Response to Anonymous Referee #2

We want to thank the referee for the positive words, helpful comments and suggestions. We have revised the manuscript according to the comments

(1)

Reviewer: The temperature dependence of HO2 calibration. As I mentioned in the previous comment, no temperature dependence of HO2 calibration was ever reported in previous aircraft HOx measurements by this technique, particularly for such strong temperature dependence (change by more than a factor of 2 from 260 K to 290 K). According to the authors, the Penn State instrument (ATHOS) needs to be corrected by 12% for such temperature change. But this is nowhere near the temperature dependence shown in this instrument. As a result, the measured HO2 in upper troposphere is higher than all previous studies, including INTEX-A, PEMT-B, and TRACE-P. Although this instrument was installed in a wing pod (compared to the Penn State instrument which is set up within the freight compartment of the DC8), the temperature in detection axis doesn't seem affected. It seems to me that major conclusions in this paper rely heavily on the temperature dependence of HO2 calibration. But this requires further investigation.
If we assume the air velocity is on average 20 m/s, the time for traveling from the first axis to the second axis is only 16(cm)/20(m/s) = 8 ms. If the authors attribute the temperature dependence of HO2 calibration factor to wall loss, which means half the signal is lost within a temperature decrease of 30 K, this wall loss rate would be extremely large. Is radial diffusion rapid enough to provide such fast wall loss? I also expect the radical plume would be a parabola shape with the peak in the center, and the radical measurement is confined to center of the flow (see Figure 2 in Donahue et al. (1996)). So even if the wall loss is extremely fast, HO2 concentration in the center may not be proportionally affected. I think the authors should examine this temperature dependence of HO2 calibration more carefully.

Response: We agree, also to our knowledge no temperature dependence of the HO_2 calibration was reported. However, this does not necessarily indicate that neither temperature effects were observed nor that data were not corrected for temperature effects. As we know from personal communication (to Hartwig Harder) HO_2 measurements conducted during the Trace-P campaign (Penn State instrument ATHOS) were corrected by 12 % for 30 K (see also the comments of reviewer 1).
The assembly of the HORUS instrument is that HO_2 is detected in a fluorescence chamber 16 cm downstream of the OH fluorescence chamber. In order to be able to detect HO_2, NO is added into the airstream to convert HO_2 into OH. The NO is added through a loop (1/8" stainless steel) which is placed in the feed through tube between the two fluorescence chambers, causing additional turbulence. During calibration the amount of OH reaching the second fluorescence chamber without adding NO is observed to subtract it from the HO_2 signal when NO is added. Depending on the pressure, different ratios of OH observed in the second chamber to OH observed in the first chamber are found (see Figure **1** in this reply). A calibration conducted during the campaign shows that not more than 60 % of the OH observed in the first axis reaches the second axis. Within the calibrated pressure range the observed ratio of OH is roughly between 25 % at 2.05 mbar and 60 % at 10.7 mbar internal pressure (see Figure 1), indicating a huge OH loss on surfaces between the detection chambers. Accordingly, HO_2 can be lost on surfaces in high quantities. Assuming a temperature effect on the HO_2 loss at surfaces, a significant change within a 30 K temperature decrease is likely.

During measurements used in this paper, internal pressures were roughly between 2 and 4 mbar.

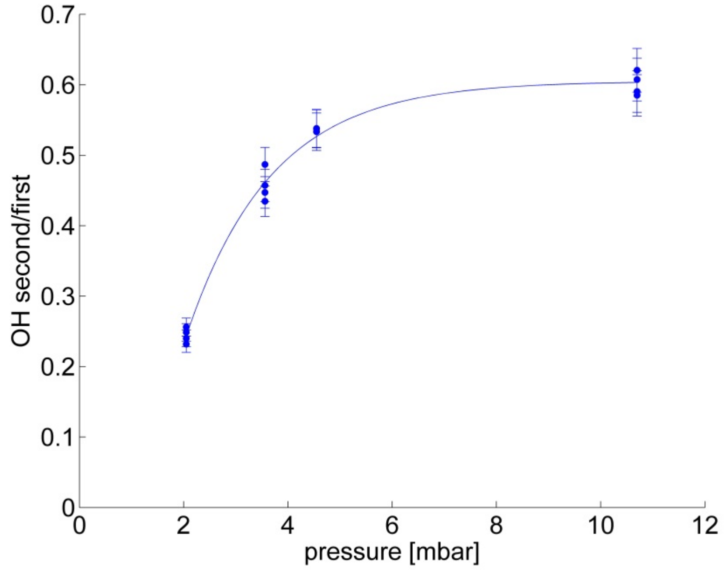

Figure 1: Ratio of observed OH radicals between second and first axes (no NO addition) at different pressures.

Additional reply to:
Reviewer: It seems to me that major conclusions in this paper rely heavily on the temperature dependence of HO2 calibration. But this requires further investigation.

