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Atmospheric Chemistry and Physics Discussions

Reply to

Interactive comment on "The influence of deep convection on HCHO and H_2O_2 in the upper troposphere over Europe" by Heiko Bozem et al.

Anonymous Referee #3

Received and published: 3 June 2017

We thank the referee for her/his helpful comments that we will address in the revised manuscript.

Summary and General Comments: Bozem and coauthors present aircraft measurements of a wide range of reactive trace gases made in the outflow of deep convection. Their observations focus on the convective redistribution of two soluble HOx precursors, HCHO and H2O2. Using measurements made in the inflow and outflow region of a single storm, Bozem et al calculate that HCHO and H2O2 are transported with high efficiency by deep convection. The manuscript describes new results and is interpreted in the context of a photochemical model. I have a series of comments that would need to be addressed prior to publication in ACP:

1) Prior measurement campaigns have used the ratio of H2O2:CH3OOH as an indicator of fresh convection due to the preferential scavenging of H2O2. Are measurements of CH3OOH available from this flight to comment on this approach? Based on the scavenging efficiencies reported here, one would expect that ratio not to be very sensitive, yet it has been shown to work well in the remote Pacific.

Answer:

Specified CH_3OOH (MHP) measurements were not made. As described in Klippel et al. (2011) the instrument used to measure H_2O_2 also provides a measurement of organic hydro-peroxides (ROOH). This measurement suffers from the different solubilities of the individual ROOHs (e.g. the solubility of MHP is only 60% of that of H_2O_2 due to the smaller Henry's law coefficient) and thus changes of the sensitivity for different ROOH. Under the assumption that all ROOH is MHP and correcting for its lower solubility, ROOH measurements can be interpreted as an upper limit for MHP (Klippel et al., 2011). The assumption that all ROOH is MHP is often justified in the free troposphere where MHP is the dominant ROOH, but not necessarily in the boundary layer (Klippel et al., 2011). The average ROOH mixing ratio in the inflow and outflow regions were 0.45 ± 0.02 ppbv and 0.68 ± 0.07 ppbv, respectively. The fact that the MHP concentration is higher in the outflow area than in the inflow indicates that the assumption that all ROOH is MHP is not justified in this case and that the ROOH partitioning most likely changes due to cloud processing. Due to the uncertainty associated with the ROOH measurements we cannot address the question raised by the referee with the available data set.

2) The authors suggest that PBL air is transported to the UT and detrained into the UT undiluted. This seems very hard to believe. Prior aircraft studies have calculated that this ratio is of order 0.2 (from measurements of CO, CH4, CO2, C2H6, and CH3OH (Bertram et al., 2007). Modelling studies have calculated this ratio to be closer to 0.25 (Mullendore et al., 2005). This suggests that convectively lofted PBL air is rapidly mixed on ascent or during detrainment into the UT. The authors should comment in more detail on how their measurements fit in the context of prior measurements since this is an important component of the measured scavenging efficiency for HCHO and H2O2.

Answer:

As pointed out on page 7, line 204 the CO ratio (outflow/inflow) (also methane, acetone and methanol) is not significantly different from unity considering their variability (1-sigma), given in the last column of Table 2, and thus entrainment did not seem to have played a role. In retrospect, this assumption might be an oversimplification. In the revised manuscript we apply a two box model to calculate outflow (OF) mixing ratios from the inflow (IN) and the entrainment (EN) according to

OF = x EN + (1-x) IN

using values for OF, IN and EN from table 1, 2 and figure 7. We derive the following entrainment rates: 24 % (CO), 26 % (CH_4), 30 % (Acetone), 19 % (methanol), indicating that roughly 75 % of the air in the outflow stems from the boundary layer. Hauf et al., (Hauf, T., P. Schulte, R. Alheit, and H. Schlager (1995), Rapid vertical trace gas transport by an isolated midlatitude thunderstorm, J. Geophys. Res., 100(D11), 22957–22970, doi:10.1029/95JD02324) concluded from a case study of a thunderstorm over Basel (Switzerland) that the cloud contained "protective cores" where air from the boundary layer was transported almost undiluted directly to the anvil. Similar observations were reported by Poulida et al. (Poulida, O., R. R. Dickerson, and A. Heymsfield (1996), Stratosphere-troposphere exchange in a midlatitude mesoscale convective complex: 1. Observations, J. Geophys. Res., 101(D3), 6823–6836, doi:10.1029/95JD03523) and Ström et al. (Ström, J., H. Fischer, J. Lelieveld, and F. Schröder (1999), In situ measurements of microphysical properties and trace gases in two cumulonimbus anvils over western Europe, J. Geophys. Res., 104(D10), 12221–12226, doi:10.1029/1999JD900188). These earlier studies corroborate that the ratio of boundary layer air in the outflow can be quite high, as has been found in our study. This question will be addressed in the revised manuscript.

Specific Comments:

Line 8: "~~the~~ Earth's"

Answer:

ok

Line 71: "project included ~~of~~ a total of"

Answer:

ok

Line 72: Give the country (Germany) of Hohn as is done for Corsica and Kiruna

Answer:
ok

Section 2.2: Was the altitude (temperature and pressure) of convective detrainment used to drive MECCA?
Answer:
yes

Line 139: What is the evidence for this? This would be an average updraft velocity of about 1 m s^{-1}. This is reasonable, but I am curious how/if this was measured.
Answer:
The statement is an interpretation of the series of cloud maps in Figure 5. The updraft velocity was not measured.

Line 209: Was the 30 ms^{-1} horizontal wind speed measured? How sensitive are the model conclusions to this number.
Answer:
Yes, these are in-situ measurements on-board the Learjet. The model results indicate that the ultimate mixing ratio in particular for HCHO is very sensitive to the processing time. The time estimated from the cloud distance and measured wind speed is similar to the processing time estimated from the model to reach the observed HCHO mixing ratio.

Section 3.3: What time of day was the model initiated? At the time of convective detrainment? This, of course, makes a strong difference in photolysis and chemical lifetimes.
Answer:
The model was constrained to measured $J(NO_2)$ photolysis rates. All other photolysis rates were calculated with the TUV model and scaled to the measured $J(NO_2)$ to account for cloud effects.

Line 310 and beyond: It would be helpful to be consistent in using either scavenging efficiency or retention coefficient.
Answer:
In our discussion scavenging efficiency accounts for all processes that ultimately remove soluble species from the gas phase (rain-out, gravitational removal of ice particle, graupel, hail etc.), while the retention coefficient describes the behavior of a soluble gas during the freezing of a rain drop. A retention coefficient of less than 100% thus indicates that some gas is released from the droplet during the freezing process. In the revised manuscript we will make sure that this difference is clearly described.