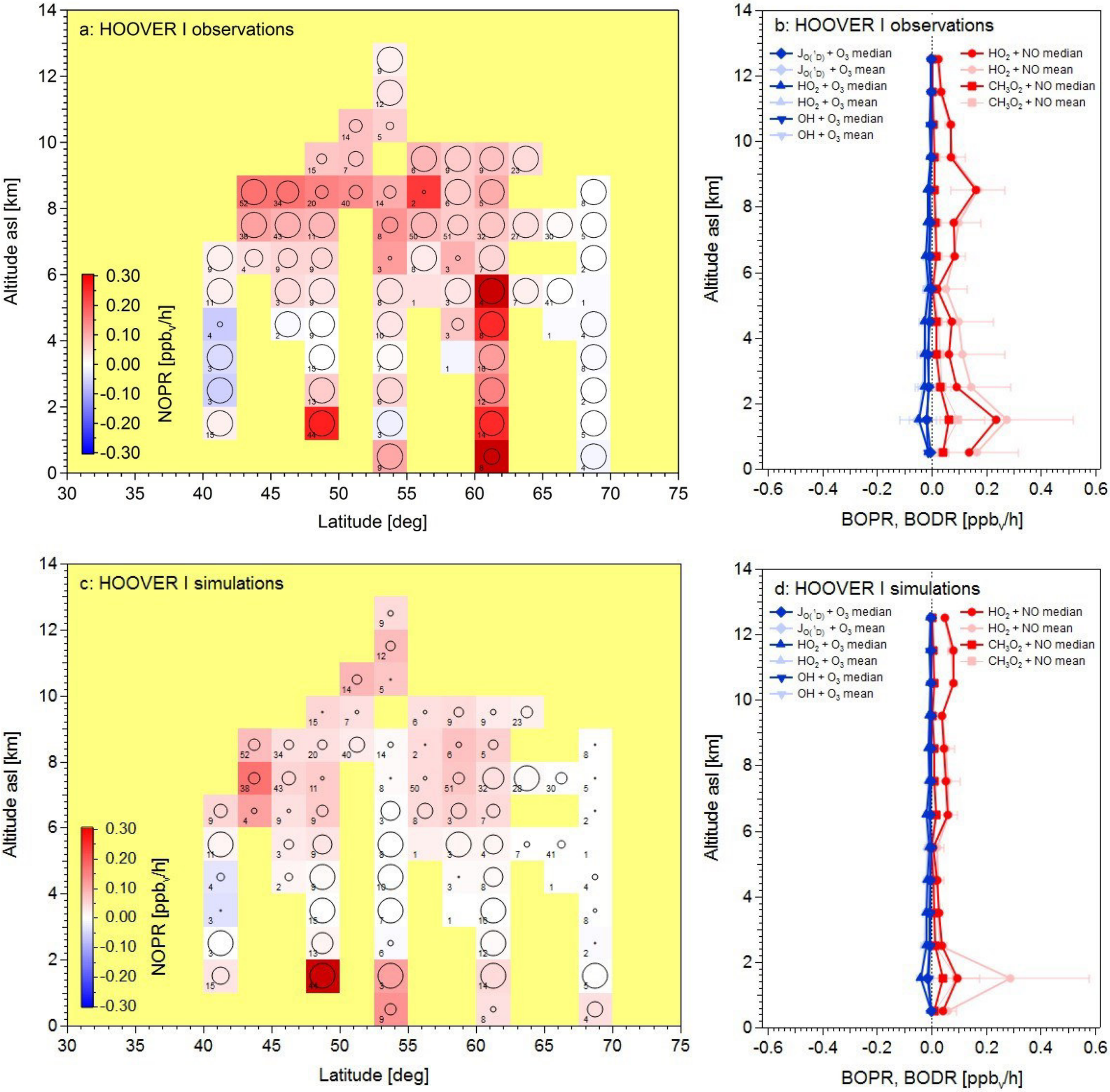


Figure 4: Net ozone production rates (NOPR) in ppbv/h calculated from in-situ data (a: upper panel) and from MATCH simulations (c: lower panel) for HOOVER I. Altitude profiles of individual production and destruction rates are shown in b (observations) and d (model simulations).

