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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.

C. Keim et al.

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Authors Comment on Anonymous Referee 1

We thank for the valuable and constructive comment, to which we reply in the following:

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 com-

plicated 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 short - and is limited to pointing out the lack of closure in the NOy 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 PAN8217;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. The referee is entirely correct, we changed this sentence acoordingly.

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. We thank the referee for completing our list. We added the two mentiond methods in the revised paper.

p.6985, L29: Please provide the full name from which the MIPAS-STR acronym is derived. We put Michelson Interferometer for Passive Atmosphere Sounding-STRatorpheric aircraft in the revised paper

p.6987, L23: Since the HNO3 measurement is used to assess the NOy deficit, a reference for how it is retrieved is appropriate. We give a reference to Ding et al., ACP, 7,

ACPD

8, S4476–S4481, 2008

p.6988, R3: This should be a right-proceeding reaction only, not an equilibrium reaction. Yes you are right, we changed it for the reviced version.

p.6989, L7: It would be appropriate to reference fig. 11 here to show that the ECMWF profile is correct. For the sensitivity study it is not important, that the profile is correct, but reasonable. As the referee notes, Fig.11 shows well, that this is the case. We add a remark in the revised paper.

p.6989, L19: It is not clear to me why the radiance decreases with increasing tangent height. Perhaps a sentence stating why this is so would be helpful to readers not familiar with the detection technique. The emitted radiance, detected by MIPAS, is (mainly) proportional to the concentration of the trace gase. The radiance is also dependent on the temperature of the emitting molecules via Planck's law. Both effects work in the same direction, a decrease of the emission with increasing altitude: the vmr of PAN as the pressure decrease with increasing altitude, so the concentration decreases. The temperature decreases with increasing alitude (until the tropopause). We tried to make the correlation clearer by adding some sentences.

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. We investigated the individual profiles of the 'easy' tropospheric gases (e.g. CFC11) and temperature. Their similiarity gave us the confidence in averaging. It should be remarked in this context, that the in situ profile is also not measured at constant position (the aircraft is not a drop sonde). Only the relative constancy of the 6 profiles makes comparison possible.

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

ACPD

8, S4476–S4481, 2008

Interactive Comment

al., ACP, 7, 257-281, 2007 for ClONO2, Clarmann et al., ACP, 7, 5861-5872, 2007 for CFC-11, and Moore at al., ACP, 8, 73-82, 2008 for CFC-22. For CH3CCl3 and CFC-113 we did no real profile retrieval, as the measured signature does not allow this. We only removed the signutures by scaling a climatological profile.

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). We thank the referee for this sugesstion, and adopted it. The following figures are renumbered adequate.

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 NOy profile in Fig. 13 makes this apparent). The referee's remark points a not well choosen expression. We used "Stability" related to the retrieval process (L12) and to the atmospheric layering (L23), what causes unclearity to the reader. L12: we do not expect a smooth profile, the retrieved PAN profile is far from smooth, but a stable, convergent retrieval. We tried to improve our expression.

p.6995, L5: Looking at Fig. 5, this isn8217;t so much "adapting the FISH measurements" as it is more closely agreeing with the FLASH measurements. The referee is entirely correct. We adapted FISH measurements for the used a priori profile for water, but here we describe a test performed with a profile adapting the FLASH measurements instead.

p.6995, L26: Is this referring to the analysis in section 4.7? Please be clearer. No. section 4.7. shows residua of two test retrievals with fixed PAN-profiles (e.g. the vmr of PAN is not changed in the retrieval). Here we test the error contribution of the choosen a priori profile. We compare the results of retrievals with two different a priori profiles (in particular: a zero profile and a midlatitude model profile). We changed the sentence.

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

ACPD

8, S4476–S4481, 2008

Interactive Comment

a local minimum in NOy. What is the PAN/NOy ratio, and how does this compare with similar previous measurements? What other NOy 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 discussion 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. We changed the discussion and conclusion part of the reviced paper, also in accordence to the second referees comments.

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

ACPD

8, S4476–S4481, 2008

Interactive Comment

distinguishable.

We adopted all the referrees suggestions

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ACPD

8, S4476–S4481, 2008

Interactive Comment