Response To Anonymous Referee #1 Comments

Comments:

1. The authors describe the difficulty in identifying co-located satellite data, but have limited their comparison to the BORTAS campaign (a small time period and small geographic area), and then compare to coincident measurements by the MIPAS instrument. This results in only three satellite occultation coincidences for comparison. Specific questions:

- What is the detection limit of the ACE-FTS PAN retrievals? What is the detection limit of the MIPAS PAN retrievals?
- How do these compare to the background concentrations of PAN?
- Could other occultations, besides the ones during July 2011, be compared?
- The three comparisons are shown in Fig. 4, but the agreement between the two satellite PAN measurements is not reported. What is the quantitative agreement?

The answer depends on whether the referee is referring to a single occultation, or to an average over many. We estimate the detection limit for ACE-FTS PAN to be around 5 pptv for a single occultation, slightly lower than the background values of 10-400 pptv reported by Wayne (2000). The detection limits for MIPAS PAN are 9 km – 20 pptv, 12 km – 30 pptv and 15 km – 50 pptv. The data has now been reported in the manuscript.

A quantitative comparison between ACE and MIPAS has now been included into the manuscript. Other occultations could potentially have been used, but since the paper is BORTAS-centric, we chose only to use measurements made during the flight campaign. We discovered three coincidences and deemed them sufficient for the comparative analysis for this publication.

2. Why haven't the authors compared the ACE-FTS PAN retrievals to aircraft measurements? In situ PAN measurements were part of the BAe-146 payload during BORTAS (Palmer et al., ACPD, 2013). Beyond BORTAS, the ACE-FTS satellite has recorded data since 2003, so other aircraft PAN measurements could be used, such as from INTEX-B or ARCTAS.

There were no coincident measurements between ACE-FTS and the aircraft during the campaigns. ACE-FTS makes a maximum of 30 occultations a day with measurements equally distributed between the northern and southern hemisphere. With so few measurements and the limited range of the instrument aircraft, it is difficult to get coincident measurements. During the BORTAS flight campaign, there were plans to direct the aircraft so that coincident measurements could be obtained since the ACE prediction tool can be used to determine the location of future ACE-FTS measurements (https://databace.uwaterloo.ca/occultations/distance.php). Unfortunately, due to the orbit of SCISAT-1 and the time period chosen for the campaign, ACE-FTS measurements were being made at more northerly latitudes, measuring the outflows from the boreal fires occuring in the Northwest territories that were tracking east across Canada towards Greenland. The aircraft was primarily dedicated to making measurements of the emissions from the fires in Western Ontario, which flowed southeasterly directly towards Maritime Canada. ACE-FTS did not start to take measurements over Maritime Canada until the very end of the campaign period when the aircraft was already packing up for the return transit flight to the UK. It is actually very disappointing, because if we we able to get some coincident measurements with the aircraft, not only could we have validated the PAN product, but a number of other pyrogenic species retrieved by ACE-FTS.

3. The current abstract is too broad, and the authors should focus on describing their new results. Specifically, the first paragraph summarizes prior work about the chemistry and transport of PAN. It should be shortened to one or two sentences. The concluding paragraph describes context and future work. It should be removed. The paper’s conclusions succinctly summarize the results, and would make a better abstract.

The abstract has been modified accordingly.

4. Some important details are missing in the current abstract and should be added.
Specifically:

- What is the detection limit for the PAN retrievals?
Approximately 5 pptv for ACE-FTS PAN and the limits for MIPAS PAN are 9 km – 20 pptv, 12 km – 30 pptv and 15 km – 50 pptv. The detection limits have now been reported in the manuscript.

- What is the precision and accuracy?

Accuracy is basically down to the systematic error, which is discussed at length in the manuscript. Increasing sample size would normally improve precision, but this would assume PAN concentrations don't show much geophysical variation. PAN formation is highly localized to biomass burning and is seasonal in nature. For a single measurement, precision is intrinsic to the instrument - the high precision of the ACE-FTS is due to the high signal-to-noise ratio (sun as light source). In order to report any meaningful information on instrument precision, repeated measurements would have to be made in the exact same geographic location, atmospheric conditions and time period, which is not really possible with ACE-FTS.

