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

Anonymous Referee #2

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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.

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.

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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.

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:

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.

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 NOx to influence the HOx budget to limit radical availability. As noted only a few lines above, you neglect the loss of NO2 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.

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 authors 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.

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.

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 CH3O2 (page 6, line 32), wouldn't it be better to calculate an average CH3O2/HO2 ratio and scale CH3O2 to HO2? This would better capture variability in the photochemical environment which should affect CH3O2 and HO2 similarly.

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.

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.

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.

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?

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”.

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.

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 NOx value that tends to have more predictable behavior. By comparing photochemistry at different altitudes for a given abundance of NOx, you eliminate the need to account for the large changes in partitioning between NO and NO2 that occur with altitude (and temperature).

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.

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.

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 O3 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).

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.

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.

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