Comment:
The main conclusion of this paper is that the constrained box model is able to reproduce the observed OH and HO_2 mixing ratios while the unconstrained global model underestimates the OH mixing ratios in convectively influenced air masses within the upper troposphere over Europe. A previous study (Klippel et al., 2011) highlighted that H_2O_2 is underestimated in the same air masses because wet scavenging is overestimated.
We added to our publication that convectively transported NO_x shifts the HO_x equilibrium towards OH. Wet deposition of NO_x is not a major NO_x sink, however, assuming NO_x is underestimated in the convectively influenced air masses would contribute to additional OH underestimation. If NO is underestimated, this missing OH source from HO_2 conversion will be higher when HO_2 is enhanced. Hence, the underestimation of OH shown by the global model in convectively affected air masses will even stronger depend on primary OH sources (like photolysis of H_2O_2) when measured HO_2 would be overestimated due to the temperature dependent calibration.

Additional reply to:
As a result, the measured HO2 in upper troposphere is higher than all previous studies, including INTEX-A, PEMT-B, and TRACE-P.

Comment
Figure 1 of Ren et al. (2008) shows the vertical distribution of HO_2 as observed during the Trace-P campaign. In altitudes higher than 7 km HO_2 mixing ratios are shown in the range between 10 pptv and 30 pptv (1-min average data).

During the HOOVER campaign at altitudes higher than 7 km, Figure 9 b (our study) shows observed HO_2 mixing ratios in the range between 5 pptv and 30 pptv. Hence, the HO_2 mixing ratios observed are comparable to those of the INTEX-A campaign.

(2)

In-flight calibration. Martinez et al. (2010) showed the in-flight calibration. Was in-flight calibration also conducted in this study? If so, is there any useful information to back up the temperature dependence of OH and HO2 calibration factor?

Martinez et al. (2010) report HO_x observations obtained in the tropical boundary layer and mid-troposphere. Good agreement was observed between ground-based and in-flight calibrations. However, HO_2 produced during in-flight calibration was always less than atmospheric HO_2 and comparable in magnitude to its natural variability during the calibration period. Therefore the in-flight calibration was used only to characterize the OH sensitivity of the instrument during the GABRIEL campaign.

The good agreement between the OH calibrations is also assumed for the HOOVER mission. According to the GABRIEL in-flight calibrations no HO_2 in-flight calibrations could be performed due to even lower H_2O mixing ratios in the mid-latitude upper troposphere over Europe.

(3)

Model comparison. I don't think the results from 3-D simulations provide much insightful information. While the authors were trying to prove that underestimate of HO2 is due to the underestimate of H2O2, there could be other possibilities. For example, such underestimate could be due to the underestimate of HCHO, which is another major source of HOx in upper troposphere (Jaegle et al., 2000). Another possibility is J value. According to Table 2, J values in global model also appear to be biased low by 30% or more. It seems to me that these possibilities could be easily examined by doing a HOx budget analysis as done in Jaegle et al. (2000), which is more convincing than the scattering plots in Figure 9-11.

We mention that HO_2 underestimation coincides with H_2O_2 underestimation (Figure 9 d, our study). Since we are focussing on the OH underestimation, we do not try to demonstrate that the H_2O_2 underestimation is a main or minor reason for underestimated HO_2. As the reviewer says HCHO and other trace gases can photolytically form HO_2. Therefore, HO_2 would most likely be higher if the simulated photolysis rate would match the observations. The coupling between OH and HO_2 would then cause increased OH mixing ratios.

However, we showed that H_2O_2 is underrepresented in the global model and that it is a significant OH source, and important to consider when OH is underestimated. As (Klippel et al., 2011) report, the global model especially has problems to reproduce H_2O_2. A sensitivity study showed that parameterisation of clouds and precipitation leads to overestimated wet scavenging of H_2O_2. However, switching off wet scavenging had no major impact on HCHO, consistent with the assumption that H_2O_2 is convectively transported while HCHO is rather locally produced.

Along with H_2O_2, NO_x is most likely convectively transported into the upper troposphere shifting the HO_x-equilibrium towards the OH (Figure 11 c, our study). The underestimated HO_2 results in a too low HO_2 conversion into OH potentially adding to the OH underestimation. Considering the reviewer's concern about the temperature dependent calibration, if the HO_2 would be reproduced by the model, the underestimation of OH could

be caused only through underestimated primary and/or cycling sources (from other species than HO_2).
A HO_x budget analysis under the aspects of background conditions and convective transport will be the subject of a follow on paper which is in preparation.

(4)
Convection transport. In section 5.2.3, why OH and HO2 are underestimated on southern flight tracks but not on northern flight tracks? Is there any reason behind this? I think the authors should provide some in-depth discussion on this.

Although we agree with the desirability of further discussion, for the southern flight tracks no NO and CO measurements are available. Therefore, no deeper analysis of the HO_x budget is possible when the OH is underestimated.
As shown by (Klippel et al., 2011) for southern flight tracks the global model has problems to resolve the observed H_2O_2 mixing ratios most likely because wet scavenging is overestimated when H_2O_2 is convectively transported. Since no NO and CO observations are available for the period when OH and H_2O_2 were underestimated by the global model, convectively influenced air masses were identified using the H_2O_2/ROOH and the OH/HO_2 ratio, both indicating convective influence on those air masses.
Comparably moderate H_2O_2 mixing ratios and photolysis frequencies were observed in this period; however the H_2O_2 photolysis is a large contributor to the primary OH production rate. Since HO_x equilibrium is shifted towards the OH, NO_x apparently is convectively transported, too. The underestimated HO_2 might also lead to an underestimated OH, since the too low HO_2 results in a too low HO_2 conversion into OH.