- Pg. 1577 line 16-17 “The retrieval method employed and errors analysis are described in full detail.” Please replace this statement with a brief description of the retrieval method and error analysis.

Correction made.

- What is the time period of the BORTAS field campaign?

12 July to 3 August 2011. The time period has already been indicated in the introduction. Now additionally included in the abstract.

- What spectral regions are used for the retrievals? What other species are fit in these windows?

Table 1 summaries all the microwindows utilized for the ACE-FTS PAN retrievals and the associated interfering species that are simultaneously recorded. Each microwindow is used for a given altitude range that minimizes the number of interfering species present in the tangent spectra used for the retrieval of the vertical profiles for each occultation.

- Pg. 1577 line 23-24: Quantify “good agreement.”
A more detailed quantitative comparison now included in the manuscript.

5. The authors should check all of the references in the introduction. Primary references should be given, rather than taking sentences from secondary references and citing the secondary references. In some cases, references should be added. Here are some examples:

- Pg. 1579 lines 7-8: "Background volume mixing ratios (VMRs) of PAN in clean air are quite variable and range typically from 10-400 ppt (Allen et al., 2005a)." This reference is incorrect. Neither Allen et al. (2005a) or Allen et al. (2005b) report mixing ratios and they don't mention this fact.

There was a mix up in the citation. The reference is actually Wayne (2000). Correction made.

- Pg. 1579 lines 9-11: "The thermal decomposition rate of PAN is highly temperature dependent, resulting lifetimes between 1 h at 298 K and about 5 months at 250 K (Glatthor et al., 2007)." This isn't an original reference. Glatthor et al. (2007) cite Singh (1987) for this fact.

Citation made.

- Pg. 1579 lines 15-16: "The thermolysis rate drops quickly with temperature, permitting extended lifetimes (Allen et al., 2005a)." Allen et al. (2005a) does not report thermolysis rates, and cite Kirchner et al. (1999) for this fact.

Correction made.

- Pg. 1580 line 19: Add reference for ACE-FTS satellite.

Citation added.

6. Some of the material presented in the introduction should be moved to the experimental section. Specifically:
- Pg. 1581 lines 3-10: Description of PAN cross sections and altitude grid of ACE-FTS data.- Pg. 1582 lines 7-23: Description of MIPAS instrument.
- The MIPAS retrieval method should be described in the experimental section, prior to the discussion of biomass burning identification.

Modification made.

7. Pg. 1583 line 17-19: "the intensities were normalized to the room temperature value." This is unclear. Did the authors scale the integrated band intensity at different temperatures to match the room temperature value? If so, change this to "the integrated band intensities were scaled to the room temperature value."

Correction made.

8. Pg. 1585 lines 19-21: ": : :once the PAN VMR profile is included in the calculated spectrum the residual values go to zero, indicating that all interfering species within the microwindow have been accounted for: : :" This is not an accurate description. The error in Fig. 2b is approximately 1%. This sentence should indicate that all interfering species within the detection limit have been accounted for.

Correction made.

9. Figure 2: Why is the average residual in Fig. 2a not centered around zero? I assume this is because the retrieval of the absorbers is being weighted by other spectral retrieval windows. For a least-squares global fit that included only this window, the average residual should be centered at zero. Please clarify in the text.

The residual is not centered at zero because PAN is an unresolved, underlying, broadband feature. There is an underlying PAN contribution throughout the entire microwindow that causes a shift in the residual into the negative when PAN not accounted for in the calculated spectrum.

10. Regarding the uncertainty discussion in Section 2.2:
- What is the precision of repeated retrievals from spectra recorded at similar altitudes or air masses?

Again, the precision of ACE-FTS PAN is difficult to determine because repeated retrievals made in the exact same geographic location, atmospheric conditions and time period are difficult to obtain because PAN is a species that is highly localized in the atmosphere and is seasonal in nature. Due to the sporadic nature of ACE measurements, precision estimates for ACE-FTS products are limited to those species that do not demonstrate much geophysical variation.

