Atmos. Chem. Phys. Discuss., 9, C10712–C10718, 2010
www.atmos-chem-phys-discuss.net/9/C10712/2010/

Atmospheric Chemistry and Physics Discussions

ACPD

9, C10712–C10718, 2010

Interactive Comment

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

D. P. Moore and J. J. Remedios

dpm9@le.ac.uk

Received and published: 10 February 2010

We thank the reviewer for their helpful and constructive comments that have improved the manuscript. One of the major comments concerned the retrieval approach as we retrieve PAN from a small "microwindow" where the signature is rather flat. We are pleased to be able to clarify this and points other raised and we understand that more detail of the retrieval is required. In the retrieval process, we firstly pre-retrieve pressure and temperature (jointly) using the MORSE scheme, then fit water vapour, ozone and nitric acid (using the microwidows 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 expected HCFC-22 radiance contribution is at the noise level in simulations (figure 1) and we do not retrieve HCFC-22 as part of the retrieval. As from the lead author's earlier work (Moore, PhD thesis, Leicester 2005), it has been shown that there is not a large variability of HCFC-22 in the UTLS on the scales measureable by the MIPAS-E along its path length of around 500 km. The important factor with HCFC-22 is the fairly rapid decrease of HCFC-22 with altitude which the climatology file used captures. When retrieving PAN finally we joint retrieve a continuum. This is described now in more detail in the text as discussed in the specific comment response below.

We tested the use of more microwindows over a larger spectral range (similar to that of Glatthor et al, ACP 2007) and found the time taken for the retrievals to be over-restrictive and discovered, from tests on a limited number of orbits, that results between the large and small windows to be similar in PAN vmr distribution. After analysing the information content from runs on simulated data, we found these four microwindows to be the most suitable for global retrievals.

Response to specific comments:

1) P22508, L8-9: I think the unapodized spectral resolution (in terms of FWHM) is 0.035 cm-1 (like the authors themselves state on P22509, L18-19).

This is true, changes made in text

2) P22508, L12: The same here: 0.0875 cm-1 instead of 0.0625 cm-1.

We agree, changes made to text.

3) P22509, L7-8: The authors should mention here, if they use the plotted range of 787–790 cm-1 for PAN retrieval.

We agree. The retrieval was made in four microwindows based on this spectral range.

ACPD

9, C10712–C10718, 2010

We have added the sentence “This range was chosen as it represents a spectral region where strong PAN emission features are present and the interference from other gases is smallest. The retrieval of PAN volume mixing ratios from MIPAS-E spectra used four microwindows in this spectral range (MW1: 787.550 cm^{-1} to 787.750 cm^{-1}, MW2: 787.925 cm^{-1} to 788.125 cm^{-1}, MW3: 788.675 cm^{-1} to 788.875 cm^{-1} and MW4: 789.375 cm^{-1} to 789.700 cm^{-1})

4) P22512, last paragraph of Section 2.1: As mentioned above, the authors should explain the PAN-retrieval more in detail: Which microwindows did they use? What is their state vector used for retrieval (e.g. did they joint-fit continuum or offset)?

The microwindows used are now mentioned in the text as discussed in the previous point. As we mention in the text (p22511, l27) we list the pre-retrieved species. We have added the sentence. “PAN is then jointly retrieved with water vapour continuum” to this paragraph as the PAN retrievals are joint-retrieved with continuum.

5) P22512, last paragraph: I do not fully understand the applied error calculation. What did the authors do by “using measured biases”? How do the cited uncertainties, e.g. 20

We follow the approach of Rodgers (2000) – inverse method for Atmospheric sounding, page 48, to calculate the expected errors on our PAN vmr data. As mentioned in the text, we base these “measured biases” on findings from the validated operational retrieval data. The likely accuracy of MORSE is better than that of the validated operational retrieval algorithm data (on which these measured biases are found). We jointly fit the continuum, rather than use a prefitted continuum, and so haven’t included this in our error budget, as is standard in retrieval theory.

6) P22513, L5: The cross-section data set of Allen et al. covers the temperature region 250–295K. Does extrapolation to much colder temperatures at the tropical tropopause (the authors state 180–200K) result in a bias of 5.2% only?

ACPD
9, C10712–C10718, 2010

Interactive Comment

The extrapolation of the PAN cross-section to temperature colder than 250 K was one area of uncertainty. In August 2003, for example, all of the data measured at the 12 km nominal altitude had a retrieved temperature of less than 250 with a mean of 222 K. By simple linear interpolation of the errors on the band intensity in Allen et al., 2005c, we calculate that the error due to the cross-section uncertainty at 180 K is 5.2%. It should be noted that the August 2003 data have no data points in the UTLS where T<180 K. We have made clear how we derived the error value clearer in the text by adding “Assuming a linear relationship between the reported spectroscopic errors reported in Allen et al. 2005c and temperature, the expected spectroscopic error is calculated not to exceed 5.2%, even at the very coldest tropopause temperatures we observe of around 180 K.

7) P22513, L19-20: The sentence “Figure 3 shows ...” is more or less a repetition of the sentence in L14-15 and should be removed.

We agree, we have removed the original sentence on l19-20 and added the words “Northern Hemisphere” to the l14-15 sentence.

8) P22513, L24-25:I think the number of degrees of freedom is also strongly dependent on the number of used tropospheric tangents.

