Response to the comments of reviewer #1 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.

This article investigates average seasonal enhancements in pollutants related to biomass burning using measurements from the MIPAS instrument. Ratios of the VMRs for different molecules are evaluated, relating relative enhancements of different constituents compared to enhancements in HCN to expectations for emission ratios from various types of vegetation, identifying when unexpectedly high levels relative to HCN suggest sources other than biomass burning. In general, it is well written and thorough, a good summary of what MIPAS sees for this class of molecule. However, there were a few issues that I felt should be addressed.

We thank Chris Boone for this overall positive assessment.

Firstly, I disagree with setting the tropopause height to 14.7 km for measurements within the polar vortex where the temperature minimum is around 20 km. I agree that the assumptions associated with the WMO definition of tropopause have broken down in that situation, but a tropopause of 14.7 km seems way too high in this latitude region. This can be illustrated by looking at the chemical make up in the vicinity of 14.7 km within the Antarctic polar vortex.

The impact of this issue is probably best seen in the distribution plots for C2H6. For seasons where high average tropopause heights are seen in the data set, low levels of C2H6 are indicated in the distribution plots. This is not a chemical (i.e., low C2H6 in the troposphere) effect. Instead, it is a consequence of including stratospheric air (with low levels of C2H6) in the average.

The obvious solution would be to use a dynamical tropopause in the analysis rather than the WMO definition. When dealing with measurements inside the polar vortex, it is possible that using a single boundary on potential vorticity (available from MERRA-2) might not suffice, and you would need to use a more sophisticated approach (doi:10.1029/2010JD014343, ”Dynamical tropopause based on isentropic potential vorticity gradients" by Kunz et al., JGR Atmospheres, 2011). The alternative would be to simply exclude Antarctic measurement where the WMO tropopause is above some threshold (15 km?). Some distribution plots would likely end up with blank regions, but that would be preferable to reporting mostly stratospheric results as tropospheric. Regions with no data would presumably all be in the Antarctic, which is the least interesting region anyway (scientifically speaking), with no significant sources of these molecules.

The reviewer is right. Setting the tropopause height to 14.7 km for geolocations in the antarctic vortex, where the WMO definition of tropopause has broken down, was no good solution. We will follow his second suggestion and exclude measurements

at latitudes south of 50°S, for which during June to November a tropopause height of more than 13.5 km was determined (cf. Figure S1 in the Supplement). The same height criterion will be applied for the region north of 50°N during December to February, since some unplausible high tropopause heights were also determined for measurements in the arctic vortex (cf. Figure S1). The updated global distributions of the pollutants have already been created. Differences to the previous plots are generally small and only visible for antarctic C2H6 during June–August and September–November. Especially the anticorrelation of the C2H6 VMRs to tropopause height during Antarctic spring (Fig. 4f) has largely disappeared. Like in the original plots there are no blank regions (no data) in the global distributions for spring, autumn and winter. The small blank regions in the Antarctic during June-August are only marginally enlarged.

The second issue I had related to internal consistency for the different molecules. Enhancement ratios are considered for each molecule separately, which admittedly already makes for a large amount of information to digest, but no synergy between the different molecules was considered. For example, unexpectedly low enhancement ratios were observed for C2H2 and C2H6 in the tropics/subtropics in October. The quite logical suggestion was made that this indicated aged emissions, with C2H2 and C2H6 levels having decreased more than HCN because of their shorter lifetimes. However, the following observation was then made for HCOOH in October (page 20, line 26):

”Thus both the high correlations as well as the ERs indicate that biomass burning is a major source of the enhanced HCOOH observed in the southern tropics and subtropics during this period."

The conclusion from C2H2 and C2H6 suggested that on average in October, the fires contributing to their enhancement in this region occurred a long time previously, long enough for the shorter lifetimes relative to HCN to have a significant effect. Then the conclusion for HCOOH in October was the opposite, that there were ”fresh" fires contributing to the HCOOH enhancement. For me, it would have been more logical to conclude that the contributions to HCOOH enhancement from biomass burning should have been relatively low because we generally have aged emissions in October (as suggested by the C2H2 and C2H6 observations), so the higher enhancement ratios for HCOOH (compared to those observed for C2H2 and C2H6) indicate biogenic sources are also likely contributing. This would be consistent with the conclusions in the paper suggesting biogenic sources for HCOOH during other time periods. Why would there be biogenic sources of HCOOH during other time periods but not this one?

In principle we definitely wanted to consider the synergy between the different molecules in the discussion in Section 4.3.2. We will add some more cross references related to the enhancement ratios obtained for the different pairs of pollutants. However, we disagree with some of the other statements of the reviewer performed above. We do not report on unexpectedly low tropical/subtropical C2H6/HCN enhancement ratios in October but state that these ERs agree well with emission ratios for savanna and grassland burning (page 18, lines 20ff). Further, we do not intend to conclude from the low C2H2/HCN enhancement ratios of October that ”the fires contributing to their enhancement in this region occurred a long time previously". Figure 3 in our manuscript shows that the fire activity in southern tropical and subtropical Africa persists well into the period September–November and that the fire emissions in South America even peak during this period. Taking this into account we explain the low C2H2/HCN enhancement ratios in October with the sentence ”Presumably this is an effect of plume aging, in this case stronger accumulation of HCN due to its relatively long lifetime (page 17, lines 15f)." To make our conclusion clearer, we

will change this sentence into ”Presumably this is an effect of plume aging, in this case stronger accumulation of HCN during persistent fire activity due to its relatively long lifetime."

