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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonality of Peroxyacetyl nitrate (PAN) in the upper troposphere and lower stratosphere using the MIPAS-E instrument" *by* D. P. Moore and J. J. Remedios

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We thank the referee for their constructive and helpful comments which have helped to improve the manuscript. The reviewer made two general comments which we are pleased to address. The first concerned the capability of MIPAS to detect PAN and whether the spectral signature could be due another gas and exactly how well does the retrieval perform in cases where the PAN concentration is closer to background levels? In the retrieval process, we take a very careful approach to the PAN retrieval. We firstly pre-retrieve pressure and temperature (jointly) using out MORSE scheme, then

fit water vapour, ozone and nitric acid (using the microwindows as used in the MIPAS operational products). We finally fit chlorine nitrate ($ClONO_2$) and carbon tetrachloride (CCl_4). These steps ensure that we have the best possible estimate of interfering gases which vary considerably with latitude. The HCFC-22 radiance contribution is calculated to be close to the noise level of MIPAS from a number of simulations (figure 1 of paper) and it not retrieved. When retrieving PAN finally it is important to note we jointly retrieve continuum, to remove these signatures. This is described now in more detail in the text as discussed in the specific comment response below.

Figure 4 was shown to highlight a case with high retrieved PAN vmr to emphasise the difference both with and without a PAN+continuum retrieval. We have taken the same orbit and simulated the same residual for 4 other scenarios: "low" (98 ppt), "average" (106 ppt), "slightly enhanced" (164 ppt) and "moderately enhanced" (379 ppt) PAN - these scenarios are based on the 12 km PAN retrievals from August 2003 with a median retrieved value of 119 ppt. We find that for all these scenarios (except the low case), the residual without PAN exceeded the 3 standard deviation level of 81 nW (the average 12 km noise in August 2003 was 27 nW/(cm^2 sr cm^{-1})). For the average residual in the retrieved data, we found that the average residual (measurement-modelled radiance) was always less than the noise value of 27 nW/(cm^2 sr cm^{-1}) over the four microwindows. We also observed the fit in the range outside the microwindows, in the regions where there are weaker PAN lines (i.e. regions that were not chosen due to the lower sensitivity to PAN changes). What we found was there was also a significant improvement in the residual in these regions. What we also try to highlight in the paper are the enhancements in PAN on a global scale. MIPAS-E is an excellent instrument with which to identify these enhancements and retrieve accurate estimates of the PAN concentrations in these regions in the upper troposphere. We have also updated figure 4 so that we include different scenarios which look at 1) a case close to the background, 2) a slightly enhanced PAN case and 3) a moderately enhanced case. Please also see the response to general comments of reviewer 1.

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We plot all averaging kernels from the retrievals as a matter of course in the output. What we see is that in the cloud-free cases the 9 and 12 km averaging kernels are well defined and can have a peak value which ranges between 0.5 and 0.7, as long as the data are tropospheric. Towards the poles, this is not the case and the averaging kernels generally peak at less than 0.2 at 12 km. There is no real meaning to an "average" averaging kernel which is why we chose to only show one case in the manuscript.

Figure 5 can also be used to look at the quality of the fit with PAN and continuum and shows the normally distributed data, with no obvious systematic bias in these data. We have also looked at estimating a detection limit for PAN in MIPAS-E data. We calculate a PAN detection limit of 55 pptv and in our August 2003 retrieved dataset, we only observe values below this vmr 1.8% of the time (287 cases out of 15611).

We tested the effect of increasing the number of microwindows over a wider spectral range (similar to that of Glatthor et al, ACP 2007) and found the time taken for the retrieval to be over-restrictive and found, from tests on a limited number of orbits, that results between the large and small windows to be similar in PAN vmr distribution. After many information content calculations on simulated data, we found these four microwindows to be the most suitable for global retrievals with the highest information content globally.

The second issue of the referee concerned the discussion of the global distribution of PAN. The main concern was slightly ambiguous as the referee could not decide whether the discussion was too short or too long. We understand, however, that some of the explanation is perhaps a little detailed with some lack of supporting evidence. What we have tried to do to answer this point is to answer the illustrations given by the referee of specific points.

referee comment 1: I find it difficult to appreciate in Figure 6 the different patterns at the two pressure levels (the peak moves from central to South Africa and the peak over Central America disappears at 201 hPa). What is happening in terms of sources

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and horizontal/vertical mixing? The same remark holds for the explanation of the double peak in Figure 10c, which would suggest predominance of vertical vs. horizontal mixing.