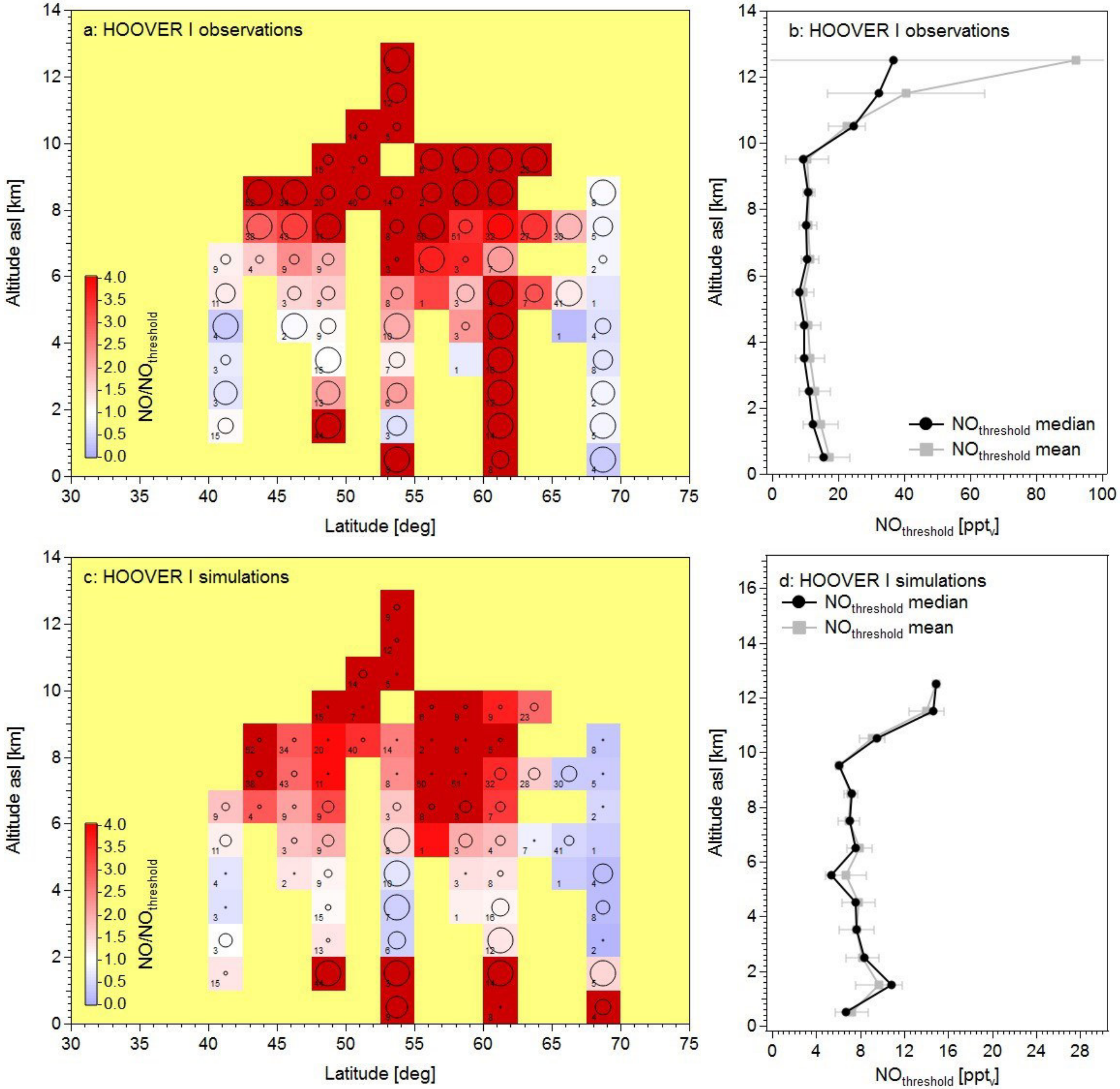
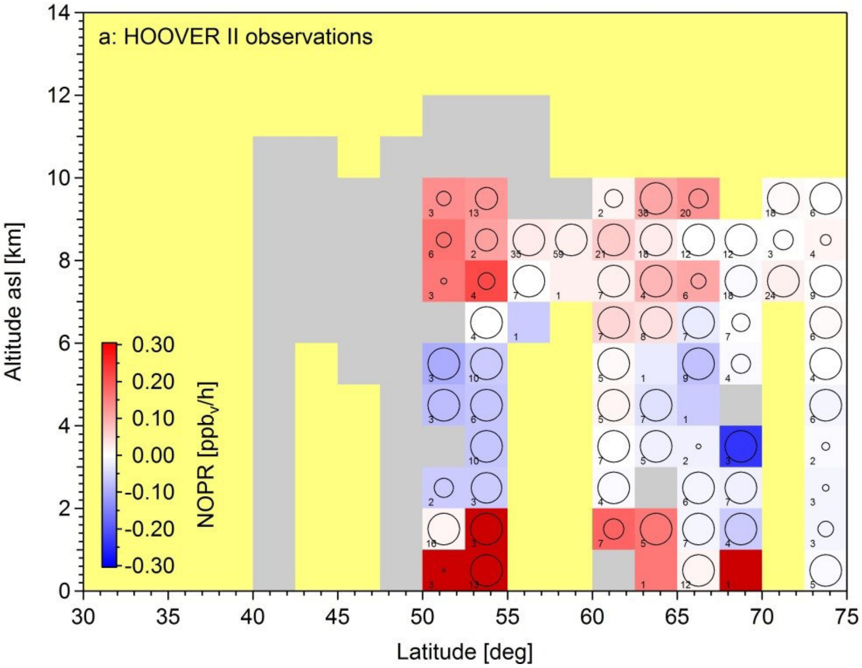
