Response to the comments of reviewer #2 on the paper ”Upper tropospheric pollutants observed by MIPAS: geographic and seasonal variations", egusphere-2024-1793

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Reviewer comments are in black, while our replies are in blue.

Overall, this is an interesting study making use of long-term MIPAS retrievals to investigate the potential sources controlling the spatio-temporal distribution of upper tropospheric pollutants. This study exploits information from enhancement ratios (ER) in comparison to emission ratios from known source types (e.g. forest fires) to determine the likely source of the pollutants. The manuscript is generally well written, figure presentation is good and would be an interesting addition to ACP. Therefore, subject to some minor comments, it is suitable for publication in ACP.

We thank reviewer 2 for this positive assessment.

1. The GFED data used in Figure 3 is from an older version (3.1). Therefore, it makes sense to exploit a newer version e.g. (vn4.1s or vn5).

We will exploit GFED version 5. The respective plots have already been created, and there are only slight differences to the original Figure 3 of the manuscript. Thus, except of referring to version 5 instead of version 3.1, the wording in the manuscript has not to be adjusted.

2. The authors use the ERs to infer source information about the pollutants retrieved by MIPAS. However, in places these statements are overall ”conclusive" and need to be weakened (e.g. Page 17 Line 33, Page 20 Line 7 and Page 9 Line 20, Page 12 Lines 21–22) without the support of e.g. a model.

On page 17, lines 29–32 we exclude biomass burning as major source of C2H6 from inspection of the observed correlation coefficients and ERs. Then we conclude on lines 32-33 that ”Both findings point to other sources of enhanced C2H6 at northern mid- and high latitudes during these months, namely accumulation in boreal winter due to the minimum in the OH cycle and anthropogenic activities." We think that these conclusions are rather cautious and list the only remaining processes for C2H6 production during these times of the year. Thus we do not see the need to weaken this statement.

The same applies to the text passage on page 20, line 7. Here we write ”There are only low to moderate correlations north of 40N, indicating that the northern hemisperic HCOOH increase in spring (cf. Fig. 5) is not caused by biomass burning but rather by oxidation of biogenic precursors."

Page 9, line 20: We will change the sentence ”In austral winter (JJA) the amounts increase slightly at southern mid-latitudes, which obviously is also due to the OH cycle." into ”In austral winter (JJA) the amounts increase slightly at southern mid-latitudes, which might also be caused by the minimum in the OH cycle."

Page 12, lines 20–22: "From October to March the C2H2 and HCN amounts at northern high latitudes are uncorrelated, confirming the dominant influence of the OH cycle and of biofuel burning on the C2H2 amounts in these regions during winter." We draw these conclusions because we think that the dominant influence of the OH cycle and of biofuel burning on the C2H2 amounts in these regions during winter is well approved in the literature. For illustration we already give a reference to Zander et al. (1991) on page 8, line 21. We suggest to add further references (e.g., Goldstein et al., 1995; Xiao et al., 2007) at this passage of the manuscript.

Goldstein, A.H., et al.:, ”Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes", J. Geophys. Res., https://doi.org/10.1029/95JD02034, 1995.

Xiao et al, 2007: see reference list.

3. The methods used in Section 4.3.2 need some more detail. From reading the text (Page 13 Lines 15–22), it is not overly clear what ESDs are and how they are calculated and why λ is needed in the regression model.

The term ESD is introduced as estimated standard deviation on page 4, line 30. We will further outline at this text passage, that the ESD is ”measurement noise transformed into parameter space by the retrieval program". The λ-term is used as a weighting parameter in the regression model to take the generally different uncertainties of the two pollutants into account. To give some more details, we will change the text passage beginning at page 13, line 18:

”In case of equal error variances for both variables, Deming regression simplifies to orthogonal regression. The λ-values required for Deming regression were determined from the ESDs given in Tab. 2 as = ESD_y^2/ESD_x^2. After averaging over the two height levels in Tab. 2, the following global λ-values were applied: ΔHCN/ΔCO: 4.42×10^{-6}, $\Delta C_2H_2/\Delta$HCN: 0.35, $\Delta C_2H_6/\Delta$HCN: 20.01, ΔPAN/ΔHCN: 0.63 and ΔHCOOH/ΔHCN: 0.75.

into

”In this regression model the potentially different uncertainties σ_1 and σ_2 of both pollutants are taken into account by introducing a parameter $\lambda = \sigma_1^{-2} \times \sigma_2^2$. We determined the λ-values from the ESDs given in Table 2 as $\lambda = ESD_1^{-2} \times ESD_2^2$. After averaging over the two height levels in Table 2, the following global λ-values were applied: ΔHCN/ΔCO: 4.42×10^{-6}, $\Delta C_2H_2/\Delta$HCN: 0.35, $\Delta C_2H_6/\Delta$HCN: 20.01, ΔPAN/ΔHCN: 0.63, and ΔHCOOH/ΔHCN: 0.75. In case of equal error variances for both variables, Deming regression simplifies to orthogonal regression.".