This is true, as long as there is sufficient information from the measurements compared to the a priori data. The PAN vmr decreases rapidly through the stratosphere and hence why we concentrate the retrieval to levels in the UTLS. We have added “(when taking 4 measurement levels in the 100 hPa and 450 hPa range)” after 3.8 on p22513, l25 to make the sentence clearer.

9) P22514, Section 3.1: Which fit parameters are used for the fit without PAN? From inspection of Figure 4 it seems as if the authors simply model the atmosphere using all joint-fitted, prefitted and climatological profiles and assume zero PAN mixing ratio.

In the retrieval process we pre-retrieved pressure, temperature, water vapour, ozone

ACPD

9, C10712–C10718, 2010

Interactive Comment

nitric acid chlorine nitrate and carbon tetrachloride, but these are not fitted in the PAN microwindows. These parameters are used for the fit without PAN. We then use the same region for the PAN retrieval (along with the continuum fit) which considerably reduces the error to within the MIPAS-E noise.

10) P22515, L8-12: There was also strong biomass burning in South America from August to October 2003.

We thank the referee for pointing this out. This is indeed the case and this has been added to the text. We have removed the list of countries in Africa containing fires as we don't think that this is necessary.

11) P22516, L25 – P22517, L12: Are there other measurements to confirm high Arctic summertime PAN amounts and other references for considerable biogenic production of PAN? Besides, boreal forest fires or long-range transport might be other possible reasons for elevated Arctic PAN.

We have recently begun analysis of PAN retrievals from MIPAS-E reduced resolution data from July 2008. These data have been compared to PAN measurements made during the POLARCAT campaign - which was designed to look at biomass burning transport from North America to Greenland. The POLARCAT in-situ data found evidence of higher PAN (up to 300 pptv) in the upper troposphere near Greenland which may have been transported from Asia. So yes, we agree that transport could be one reason for the elevated Arctic concentrations. We have re-written p22517 l8 to read "It is possible, therefore, that the enhancement of PAN over Western Siberia may be linked with enhanced acetone vmrs." After this sentence we have added the sentence "We cannot, however, rule out the possibility that long-range transport might be causing, or contribute to the elevated PAN vmrs." To include the possibility that long-range transport could also be a contributing factor.

12) P22518, L1 and L3: C7998 Please change "PV" into "PVU" and explain the definition of 1 PVU.

ACPD
9, C10712–C10718, 2010

These changes have been made in the text and PVU has been defined as potential vorticity unit

13) P22518, L19: Low PAN at 10N: Why are the “PAN vmrs suppressed” here due to temperature. Is it warmer than at 0N and 20N?

Yes, we agree this comment may lead to some confusion. From zonal analysis of the vertical wind field data from ECMWF operational data (which we didn’t show in the paper), we observed the strongest vertical wind speeds at 10N (i.e. the Inter-tropical convergence zone was centred over 10N at this time of year). What is very interesting, but beyond the scope of this paper, is that the highest PAN vmrs occur in regions of “weak” vertical convection – around 0 to -0.02 Pa s^{-1}. In regions of stronger vertical ascent - > 0.02 Pa s^{-1} the PAN vmrs are suppressed, possibly due to enhanced latent heat release in the convective cells which shortens the PAN lifetime. It may be that there is an “optimised” convective range for PAN vertical transport. We have taken out this line from the paper as it will need further investigation outside the scope of this paper.

14) P22518, L5-7: Cross-isentropic transport inferred from Fig. 10: For me it looks rather like a troposphere-to stratosphere gradient than like similar PAN values in the upper troposphere and lower stratosphere. Did the authors check, if enhanced stratospheric PAN might, at least to a certain degree, be mocked by tropospheric PAN by smearing by the averaging kernels.

The averaging kernels in the UT, on the whole, are well-defined: by which we mean that the width of the averaging kernels are around 3-4 km with little overlap between adjacent measurement levels. In fact, figure 3 shows this quite nicely at the nominal 6, 9 and 12 km levels (black, red and green lines respectively). We find that the width of the 15 km averaging kernel does increase markedly in many cases, similar to figure 3. We agree that this could indicate that the lower stratospheric PAN is, in fact partly tropospheric in nature and cause some degree of smearing. We have taken out this

ACPD

9, C10712–C10718, 2010

sentence.

15) P22518, L19-24: Is a similar pool south of 70S also visible in other tropospheric tracers?

We have looked at the other gases retrieved for this period (H_2O, O_3, HNO_3, $ClONO_2$ and CCl_4) and there does not appear to be a similar pattern in these data.

16) P22519, L8-9: I think, the Sahel region is not in Central-Southern Africa but south of the Sahara, where nearly no fire counts were made in August.

We agree with this comment. The words “in the Sahel region” have been removed from the text.

17) P22519, L22ff: Do the authors mean here, that on 18 October the average in the biomass burning region on 180 hPa is comparable to the average over the South Pacific on 275 hPa?

Yes, this is correct. We have added the words “at 275 hPa” after the words “South Pacific” on p22519 l24 to distinguish this fact.

18) P22536, Figure captions: The authors should explain that the white, red and blue curves indicate theta levels and ± 2 PVU.

We thank the referee for noting this. We have made these changes.

Technical corrections: We thank the referee for the technical corrections. They have all been implemented in the paper.

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

ACPD

9, C10712–C10718, 2010

Interactive Comment