Since the atmospheric lifetime of HCOOH is even somewhat shorter than that of C2H2, the reviewer rightly points out the discrepancy between our conclusions from the October ERs of C2H2/HCN (”Presumably this is an effect of plume aging ...") on page 17 lines 15f and our conclusions on HCOOH/HCN (”Thus both the high correlations as well as the ERs indicate that biomass burning is a major source of the enhanced HCOOH observed in the southern tropics and subtropics during this period.") on page 20, lines 26f. Therefore we will change this sentence into ”Thus the high correlations indicate that biomass burning is a major source of the enhanced HCOOH observed in the southern tropics and subtropics during this period." and add the sentences ”However, contrary to the other short-lived pollutant C2H2, the October ERs of HCOOH have not yet decreased considerably with respect to the emission ratios for savanna or tropical forest fires. This is an indication for additional contribution of biogenic release or of secondary production to the observed HCOOH amounts, feigning exclusively fresh pollution by biomass burning only."

As the authors indicate, the different vertical resolutions HCN and the other molecules will impact the accuracy of the ratio. They report that degrading C2H2 to HCN resolution yields ”on average" 10% lower C2H2. It was not clear what conditions were being averaged over. Over the global set? The vertical resolution changes with latitude, and so does the tropopause height, which could compound the systematic error. Since the vertical resolution for C2H2 is larger at 14 km than it is at 8 km, presumably the impact would be smaller in the tropics than near the poles because there would be less of a resolution mismatch.

The value of 10% lower C2H2 was estimated from a restricted dataset of 154 MIPAS-orbits of January, February and October 2009, averaged over all latitudes. On behalf of the reviewer’s comments, we performed additional estimations for different regions, e.g., the area 45°–90°N or the southern tropics and subtropics. The outcome was similar to our original estimation. We will give a more detailed estimation in the updated manuscript by changing the wording on page 14, lines 5-6, from

”However, degradation of, e.g., the C_2H_2 profiles to the height resolution of HCN on average resulted in 10% lower C_2H_2 VMRs, which would lead to 10% lower ERs only."

into

"However, degradation of a sample of C_2H_2 profiles of 154 orbits to the height resolution of HCN by the use of Gaussians representing the differences in vertical resolution on average resulted in about 5% lower VMRs in the southern tropics and subtropics and 10% lower VMRs at northern mid- and high latitudes, which would lead to 5–10% lower ERs only."

Regardless, an error of 10% is probably low compared to the uncertainty from the unknown ”emission age" of the air, due to the different lifetimes of the molecules being ratioed. That could perhaps be stressed more when comparing observations of enhancement ratios to emission ratios for various types of vegetation. It is difficult to make definitive statements of agreement / disagreement with the expectations for a particular type of vegetation without knowing how long ago the fire occurred.

We already mention the precautions to be taken with respect to the unknown "emission age" of the air on P13, L33ff. As suggested by the reviewer, we will additionally point out this fact in the discussion of the ERs of the short-lived pollutants C_2H_2 and HCOOH with HCN by changing the passage on page 16, lines 20ff from

"The mean $\Delta C_2H_2/\Delta HCN$ enhancement ratio obtained for February for the region above northern tropical Africa and the Middle East is 0.80±0.17 (Fig. 10b). This value - also after a 10%-subtraction as discussed above - is in good agreement with the emission ratio for the dominant burning process in northern tropical Africa, namely savanna or grassland fires (0.73)."

into

"As already mentioned, the considerably shorter lifetime of C_2H_2 compared to HCN is an issue in the interpretation of monthly composites of $\Delta C_2H_2/\Delta HCN$ enhancement ratios. Nevertheless, the mean ER obtained for February for the region above northern tropical Africa and the Middle East is 0.80±0.17 (Fig. 10b), which - also after a 10%-subtraction as discussed above - is in good agreement with the emission ratio for the dominant burning process in northern tropical Africa, namely savanna or grassland fires (0.73)."

and by adding the sentence

"However, when discussing $\Delta HCOOH/\Delta HCN$ enhancement ratios, the same caveats have to be taken into accout as for $\Delta C_2H_2/\Delta HCN$."

on page 19, line 30 after "... enhanced HCOOH."

Minor comments:

Page 7, line 6: but ca also be caused, ca -> can

Will be corrected.

Page 7, line 16: "caused by confinement of pollution mostly from South- and South-East Asia (see, e.g., Vogel et al., 2015) inside the Asian Monsoon Anticyclone (AMA)."

Not just confinement; vertical transport within the monsoon region carries pollution toward the upper troposphere, increasing the measured enhancement for a point 2 km below the tropopause.

We will change the sentence into "This feature is caused by vertical transport of pollution mostly from South- and South-East Asia within the Asian monsoon region towards the upper troposphere and subsequent confinement inside the Asian Monsoon Anticyclone (AMA) (see, e.g., Vogel et al., 2015).

Sometimes "Table" is written out fully and sometimes it is abbreviated as "Tab."

We will write "Table" throughout the text.

Figure 8: North Africa is labelled as NAFR but is referred to as NAF in the text.

We will label North Africa as NAF in Figure 8.

Page 17, line 26: Like for HCH versus CO, HCH -> HCN

Will be corrected.

Page 19: no reference to Figure 13 in the text

We will reference Figure 13 after the sentence on page 19, line 26.