- What is the change in the PAN retrievals change as you vary the HCFC-22, CFC-114, and other species within their uncertainty? Is it consistent with the 1% estimate?

These are all very weakly absorbing molecules, but their VMRs are not floated in the retrieval. Since there are no systematic features in the residuals, we make the assumption that the error contribution is small. The effect of removing these species from the retrieval is negligible and has little effect on the overall uncertainty.

11. Regarding the comparison:
- Pg. 1590 lines 8-14: The authors mention calculating correlation coefficients. Please report the results.

The results reported in Figure 3 have now been included into the main text.

- Pg. 1592 line 9: Quantify “excellent agreement.”

Sentence rewritten accordingly. The remark was intended to call special attention to the similarities in the profile shapes recorded by both instruments. Comparison now quantified.

- Fig. 4 center panel: Why is one MIPAS profile an outlier?

The MIPAS outlier has been remove from the plot for 2011-07-23. The profile was not so much an outlier than a MIPAS measurement made off the same plume that was measured by ACE-FTS.

Minor comments:

- Throughout: Please edit to remove casual/colloquial text. This includes “bring the data together”, “naively expect”, “go to zero”, “instrument peers through”, “measurements at low altitutes are cut off”.

Text corrected.

- “Boreal” should not be capitalized. Change on pg. 1577 line 14, pg. 1577 line 22, and elsewhere.

Text corrected.

- Pg. 1578 line 19: Punctuation error. Remove ", smog" and the semicolon.

Text corrected.

- Pg. 1579 line 7 – pg. 1580 line 7: This paragraph should be edited to remove repetition.

Changes made to the paragraph accordingly.

- Pg. 1579 line 12: Give the photolysis wavelengths for PAN.

Wavelengths have now been included in the manuscript.

- Pg. 1580 line 20: "coverage in the infrared covering" should be "coverage in the infrared, covering"

Text corrected.

- Pg. 1580 line 27: "Through the new: : :" should be "In the new: : :"

Text corrected.

- Pg. 1583 line 13: "is strongly interfered by the presence" fix grammar.

Text corrected.

- Pg. 1588 line 9: "VMRS" should be "VMRs".

Text corrected.

- Pg. 1588 line 12: "VMRs values" should be "VMR values"

Text corrected.

- Pg. 1590 line 1: "during approximately two days earlier" should be "approximately two days earlier".

Text corrected.

- Pg. 1590 lines 24-26: "After sequential joint-retrieval with continuum of, in order, pressure/temperature, water vapour, O3, HNO3, ClONO2, and CCl4: : :" I can't understand this sentence. Do the authors mean that gases were simultaneously retrieved in multiple spectral windows? Clarify.

The gases are retrieved in this order. The microwindows used are optimised for the particular gas (i.e. the PAN microwindow is not used for P/T, H2O retrieval etc.) This is the same approach as the MIPAS operational product retrievals. Clarification in the made in the manuscript.

- Pg. 1591 lines 8-10: What is "PAN field from TOMCAT model data"?

The MIPAS PAN a priori are constructed from TOMCAT model data averaged over June, July and August (i.e. summer) from 2003. We assume little year-to-year change in PAN VMR.

- Pg. 1591 line 14: “derived the measurement” should be “derived from the measurement”.

Correction made.

- Every reference is followed by a spurious number.

Numbers added due to some error in the typesetting process of the document for publication in ACPD. They do not appear in the tex file of the original submitted manuscript.

- Spell out numbers less than 10.

Changes made where appropriate.

Specific Comments:

Page 31630, Abstract: Although the abstract is well written, it says very little about the results of the paper, focusing instead on a description of the BORTAS campaign. Some additional information should be provided, summarizing the conclusions of the work.

Additional information has been appended to the abstract.