Minor comments:
(1)
In section 4.1, could the authors give some brief introduction on the MESSy? It is not clear how this interface works.

We added:
"... by Jöckel et al. (2005). MESSy formally describes a way to connect different process and diagnostic submodels to a more comprehensive model system. The key ideas are the modular, object oriented approach, and the strict separation between model infrastructure (such as data exchange, input/output, memory management etc.) from the actual scientific content (e.g. the parameterisations, numerical solvers, etc.) into 4 different software layers. Information about the implementation of the recent (2nd generation) MESSy infrastructure has been documented by Jöckel et al. (2010)."

(2)
Page 30633, "Observed HO2 mixing ratios exceed the INTEX-(N)A, PEM-(T)B and TRACE-P observations." I think authors should be more quantitative on this.

Changed accordingly.

(3)

Page 30636, "HO2 is almost always underestimated even if the H2O2 is well reproduced by the model, as seen in Fig. 9d." This tells me that underestimate of H2O2 may not be the only reason for underestimate of HO2.

While the global model underestimates HO_2 systematically, the OH is underestimated when the global model underestimates H_2O_2 mixing ratios in convectively influenced air masses. Since NO_x is also enhanced in these air masses an underestimated HO_2 conversion might cause an extra underestimation of OH. We added:
"Coupled convective transport of H_2O_2 and NO_x and local NO_x formation by lightning might lead to an underestimation of H_2O_2 and NO_x in the convectively influenced air masses in the upper troposphere. Therefore, a contribution to the underestimation of simulated OH can be expected from underestimated HO_2 conversion into OH."

(4)

Page 30637, "Figure 10b indicates in the same area a correlation between the degree of OH underestimation and the underestimation of NO. Thus, a missing HO2 conversion rate is likely responsible for the OH underestimation." I don't understand this sentence.

The area within the red ellipse shown in Figures 10 a and b highlights data points were OH is better reproduced the higher the NO ratios are and the lower the H_2O_2 ratios are. In contrast to the data shown in the blue ellipse (same Figures), here OH is underestimated when the model reproduces the H_2O_2 since then the HO_2 conversion rate is underestimated because of underestimated NO mixing ratios.
We added:
"…since OH is better reproduced at higher NO ratios (modelled to observed) and lower H_2O_2 ratios. In contrast to the data shown in the blue ellipse (same Figures), here OH is underestimated when the model reproduces the H_2O_2."

(5)

Page 30640, "The model tends to underestimate not only H2O2 but also NO mixing ratios in convectively transported air masses." I couldn't find any description on this from the section of "influence of convective transport" (Section 5.2.3). How did you get this conclusion?

We added:
"For the southern flight tracks NO and CO measurements were not available. As indicated by the OH/HO_2 ratio, along with peroxides, NO_x was convectively injected into the upper troposphere shifting the HO_x equilibrium towards the OH. Underprediction of HO_2 then results in a stronger OH underestimation, since a primary OH source (photolysis of H_2O_2) as well as HO_2 cycling (with NO) into OH is underestimated."

(6)

Is Fig. 10a a zoom-in version of Fig. 9c? But they look very different. This definitely should be clarified.

We added:
"Figure 10a is a cut-out of Figure 9c. To highlight the statement the colour coding was adapted."

Reference

Donahue, N. M., Clarke, J. S., Demerjian, K. L., and Anderson, J. G.: Free-radical kinetics at high pressure: A mathematical analysis of the flow reactor, J. Phys. Chem., 100, 5821-5838, 1996.

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., Fischer, H., Klüpfel, T., Gurk, C., Königstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Williams, J., and Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements, Atmos. Chem. Phys., 10, 3759-3773, 10.5194/acp-10-3759-2010, 2010.

Reference

Klippel, T., Fischer, H., Bozem, H., Lawrence, M. G., Butler, T., Jockel, P., Tost, H., Martinez, M., Harder, H., Regelin, E., Sander, R., Schiller, C. L., Stickler, A., and Lelieveld, J.: Distribution of hydrogen peroxide and formaldehyde over Central Europe during the HOOVER project, Atmos Chem Phys, 11, 4391-4410, DOI 10.5194/acp-11-4391-2011, 2011.

Ren, X. R., Olson, J. R., Crawford, J. H., Brune, W. H., Mao, J. Q., Long, R. B., Chen, Z., Chen, G., Avery, M. A., Sachse, G. W., Barrick, J. D., Diskin, G. S., Huey, L. G., Fried, A., Cohen, R. C., Heikes, B., Wennberg, P. O., Singh, H. B., Blake, D. R., and Shetter, R. E.: HO(x) chemistry during INTEX-A 2004: Observation, model calculation, and comparison with previous studies, J Geophys Res-Atmos, 113, Artn D05310, Doi 10.1029/2007jd009166, 2008.