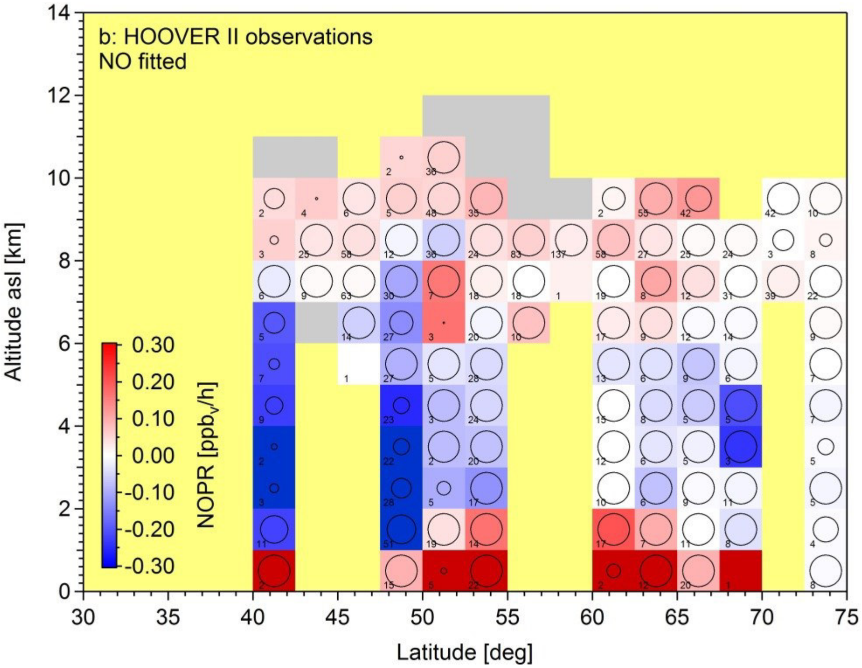