Response To Anonymous Referee #2 Comments

General comments:

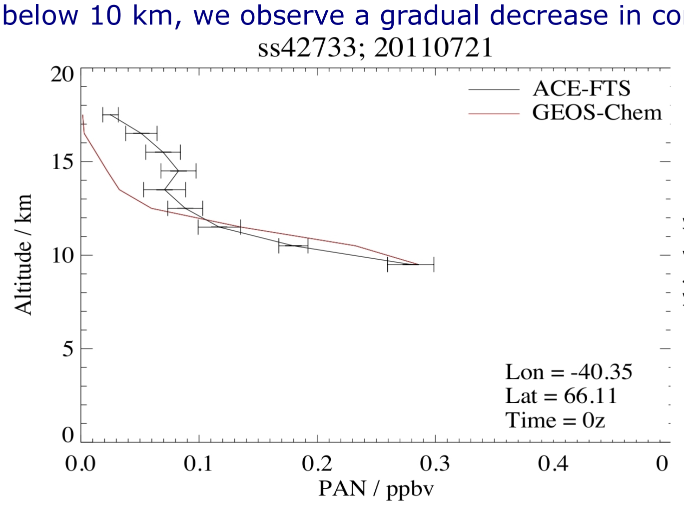
The paper focuses primarily on the background of PAN chemistry and the retrieval algorithms and error assessments. Only a single printed page is devoted to results (sections 5 and 6), followed by a short conclusions. This work thus falls short of addressing the science questions raised in the introduction, such as how the measurements here provide constraints on the role of biomass burning impacting UTLS chemistry. The authors could easily have dug deeper to assess questions such as how their measurements compare to e.g., the GEOS-Chem modeling work from the BORTAS campaign, or other modeling analysis on the global scale in comparison to the ACE-FTS global retrieval set. They could have also examined the impact of biomass burning on global PAN distributions via their HCN indicator rather than simply presenting global PAN distributions, which at the moment are a bit disconnected from the themes of the paper laid out in the introduction.

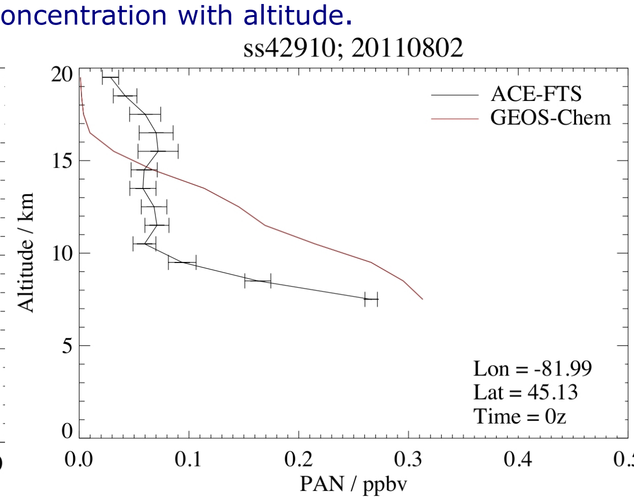
First and foremost, this publication was intended as a validation paper and as an announcement of the availability of the new ACE-FTS PAN data product. The primary focus of this paper was the detailed description of the retrieval method and validation of ACE-FTS PAN and NOT an in-depth investigation of the formation of PAN, its growth rate and subsequent chemistry in Boreal biomass burning plumes. An analysis of PAN and other pyrogenic trace species retrieved by ACE-FTS in the remote detection of boreal biomass burning plumes is reported in a completely separate publication submitted to the BORTAS special issue of ACP.

Tereszchuk, K. A., González Abad, G., Clerbaux, C., Hadji-Lazaro, J., Hurtmans, D., Coheur, P.-F., and Bernath, P. F.: ACE-FTS observations of pyrogenic trace species in boreal biomass burning plumes during BORTAS, Atmos. Chem. Phys. Discuss., 12, 31629-31661, doi:10.5194/acpd-12-31629-2012, 2012.

