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Comment

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 #1

Received and published: 21 April 2008

This paper relates to aircraft-based remote-sensing measurements of PAN taken in the upper troposphere and lower stratosphere (8 - 18 km) over continental Brazil in February 2005. The focus is primarily on issues relating to accurate retrieval of the vertical PAN profile from limb measurements of emission spectra obtained by the MIPAS-STR instrument. Detection of PAN via remote sensing is a fairly new technique and is complicated by the multitude of bands that interfere with the broad PAN emission peak. The authors do a thorough job of assessing these difficulties, which is a necessary step for any new technique to be widely accepted. The discussion is quite short - perhaps too

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short - and is limited to pointing out the lack of closure in the NO_y budget. The paper is generally well written; the phrasing is awkward in places, but not so much as to cause misinterpretation of the results or conclusions. This paper is suitable for publication in ACP, with some revisions as outlined below.

As a final note, though the results presented here are of reasonable magnitude, future validations against in-situ measurements of PAN should be made a priority if remote-sensing measurements are to be widely accepted within the scientific community.

Specific Comments

p.6984, L22: The authors might add the caveat that PAN's deleterious effects on plants and animals is only an issue at fairly high concentrations, even higher than what is found in typical urban smog episodes. Alternatively, provide references for this statement.

p.6985, L15: In this list, the authors should also include thermal dissociation-chemical ionization mass spectrometry (TD-CIMS, see Slusher et. al. (2004), JGR) and thermal dissociation-laser induced fluorescence (TD-LIF, see Day et al. (2002), JGR). Note that the latter can only detect sum peroxy nitrates, but this is typically 80 - 90 percent PAN.

p.6985, L29: Please provide the full name from which the MIPAS-STR acronym is derived.

p.6987, L23: Since the HNO₃ measurement is used to assess the NO_y deficit, a reference for how it is retrieved is appropriate.

p.6988, R3: This should be a right-proceeding reaction only, not an equilibrium reaction.

p.6989, L7: It would be appropriate to reference fig. 11 here to show that the ECMWF profile is correct.

p.6989, L19: It is not clear to me why the radiance decreases with increasing tangent

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height. Perhaps a sentence stating why this is so would be helpful to readers not familiar with the detection technique.

p.6991, L12: Does natural (e.g. real) variability in the concentrations over the 6 averaged profiles affect this analysis? In other words, is it safe to assume that profiles are constant over the rather large (>100 km, I believe) measurement swath? This is currently not considered as a source of error/variability in section 4.8.

p.6991, L23: If a reference is available detailing the validity of using the given bands for retrieval of these species, please provide it.

p.6992, L2: Given that Fig. 12 appears so early and is not really discussed later, it might be better to move it up (i.e. renumber as Fig. 5 or 6).

p.6992, L12: What is meant by "instabilities"? Please be more specific. A smooth profile should not necessarily be expected, as there are often thin layers of pollution or other air masses throughout the troposphere (indeed, the NO_y profile in Fig. 13 makes this apparent).

p.6995, L5: Looking at Fig. 5, this isn't so much "adapting the FISH measurements" as it is more closely agreeing with the FLASH measurements.

p.6995, L26: Is this referring to the analysis in section 4.7? Please be clearer.

Discussion: Though this data is preliminary, some discussion of or speculation on the results is warranted. Why is there a maximum at 10 km? This seems to coincide with a local minimum in NO_y. What is the PAN/NO_y ratio, and how does this compare with similar previous measurements? What other NO_y species could be contained in the deficit? N₂O₅? Alkyl nitrates? HONO? Is it possible to retrieve these in the MIPAS-STR spectra? This measurement technique is quite new, thus it is important to demonstrate how these measurements can be used to understand the atmospheric chemistry of the upper troposphere and lower stratosphere.

p.6997, L5-12: These comments are analysis/comparison and thus belong in the dis-

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cussion section. Furthermore, the argument of seasonality is questionable. The lifetime of PAN is on the order of months at these altitudes, thus (neglecting transport) one might expect the opposite: higher concentrations at the end of the dry season due to a buildup of PAN throughout the burning period.

Technical Corrections

p.6984, L14: highest reported in the literature.

p.6984, L16: in-situ.

p.6991, L5: just large enough to avoid oscillations.

p.6994, L24: which PAN is also retrieved.

p.7004, Fig.1: Add a key for the altitude color-coding.

p.7010, Fig.7: Change axis labels to specify the measurement altitude and the averaging altitude (or otherwise make the labels more specific).

p.7013, Fig.10: change legend term "Spectroscopy" to "PAN x-section" to match the discussion in section 4.8.

p.7016, Fig.13: It is difficult to tell the PAN and HNO₃ colors apart, especially in the lower half of the plot; the authors might want to change these to make them more distinguishable.

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

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