Figure 5: Ratio of NO to NO_{th} deduced from in-situ data (a: upper panel) and MATCH simulations (c: lower panel) for HOOVER I. Altitude profiles for NO_{th} are given in panel b for the observations and in panel d for model simulations.


a: HOOVER II observations
Altitude asl [km]
0
2
4
6
8
10
12
14
Latitude [deg]
30
35
40
45
50
55
60
65
70
75
NOPR [ppb$_v$/h]
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30


b: HOOVER II observations
NO fitted
Altitude asl [km]
0
2
4
6
8
10
12
14
Latitude [deg]
30
35
40
45
50
55
60
65
70
75
NOPR [ppb$_v$/h]
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30

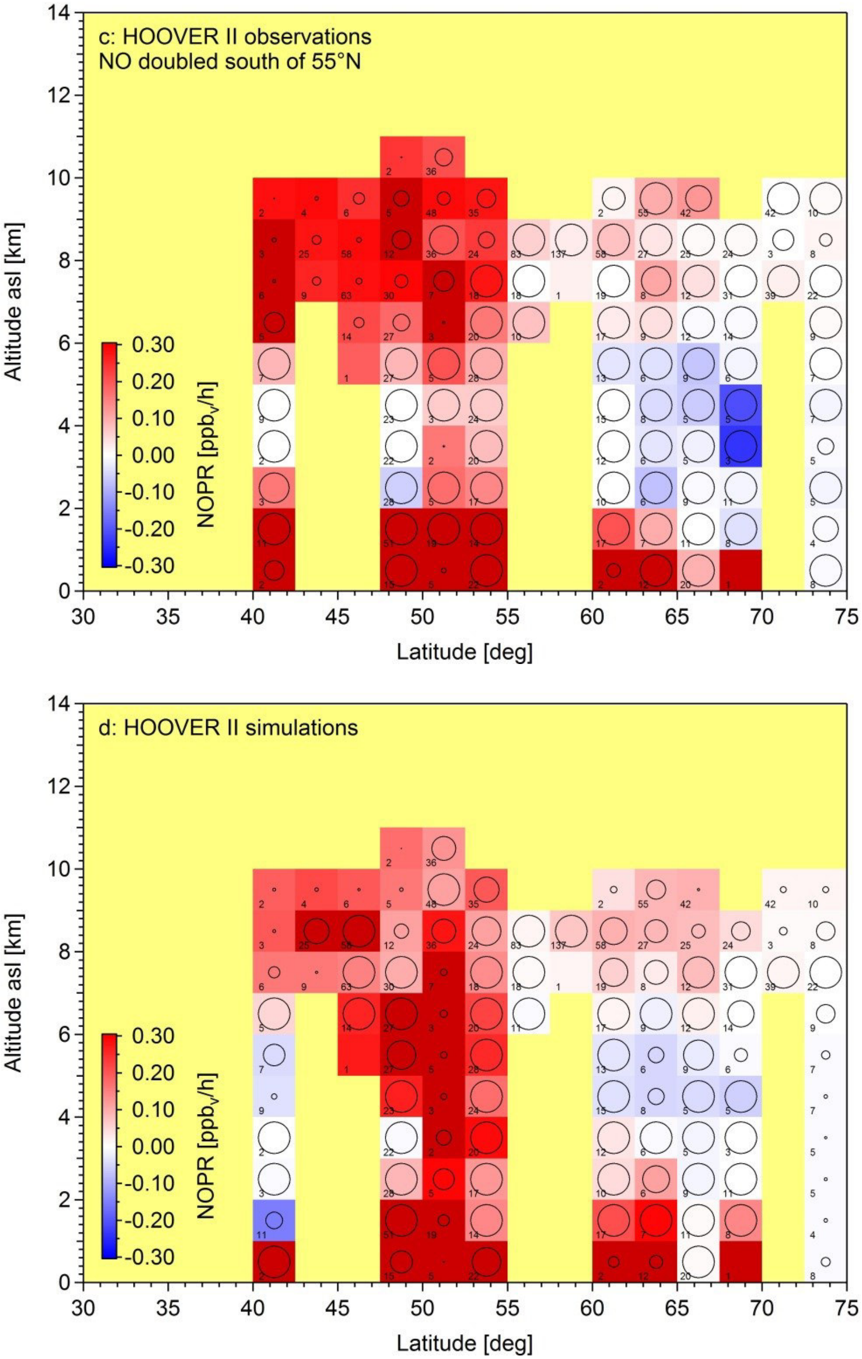


Figure 6: Net ozone production rates (NOPR) in ppbv/h calculated from in-situ data (a), fitted NO (b), double NO (c) and from MATCH simulations (b) for HOOVER II.