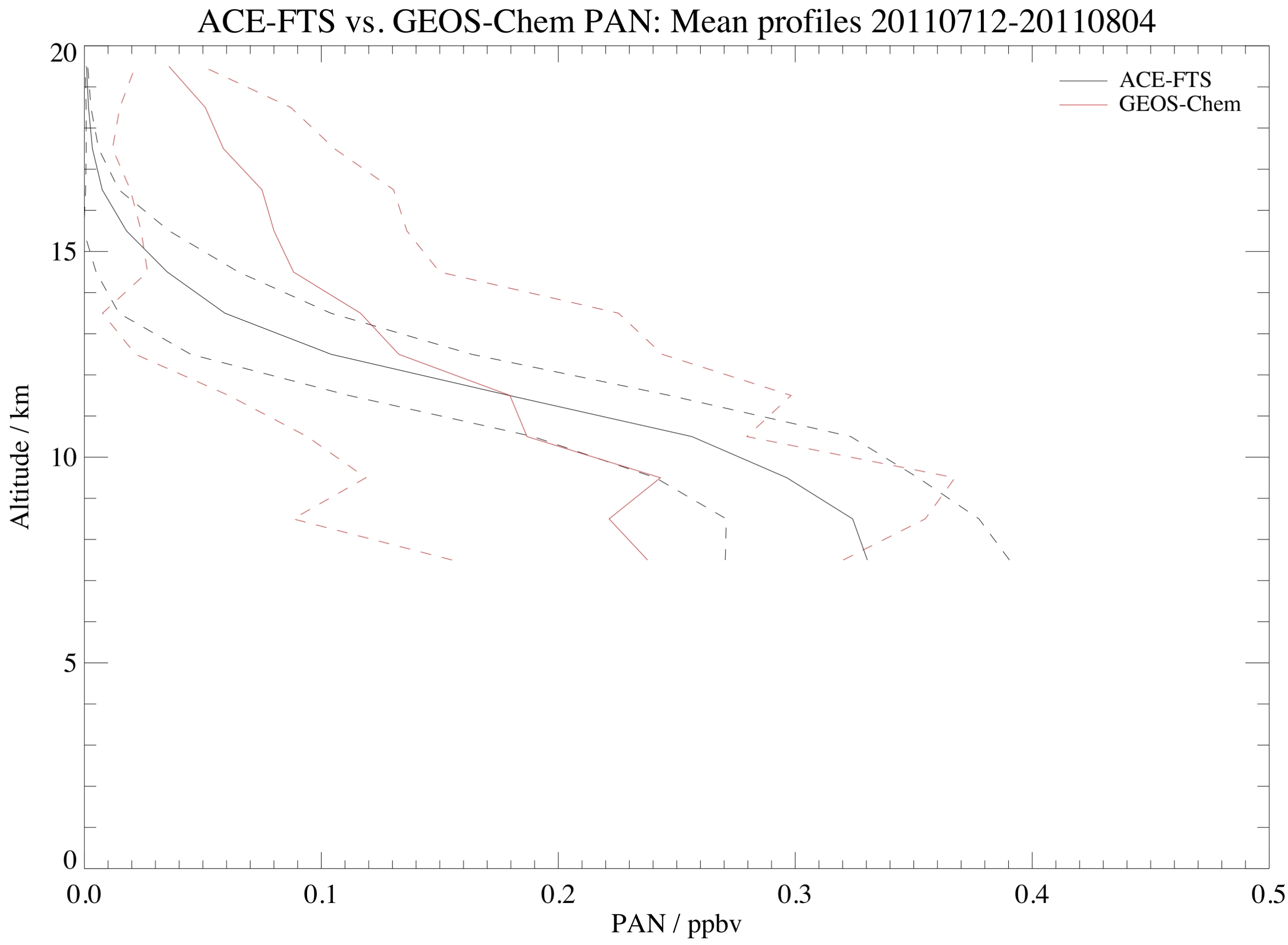
We initially intended to include comparative model data in this paper, but the results of the model output were not very convincing. Below are examples of the comparisons made with GEOS-Chem and ACE-FTS.

Firstly, occultation ss42733, which is one of the occultations compared to MIPAS in the paper. The output from the model emulates the concentration profile measured by ACE-FTS and seem to be in fairly good agreement, but upon further inspection of the comparisons with other occultations containing measurements of boreal biomass burning, we see that the model can be quite erroneous. The corresponding GEOS-Chem output for occultation ss42910 compares poorly with the satellite measurement. Instead of showing a defined plume profile with enhancements in PAN below 10 km, we observe a gradual decrease in concentration with altitude.