4. In Section 4.3.2, why focus on individual months instead of the seasons as used earlier in the manuscript and why choice those specific months (i.e. Feb, Apr, Jul, Oct)?

In Section 4.3.2 we focus on individual months, because the differences between late boreal winter (Feb) and boreal spring (Apr) in the northern hemisphere as well as the differences between austral winter (Jul/Aug) and austral spring (Oct) in the

southern hemisphere become more obvious in this representation. For these reasons we do not want to change the discussion to seasons here.

Page 9 Line 17: Reword ”even better visible" to something like ”more evident".

We will change ”even better visible" to ”more evident".

Page 9 Line 18: Can you provide a motivation for looking at 11 km (e.g. why not 10 km)?

Actually the global distributions of C2H6 and of the other gases in Figure A2 are presented at 10 km altitude. ”11 km" is a typo, which will be corrected. For the reason of consistency, the C2H2 and HCN enhancements in Figure A1, which are presented at 11 km, will also be presented at 10 km.

Page 16 Lines 14-19: Suggest rewording as not overly easy to follow.

We will change the wording from

”High correlations between C2H2 and HCN occur in even larger regions than for HCN and CO and they are generally stronger, often reaching values of r = 0.8 or above (Fig. 10, left column). Again, the focus is above North-East Africa, the southern tropical Atlantic and the North Pacific in February and April. In August, there are high correlations at northern mid- and high latitudes, above tropical Africa, in the AMA region and above the southern Indian Ocean, and in October very high correlations above the southern tropical Atlantic, South Africa, the Indian Ocean and Australia. All these features strongly point to biomass burning as common source of C2H2 and HCN."

into

”High correlations between C2H2 and HCN occur in even larger regions than those between HCN and CO and they are generally stronger, often reaching values of r = 0.8 or above (Fig. 10, left column). Again, strong correlations are found above North-East Africa, the southern tropical Atlantic and the North Pacific in February and April, and at northern mid- and high latitudes, above tropical Africa, in the AMA region and above the southern Indian Ocean in August. In October there are very high correlations above the southern tropical Atlantic, South Africa, the Indian Ocean and Australia. All these features strongly point to biomass burning as common source of C2H2 and HCN."

Page 16 Line 28: Add ”a" between ”as" and ”possible".

Will be done.

Page 17 Line 28: This line needs rewording as not clearly written. Also, what is the ”two times larger relative retrieval error" based on? Is this from the literature, the data product, do you calculate this?

This value was calculated from the ESDs associated to the retrieved VMRs. For more clarity we will change the sentence

”But it has to be considered that a certain part of the weaker correlations is due to the up to two times larger relative retrieval error of C2H6 as compared to C2H2."

into

”But it has to be considered that a certain part of the weaker correlations is due to the large retrieval error of C2H6 (see Table 2), which results in an up to two times larger relative retrieval error of C2H6 (error divided by VMR) as compared to C2H2."

Page 18 Line 33: Add ”any" between ”hardly" and ”information".

Will be done.

Page 21 Line 8–9: This sentence needs rewording as difficult to follow.

The sentence

”The reason is the minimum of their dominant reactant of C2H2 and C2H6, the OH radical, as well as enhanced biofuel and fossil fuel burning during winter."

will be changed into

”The reason is the minimum of their dominant reactant, the OH radical, as well as enhanced biofuel and fossil fuel burning during winter."

Page 21 Line 22: Add ”an" between ”as" and ”important".

Will be done.

Page 21 Line 26: Replace ”better" with e.g. ”stronger".

Will be done.

Page 22 Line 24: Replace ”become better" with ”becomes more".

Will be done.

Table 2: For ”a" why give the value as ppbv. For consistency and presentation, keep as pptv.

Ok, we will give the values for CO in pptv.

Table 3: Same as Table 2, why use ”a"? Best to use consistent units and not a %.

Ok, we will specify the HCN/CO enhancement ratios in Table 3 consistently in pptv/pptv. We will perform the same update in Table 4 as well.

Figure 6: Panel title and x/y-axes are missing for PAN.

We do not see any differences between the depiction of PAN and of the other gases in Figure 6.

Figure 8: I do not understand the delta HCN / delta CO units of 0.01 pptv/pptv while the colour bars show ER %.

The reviewer obviously means Figure 9? Consistently to the changes requested above, we will plot the HCN/CO enhancement ratios in Figure 9 in pptv/pptv as well. Thus, ”0.01 pptv/pptv" will be changed into ”pptv/pptv" in the figure captions, and the colour bar units will also be changed from ”%" into ”pptv/pptv."

Figure 3: For the colour bar units, what is 10 to the power of? Just says ”10”.

In the original Figure 3 the numbers at the colour bar should have been added as exponents to ”10". To make things clearer, we will update Figure 3, with the numbers 10^{-2}, 10^{-1}, ..., 10^{3} at the left side and the unit g m^{-2} at the top of the colour bar.