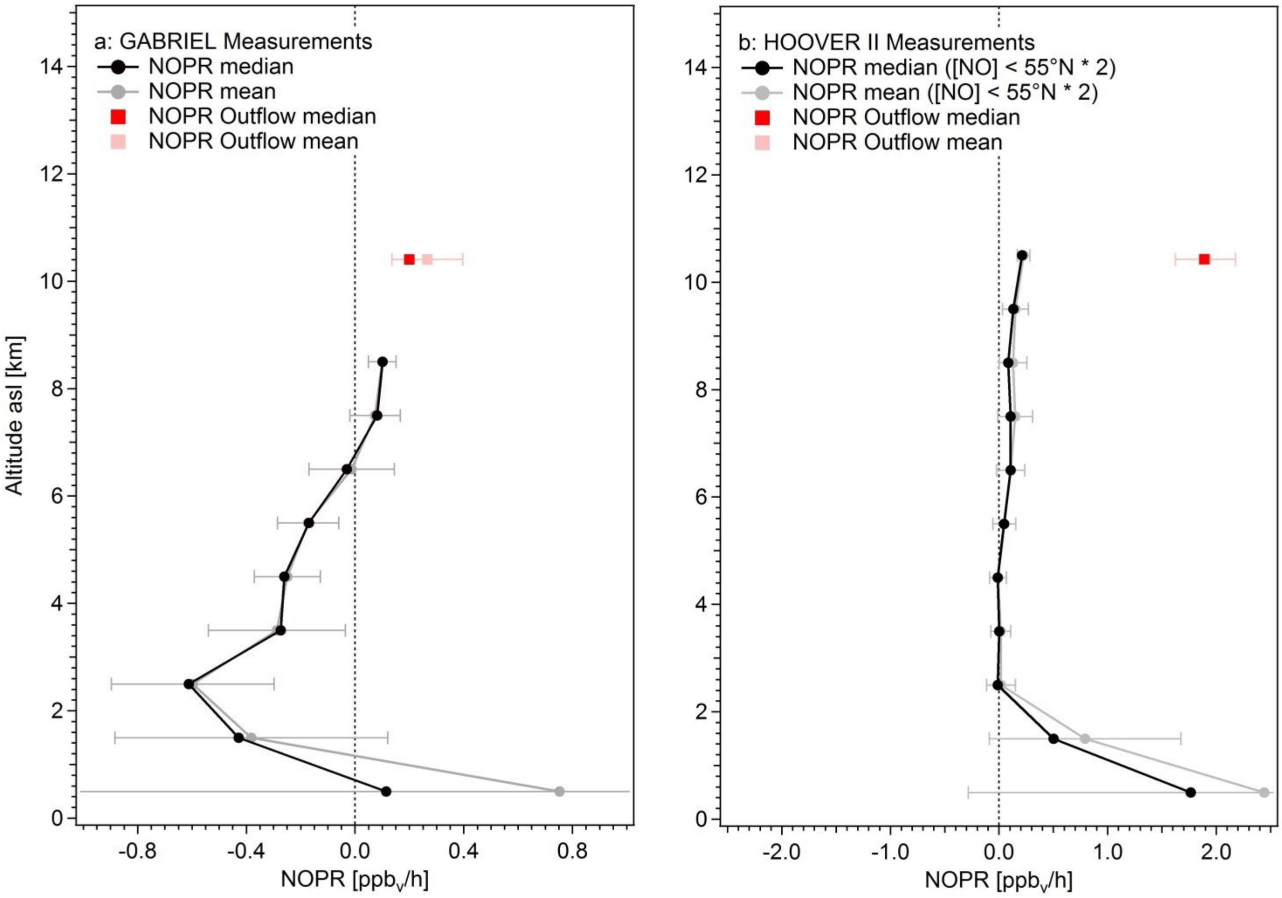


Figure 7: Net ozone production rates (NOPR) in ppbv/h (red squares) calculated from in-situ data for convective events during GABRIEL (a: left panel) and HOOVER II (b: right panel) relative to campaign average profiles (black).