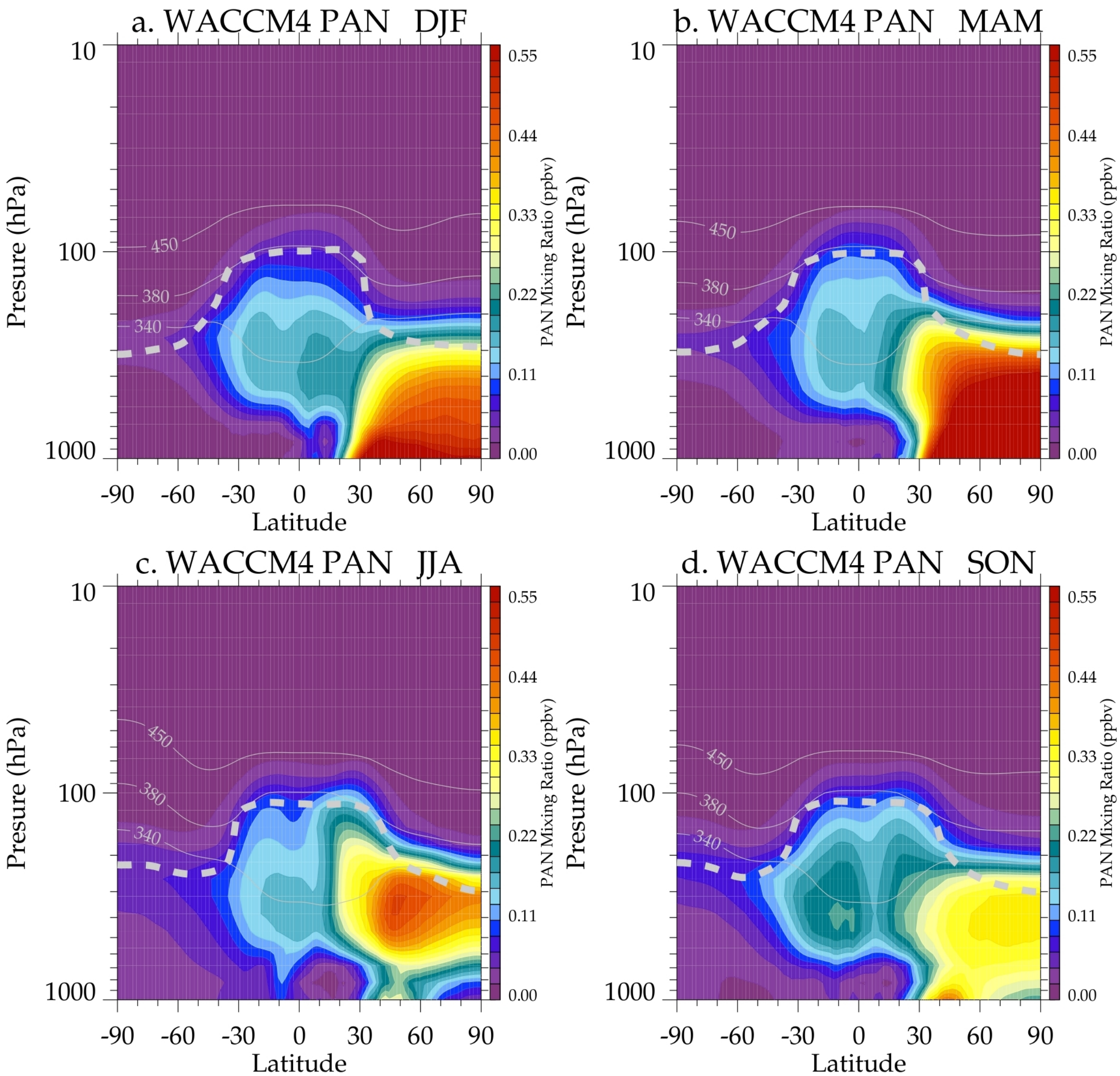


The same behavior is observed in the mean profiles calculated from the occultations containing measurements of boreal biomass burning during the period of the 2011 flight campaign. The mean profile for the ACE-FTS data is what should ideally be observed, i.e. enhancements in PAN in the the middle and upper troposphere and then a sharp cut-off at the tropopause with concentrations of PAN in the stratosphere dropping to near zero. This is clearly not observed in the the mean GEOS-Chem profiles, it instead demonstrates an almost linear decline in concentration with altitude.



