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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 #2

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

This is an interesting study that represents important research that should be of interest to readers of this journal. The results of this research will add to a growing list of studies dealing with the important topic of convective transport of reactive radical precursors to the UT and LS. This paper is within the scope of ACP and meets the scientific quality of this journal. However, after having said this, this reviewer has some major concerns regarding the results as presented and would like to see more supporting evidence in the areas discussed below. Accordingly, this reviewer believes this paper should be accepted for publication after some **major revisions** are made.

First, CO and CH_4 may not be the best species to account for entrainment/dilution during both vertical transport as well as horizontal transport out of the anvil. As shown, the contrast in mixing ratios between the convective outflow (OF), the free troposphere, and the boundary layer inflow (IF) are small and thus information on the entrainment rates may not be reliable. Measurement of other species with much more dynamic vertical profiles like various hydrocarbons would be preferable in determining entrainment rates. Can the authors employ their canister measurements of hydrocarbons like i/n butane and i/n pentane and their ratios to address this as well as to further verify that the outflow is coherently related to the inflow?

Answer:

We partly agree that CO and in particular CH_4 are not ideal tracers to estimate entrainment rates. While the referee's criticism is correct that the dynamical range of CH_4 is small throughout the troposphere, this is not necessarily true for CO: median mixing ratios in the inflow and outflow region are 127 ppbv and 118 ppbv, respectively, while the background mixing ratio in the upper troposphere is 63 ppbv and the mixing ratio in the middle troposphere 90 ppbv. Taking into account the variability (instrument's precision and atmospheric variability) these differences are large enough (and significant at least for the contrast between inflow and entrainment regions) to permit a calculation of entrainment rates. Please note that there are also other tracers, e.g. methanol or acetone that can be used for this purpose. NMHC ratios, at least from canister measurements, are not suitable for this purpose in our case. In fact the number of samples is rather limited (24 canisters with a volume of 0.8 l each) and on this particular day two flights were performed, so that only 12 canisters were filled during the second flight on which our study is based. Additionally, one has to take into account that the sampling itself takes more than

several seconds (lower troposphere) to several tens of seconds in the upper troposphere, so that rather large horizontal and vertical averaging takes place over filling one canister. The data base on NMHC is thus insufficient to perform a similar analysis as done in Fried et al., 2016.

Nevertheless, given the near unity CO OF/IF ratio of 0.93, one cannot assume that entrainment does not exist. It's hard to imagine there is no entrainment dilution during convective transport from the BL to ~ 10 km, followed by no entrainment dilution of UT background air during the OF. Can these assumptions be wrong? Very similar CO OF/IF ratios were measured during DC3, and yet entrainment was still found to be important. In fact, using your CO IF and OF values in the altitude dependent entrainment model of Fried et al. [2016] with estimates of your background CO values in each 1km altitude bin, I get a net entrainment rate of 3.6%/km. Using this entrainment rate, I calculate that the HCHO value at the storm core should be ~ 2.054 ppbv, which should then be used to compare with your 1.45 ppb OF value, which has to be further modified for production and destruction. Even though my calculations are crude (mixing together entrainment from vertical transport and horizontal outflow in the anvil), they serve to illustrate that dilution of background air should not be ignored.

Answer:

We agree with the referee that the CO (and other species) OF/IF ratio of 0.93 indicates dilution of the outflow to some extent. As pointed out on page 7, line 204, this ratio (and others like methane, acetone and methanol) is not significantly different from unity based on the variability (1-sigma) given in the last column of Table 2. We nevertheless agree that this assumption might be an oversimplification. Therefore we applied a two box model to calculate OF mixing ratios from the Inflow (IN) plus 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). Assuming an average value of 25 % entrainment we calculate maximum mixing ratios for HCHO and H_2O_2 at storm core of 2.05 ppbv and 1.82 ppbv, respectively. Please note that the HCHO value is identical to the estimation made by the referee based on entrainment rates taken from Fried et al., 2016.

In the revised manuscript we will add this analysis and use the derived starting values in a sensitivity run of the box model to account for photochemical modification of HCHO and H_2O_2 in the outflow.

However, my second and biggest concern relates to the appropriate IF values to use for this analysis. The authors attempt to address this in their discussion section on page 11, by stating that although it is not possible to unambiguously identify the inflow area, their HCHO and H2O2 boundary layer mixing ratios near Dresden are similar to other boundary layer observations during HOOVER II and should thus be representative of the convective IF values. However, as shown by Fried et al. [2016] if this assumption does not hold, then one can obtain both higher (~80%) and lower (~20%) HCHO scavenging efficiencies (SEs), depending upon the circumstances.