We feel that a thorough trajectory analysis is outside the aims of this observation paper. We have looked at zonal behaviour (as shown in figure 10) and also analysing the vertical wind velocity as a function of latitude we see highest PAN vmrs in regions of weak ascent, suggesting that vertical transport is an important mechanism. To look at horizontal transport relevant to January 2003 we looked at the 300 hPa average wind field operational data from ECMWF. In the UT, for this period, we see several dominant regimes. Air over central America, for example, is likely to transported eastward at speeds approaching 25 m/s on average in the UT. Conversely, horizontal winds over central Africa are much lighter, less than 10 m/s on average, implying a longer residence time. The Inter-tropical convergence zone (the area of strong vertical ascent in the tropics) is aligned across this region in January and is likely to explain why the broad-scale patterns are similar at 300 hPa and 201 hPa. It is possible that one mechanism dominates the other in the global average, but beyond the scope of this observation paper to explore further.

referee comment 2: The measurements give similar vmrs for PAN in the UT and the LS. Is this expected (is PAN expected in the stratosphere at all)? How to explain this feature? Have the authors checked if that was not an artifact of the retrieval due to the high correlation between the different altitudes?

We were very careful in the retrieval set-up to reduce the “correlation length” in the a priori covariance matrix to 6 km to reduce the ambiguity and vertical smearing likely to arise in the data from over-smoothing. The averaging kernels we show in figure 3 show nicely that the measurement resolution is somewhere between 3 and 4 km in the mid-latitude case. We certainly would not expect very much PAN to reach the stratospheric “overworld” – which we take as theta > 380 K and our observations show this. We may expect some reversible isentropic mixing of PAN to the LS. We have looked at the

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correlation between adjacent levels and the relationship is not significant. This follows on from point i) however; we may actually expect some correlation in certain regions (i.e. Southern Africa) where strong vertical ascent is the dominating mixing factor.

referee comment 3: Growing plants is suspected as a source of PAN through the release of acetone in NHsummer. Would that not affect the distributions globally (e.g. tropical forests?)? Have the authors considered the strong fire activity at high northern latitudes in 2003?

Although it has been shown that acetone is produced in tropical forests, we believe that our results also show that there is a possibility that the increase in PAN during the summer months could be linked to boreal forests or another mechanism specific to the Northern Hemisphere. As the timescale for hemispheric transport (1 year) is longer than that for the lifetime of PAN/acetone, this is why we see the hemispheric gradient. It is outside the scope of this paper to explore the link further although it should lead to other work to investigate the origin of the PAN enhancement through chemical transport model runs.

referee comment 4: Overall the issue of sources, vertical and horizontal mixing vs. PAN lifetime is poorly addressed. I acknowledge this is a difficult topic and probably outside the scope of this paper. I would therefore rather suggest keeping the geophysical discussion to a minimum and more centered on the actual observations.

As the referee states, the aim of this work is to show the first observed seasonality of PAN in the upper troposphere as measured from space rather than apportion the issue of vertical and horizontal mixing (which would have to be done in a coupled paper with a chemical transport model). The next step of the work is to look at this and try to understand the origin of the PAN distribution and how well it fits with our understanding derived from chemical transport models. Quantitative strides have been made to this end. We have modified the illustrations made by the reviewer to minimise the geophysical discussion.

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We now attempt to answer the specific comments:

1) Page 22510, line 15-17: What are the diagonal elements of Sa? 300% at all levels as stated later page 22512?

For the PAN data, the diagonals were set to 300%. We have added “which was set at 300% for PAN” to this sentence.

2) Page 22510, line18: The elements of Sy are set to zero. Does that comes to assuming there is no noise correlation between altitudes (as written) or that there is no noise correlation between the different spectral samples?

This statement was incorrect in the original manuscript. Due to the fact that the MIPAS level 1b data is apodized we need to take into account the correlation between nearby spectral points and have off-diagonal correlation values for these. In the text we have added the line “The apodization of MIPAS-E spectra, with a strong Norton-Beer function, introduces noise correlation into the measurement covariance matrix S_y. These were included in the off-diagonal elements of S_y in MORSE after being derived from the MIPAS-E apodized instrument line shape.”

3) Figure 3 and associated text on Page 22513: It would be simpler for the discussion if the right vertical axis was given in terms of altitude. Please also check the DOFS: On line 24, it is 3.7 but in the Figure it is 2.7.

The right-hand axis has been changed in the figure so that it is easier to convert between pressure and altitude. The number of DOFS for this case is 2.7, the text has been changed accordingly.

4) Text page 22514 and caption of Figure 3: Instead of the technical orbit and scan numbers, it would be better to specify latitude/longitude and time.

We have added the information ”(from 4 August 2003, 41N, 91W)” into the text and caption to make the position and time of measurement clearer.

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5) Figure 1: The total contribution seems to be the black line. On my printed copy at least, the legend refers to a blue line.

This has been corrected on a revised figure, the key has been altered so that “total” is now black.

Technical comments:

We thank the referee for pointing out the technical corrections, all changes have been made within the text and references.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22505, 2009.

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Interactive Comment