Unconvinced by the GEOS-Chem output, we sought to make comparisons with the WACCM4 model, but to no avail. The output for the WACCM4 model was generating much higher PAN mixing ratios (more than twice as large in magnitude) than ACE-FTS. In addition, when calculating the the global distributions of PAN from the WACCM4 model (see below), we do not observe any seasonality in the distribution of the PAN concentrations.

It was ultimately decided that until the model problems for PAN were assuaged, model data was to be omitted from this paper and would be the focus of a separate, future, publication.



Specific comments:

The authors discuss retrieval error in detail, but what are the lower detection limits of PAN measurements from ACE-FTS and MIPAS?

Approximately 5 pptv for ACE-FTS PAN and the limits for MIPAS PAN are 9 km – 20 pptv, 12 km – 30 pptv and 15 km – 50 pptv. The detection limits have now been reported in the manuscript.

Throughout: italicize subscripts x and y on NOx and NOy

Correction made.

1588.9: Rather, these are measurements of biomass burning impacted air masses, not the emissions themselves.

Correction made.

Fig 3: This might be better presented with the panels side by side, rather than attempting a single column layout.

Format change made.

1591.25: Can the authors provide an example of the back trajectory analysis? Also, regarding the attribution of plumes to specific biomass burning events / locations, how would the impact of multiple plumes beneath the trajectory be disentangled?

I would rather provide a citation to the other ACE paper for BORTAS (below) which covers these aspects in more detail instead of repeating the exact same content in both manuscripts. To track the outflows from multiple sources, animations were created using IASI CO measurements. The movement of pyrogenic outflows were monitored over a period of days leading up to the time of the ACE-FTS measurement to determine the origin of the plumes and whether there is convergence from more than one source.

Tereszchuk, K. A., González Abad, G., Clerbaux, C., Hadji-Lazaro, J., Hurtmans, D., Coheur, P.-F., and Bernath, P. F.: ACE-FTS observations of pyrogenic trace species in boreal biomass burning plumes during BORTAS, Atmos. Chem. Phys. Discuss., 12, 31629-31661, doi:10.5194/acpd-12-31629-2012, 2012.

Section 6: Why do the authors only construct a global PAN distribution from ACE-FTS and not MIPAS?

The global distribution and seasonality of PAN has already been published by Moore et al. 2010 (figure 10). Reference will be made to this work.

Seasonality of Peroxyacetyl nitrate (PAN) in the upper troposphere and lower stratosphere using the MIPAS-E instrument, Atmos. Chem. Phys., 10, 6117-6128, 2010.

Section 5: The inter comparison between the ACE-FTS and MIPAS coincident profiles provides a nice opportunity. However, the treatment is a bit lax. Can the agreement be statistically quantified, rather than just referred to qualitatively as "good", and then later as "excellent"? Further, the authors state that the profiles lie with the associated measurement errors, but from the plots this does not always appear to be the case. Please explain. Lastly, there is one MIPAS profile in the second and third comparison that is wildly different. What is happening there?

Quantitative analysis added to manuscript. The outlier is basically a MIPAS measurement that is off-plume and measured a different air mass than that measured by ACE-FTS. The MIPAS outlier has been removed from the plot for 2011-07-23.

1591.10: Given that the authors are showing here the influence of biomass burning on PAN, and biomass burning can have substantial annual variability, it is surprising to read that PAN does not. Also, it wasn't clear if they were referring to the TOMCAT simulations or MIPAS measurements here with regards to the small variability.

1591.14: derived from the

Correction made.

1591.14: Can degrees of freedom be calculated to quantify the fraction of information coming from the retrieval vs a priori, as are done for e.g., TES nadir retrievals?

Yes. The degrees of freedom are discussed in detail in the paper by Moore et al. 2010.