Answer:

We agree that establishing a connection between the timing and location of the inflow area and the corresponding outflow of a convective system is the most critical aspect of this study (and

others, as demonstrated by Fried et al., 2016). Unfortunately, Lagrangian experiments are not possible, so the only way to establish an unambiguous connection between in- and outflow would be through the use of an artificial tracer released in the inflow area, ideally from a second airplane. Here we have to rely on sequential measurements first in the outflow and later in the potential inflow area. Due to the time shift associated with the vertical transport and the movement of the convective system itself it is not possible to determine the correct inflow area. So an inflow area is only representative if it is rather homogeneous with respect to space and time. We interpret the fact that several conservative tracers show similar ratios between in- and outflow as an indication that this assumption is fulfilled here. Additionally, Fig. 6 of Klippel et al. (2011) indicate that HCHO and H_2O_2 mixing ratios in the boundary layer are within the range of observations made during all HOOVER II flights in the latitude belt from 50°N – 57.5°N. Additionally we checked that the wind direction in the boundary layer is such that an inflow into the approaching storm can be assumed, as has been done by Fried et al., 2016. It is not possible to determine the height of the layer from which the inflow takes place. While CO and e.g. some NMHC might be well mixed in the continental boundary layer (CBL), this is not the case for H_2O_2 and to some lesser extend HCHO that exhibit strong gradients in the CBL and across the boundary layer (e.g. Klippel et al., 2011). So we agree with the referee that appropriate IF values are the most critical, but we do not see a way to address this question other than we have done.

In particular, large changes in boundary layer isoprene mixing ratios, as one example, can cause erroneous HCHO SE determinations unless one can be certain that the inflow is related to the outflow.

Answer:

Isoprene concentrations in the in- and outflow area were measured with a PTR-MS (Colomb et al., 2006, doi:10.1071/EN06020). There are only 3 data points yielding 0.13 ppbv (OF) and 0.12 ppbv (IN), which are below the instrument's detection limit. Thus we conclude that isoprene has no significant influence on secondary HCHO formation in the outflow. As shown in our model studies, both HCHO and H_2O_2 instead show a tendency for decreasing mixing ratios due to the direct proportionality of the sink term to the concentrations itself.

The authors need to provide more convincing evidence to this effect in order to reconcile if their much lower SEs with other studies for both HCHO and H2O2 are caused by this or by differences in storm dynamics and microphysics. Do the authors have measurements of isoprene and/or any other sources of HCHO in the boundary layer to help this agrument? Simply invoking differences in ice retention factors cannot explain the lower HCHO and H2O2 SEs in the present study with the DC3 results. As discussed in the DC3 studies in the case of HCHO, large changes in calculated HCHO ice retention factors from 0.25 (and most recently 0.15) to 1.0 all result in calculated HCHO SEs near 100%. It is only when HCHO is completely degassed from ice (ice retention of 0) can the modeled results reproduce the ~ 50% SE results deduced from measurements. There is no scenario where changing the ice retention factor produced lower SE results. Likewise, for H2O2 Bela et al. [2016] and Barth et al. [2016] in their simulations found that with H2O2 ice retentions $\geqq$ 0.25, the H2O2 SE approached 100%, and with ice retentions

of 0, one obtains H2O2 SEs of 80% ± 12%. Again, ice retention factors cannot explain the differences.

Answer:

Assuming a 50 % scavenging efficiency for HCHO and a mixing ratio of 1.45 ppbv in the OF or 2.05 ppbv estimated at the cloud core would yield an IF mixing ratio of 3 – 4 ppbv. The same calculation for H_2O_2 assuming an SE of 80% and a cloud top mixing ratio of 1.25 and 1.82 ppbv, respectively, yields an H_2O_2 mixing ratio in the inflow area of 6 - 9 ppbv. Based on the observations of both species during HOOVER II (Klippel et al., 2011) the simultaneous occurrence of these mixing ratios for both species, in particular at the same altitude, is very unlikely. Assuming the scavenging efficiencies determined from the DC3 campaign seem to yield inconsistent results.

Therefore, the authors need to seek other explanations for the differences with DC3 results. Can differences in storm dynamics and microphysics be the cause or can differences in IF and OF airmasses be the cause? In the case of the former, the authors should try and contrast differences between the studied storms here and DC3. To eliminate the latter, the authors need to provide more convincing evidence that the IF is related to the OF. In addition, the authors need to raise the possibility that in contrast to most DC3 measurements acquired in the anvil, the measurements here were obtained in clear air and this may allow the hydrometeors a chance to evaporate, thereby degassing the dissolved species resulting in low SEs.

Answer:

Differences in the storm dynamics and microphysics between DC3 and HOOVER cannot be investigated since these details are not available for HOOVER. Contrary to DC3 HOOVER was not a coordinated campaign to study convective transport. Here we rely on a single event study, based on the measurements from one aircraft. As pointed out in Fig. 8, and unfortunately not mentioned explicitly in the description of the observations in section 3.2, all measurements were performed in cloud free air. So the referee's suggestion that the differences to DC3 might be due to degassing from evaporating hydrometeors is a potential explanation that we will address in section 4 (Discussion and conclusions) of the revised manuscript.