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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vertical profile of peroxyacetyl nitrate (PAN) from MIPAS-STR measurements over Brazil in February 2005 and the role of PAN in the UT tropical NO_y partitioning" *by* C. Keim et al.

Anonymous Referee #2

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General Comments

This is a generally interesting paper looking at the important issue of measuring vertical profiles of peroxyacetyl nitrate in the upper troposphere and determining its role in tropical NOy partitioning. The period of focus is February 2005 over Brazil.

The paper's strength is the clear description of the retrieval of the PAN profile from the MIPAS-STR aircraft instrument and the clear indication of PAN retrieval capability at close to 2 km vertical resolution. In my opinion, there are some issues of clarification

required for the PAN retrieval and errors but good attention has been paid to the most critical points. Hence what is mainly required is complete clarification of the errors for the comparison to the NOy data but the main conclusions are likely to be unaltered. Therefore the points below are intended to provide some robustness to the conclusion on NOy.

The paper's weakness is the shortness of the discussion section and the lack of information on the measurements from the SIOUX instrument and complementary instruments on the Geophysica. In particular,the critical issue is the inter-comparison of the SIOUX NOy, NO and inferred NO2 with the MIPAS-STR PAN, HNO3 and ClONO2 including a proper accounting for the errors and vertical resolution. Further there should be a more careful definition of NOy, including bromine nitrate, N2O5 and all peroxynitrates such as PPN. For example, Hegglin et al., ACP, 2006 define their chemiluminescence measurement of NOy as the sum of NO, NO2, NO3, HNO3, HNO4, HONO, PAN, RONO2, ClONO2, 2xN2O5, BrONO2, organic nitrate and particulate nitrate of less than 1 micron diameter.

In my opinion, three main areas should be addressed in the revisions to the paper and would result in a more robust conclusion.

1) there should be a more detailed description of the SIOUX instrument, and in particular the errors on NOy, NO and NO2 (which depends also on errors in the input data for computation of NO2). For example,Patz et al, ACP, 2006 show that different NOy measurements can differ by 7%. The error for the SIOUX measurements may be less than this but this is not given. Is there any sensitivity to nitrate in small particles? What about interferences such as HCN.

2) the inter-comparison of the data sets should more carefully take into account the errors in the individual data sets and of the total NOy. In other words, a plot should show the final difference of NOy minus all the individual measurements compared to the root-sum-square error of all the measurements (including NOy, NO and the inferred NO2).

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This is the only way to be sure that the difference is greater than the measurement errors although I suspect this is the case.

3) in utilisation of data sets of differing vertical resolution, it is usual to degrade the in situ data to the resolution of the remote sensing measurement. This has not been done here. There is certainly some value to presentation of the detailed aircraft measurements and I suggest this should be retained. However, I suggest that the comparisons of Figure 13 also need some improvement to be sure of the conclusions. The in situ measurements should also be degraded to the vertical resolution and sampling of MIPAS-STR in a companion plot (could make Figure 13 a two panel plot). I am not sure why the MIPAS data are presented as piece-wise vertical profiles but in this second plot we could simply see the averaged mixing ratios for the layer. Also the authors should comment on and explain the implications of the apparent finer-scale structure in the in situ data - there seems to be atmospheric layering present i.e. the NOy profile does not have the same shape as the assumed nitric acid and PAN profiles (why are there gaps in the in situ data in Figure 13?).

The conclusions need to be made much more robust also. For some reason there is little mention of one of the primary parts of the paper, i.e. are we really seeeing a gap in the NOy budget and what is the importance of this? If correct, the paper would add to the evidence for a substantial fraction of NOy being tied up in non-NOx,PAN,HNO3 sources. To my mind, it also certainly suggests that the NOy data from the Geophysica are difficult to interpret without more information on the individual organic components and possibly radical chemistry. What is the evidence for discounting biomass burning and transport events? Are the measurements in daytime or not (expect daytime) since the suggested alternatives of HO2NO2 and CH3O2NO2 are likely to be much smaller at night?

Specific comments

The paper title should be re-considered and the second part of the title changed from

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"the role of PAN in the UT tropical NOy partitioning" to something perhaps like "its contribution to tropical NOy partitioning" or "comparisons with NOy profiles measured by the SIOUX instrument".

1) Define all acronyms: MIPAS-STR, SIOUX, KOPRA/KOPRAFIT.

2) P6985, L12: The authors refer to Tanimoto et. al who suggest PAN levels typically of <0.1 ppbv. Is this only true for Asia, or globally? At which altitudes in the atmosphere is this work valid?

3) p6987. Figure 1. It would be useful to see on this plot the related altitudes of the SIOUX in situ measurements, e.g., by colouring the flight path with the same altitude scale of colours.

4) P6987, L16: How do the authors filter for cloud in their spectra? Do they use the cloud index technique of Spang et. al (2004) [Advances in Space Research]? If so, please include the reference. Also, it would be good to be quantitative on the cloud measures observed, e.g. list the minimum cloud index in the MIPAS-STR profiles.

5) P6987, L25: Please provide more details of the HNO3 retrieval as this is also important for the NOy problem, For example, which spectral range is used? What are the important contaminants? How are these treated? A particular point is that the spectral data source for HNO3 should be given as this can change the HNO3 values by up to 15%.

6) P6992, L2: why is the plot of all five pre-determined species listed as figure 12? (i.e. at the very end of the paper) This should be moved to figure 6/7. Also, it would be good to have a brief indication of the level of agrement with expected tropospheric values for these species which would also help with point 9 below.

7) P6992, L5: Is the tangent height radiation offset for calibration errors considered in the overall error budget or is it assumed that this retrieval does not influence the PAN retrieval? Is this the same as radiometric calibration error?

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8) P6992, L7: Are all spectra below 8 km cloudy? Or is this due to high water vapour contamination. This is not important for the paper , but the author should keep this issue in mind for future work.

9) P6995, L8: Why is an error of 5% assumed for all contaminants? What is the assumption based on? Please expand.

10) P6995, L20: Similar to the last point; is there a reference for the assumption of a gain calibration error of 2%? If so, please add. If not, please justify.

Technical corrections:

There are numerous minor errors which need to be corrected. A few are given here.

P6984, L8: please change CFC-22 to HCFC-22 as this is how the compound is more generally referred to in the literature (although CFC-22 is still technically correct)

P6984, L23: change "firstly found" to "first discovered"

P6989, L14: change the word "on"; to "to"

P6991, L1: "xa" should be written as a vector

p6994, L1: change "like described" to "as described"

P6994, L14: please remove the word "in"

p6994, L15: change "like" to "errors such as"

P6996, L3: remove the first instance of the word "in" and replace with "at"

P6997, L4: please remove the word "tropic" and insert the phrase "in the tropics"; after the word "spectra".

Figure 3 might perhaps look better as one plot with the y-axis in log format. At the moment the plot is also very busy. The figure would also be clearer if, say, only contaminants with a signal greater than the MIPAS-STR noise were included.

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Figure 11: It would be useful to also show the absolute difference between the MIPAS-STR and ECMWF/TDC profiles. These could be included in figure 11b.

Figure 13. The authors may want to change the colour scale for the plot. At the moment, it is quite difficult to distinguish between the PAN and HNO3 colours.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6983, 2008.