Seasonality of Peroxyacetyl nitrate (PAN) in the upper troposphere and lower stratosphere using the MIPAS-E instrument, Atmos. Chem. Phys., 10, 6117-6128, 2010.

The degrees of freedom for the mid-latitude retrievals during BORTAS range between 2 and 4 in general.

Below is the PAN averaging kernel for the closest ACE/MIPAS coincident measurement (ss42733). Included are the degrees of freedom (dfs) of 4.11 and shannon information content (shn) of 1.31. Typically between 2 and 4 dfs for mid-latitude profiles during July 2011.

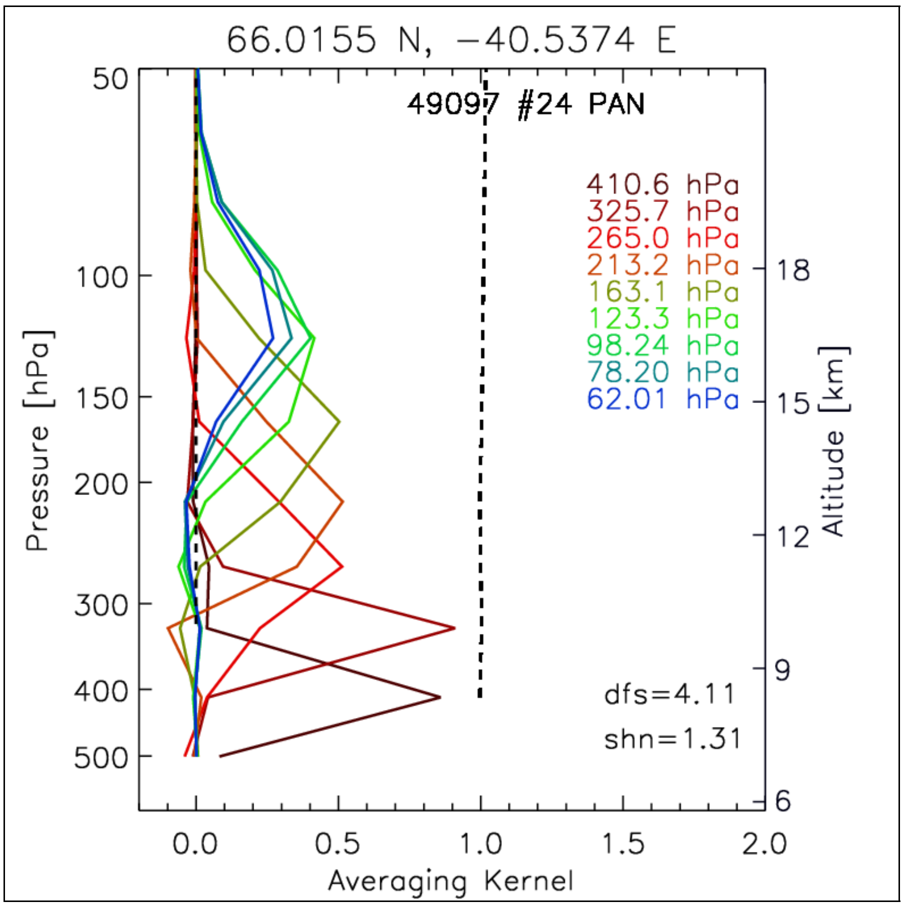


Fig 4: What is the origin of the mid trop and UTLS local maximums in the PAN concentrations over Antarctica in JJA?

Most likely from the outflows of large fires occurring in the Australian savanna, like those observed during the Black Saturday bushfires in February 2009. The pyrogenic updrafts generated from large fire can loft biomass burning plumes high into the upper troposphere and cause perturbations which can result in the strat-trop exchange of air masses. The PAN in the biomass burning emissions trapped in the cold lower stratosphere would have extended lifetimes and because JJA corresponds to the winter months in Antarctica, the lack of sunlight would inhibit the photolysis of PAN, resulting in even longer atmospheric lifetimes.

Specific Comments:

Page 31630, Abstract: Although the abstract is well written, it says very little about the results of the paper, focusing instead on a description of the BORTAS campaign. Some additional information should be provided, summarizing the conclusions of the work.

Additional information has been appended to the abstract.