

The manuscript by Fischer et al., presents tropospheric measurements of satellite retrieved peroxyacetyl nitrate (PAN) over North America and investigates the changes in concentrations linked to fires. Overall, the manuscript would be a nice addition to the existing literature (e.g. Payne et al., 2014, 2016) as there are limited flight campaigns measuring PAN and MIPAS can only retrieve it in the UTLS. The compositing of TES PAN retrievals under smoke plumes is also an interesting way to investigate potential enhancements of PAN related to fires. Therefore, once the comments below are addressed, this manuscript should be accepted for publication in ACP.

Major comments:

As TES is the only satellite currently measuring lower tropospheric PAN (to the best of my knowledge anyway), it would be useful to see the spatial distribution of PAN at different tropospheric levels. In neither this paper nor the Payne et al., (2014, 2016) manuscripts, there are very few spatial maps of TES PAN. In Payne et al., (2016), Figure 1a shows a noisy spatial distribution of TES PAN in the tropics. Therefore, it would be useful if this study could add another figure (e.g. between Figure 1 and Figure 2) showing the PAN distribution over N. America (e.g. the July 2006-2009 average on a regular grid instead of individual retrievals on several tropospheric levels) highlighting the average PAN hotspots and potential outflow of PAN from source regions.

*We agree that showing a spatial distribution is interesting. Exactly as suggested, we have added the July 2006-2009 average on a regular 2x2 degree grid. However, we have only done this as a tropospheric average. As discussed in Payne et al. (2014) and also in Section 2.1, the TES PAN retrievals do not provide information on the vertical variation of PAN. In all cases, the degrees of freedom for signal, or number of independent pieces of vertical information in the retrieval, is less than 1.0. To address the true spirit of this suggestion we have also added a panel that shows all the data points individually; this allows readers to see the noise in the data. We also include the entire region of retrievals that were processed so that readers can view the distribution off-land as well. We have added another paragraph describing this new Figure (now Figure 2 as suggested) in section 2.1.*

*“Figure 2 shows the July 2006 – 2009 tropospheric average PAN. When all the existing TES data is gridded, there are several large patterns that emerge. 1) Average tropospheric PAN mixing ratios in the TES observations generally increase with latitude during the month of July over North America. 2) Average tropospheric PAN mixing ratios generally decrease from west to east. 3) As can be seen in later figures, there are relatively few retrievals per grid box over the southwestern U.S. Though there are relatively few samples (~5-20 per 2x2° grid box), relatively high mixing ratios (0.6 ppbv) are observed over the Colorado Front Range.*

The presentation of the manuscript needs to be improved as several of the Figures have been mislabelled in the text and it is difficult to follow. In Figure 7, there is reference to red lines, but all the lines are grey/black, again making it difficult to read the paper.

*We apologize for the labels on the original Figure 7. We changed the lines from red to black and color-coordinated the dots with the original Figure 6, and then it looks like only half of the caption for the original Figure 7 was updated. We have fixed this.*

Section 3.3 needs to be made clearer as discussion of the PAN:CO ratios is rather rushed. For instance, adding some equations into Section 3.3 on how the enhancement ratios are calculated would be useful. Again, as Figure 7 has misleading colours, it is difficult to work out what the authors are trying to say in this section.

*We sincerely believe that this section is now much easier to understand with the caption for Figure 7 (now Figure 8) corrected. As indicated in the comment above and noted by the second reviewer, we mislabeled black lines as red in the submitted caption. There was also an incorrect reference to Figure 7 (now Figure 8) in Section 3.3, which should have pointed readers to Figure 6 (now Figure 7). Now that these typos*

*have been fixed, this section should be much easier to follow. However, as suggested by the reviewer, we have also added an equation describing the calculation of the PAN enhancement ratios, and several sentences at the start of the section that point readers to a reference that discusses enhancement ratios and their pitfalls (Yokelson et al., 2013). There are two key points to this section, and we now state both of them in the introductory paragraph. 1) The tropospheric PAN enhancement ratios from TES fall within the range of relevant aircraft measurements over North America. 2) There are many pitfalls associated with using enhancement ratios as observed from TES to study the evolution of PAN in the smoke plumes we have identified here.*

Minor comments:

P1 L68: Would be good to reference of Ungermann et al., (2016) who investigate PAN in the summer-time Asian monsoon region using Earth observation measurements. On Line 62-64, the authors states “much of our understanding of the distribution of PAN outside urban areas rests on data from aircraft missions interpreted with global chemical transport models”. I think it would be useful to reference a few papers that have utilised CTMs and satellite data to investigate PAN (e.g. Fadnavis et al., 2014; Pope et al., 2016).

*Thank you very much for pointing out these newer references. We have added citations to all of them in the suggested locations.*

P2 L102: What do the authors mean by “True profiles”? In Figure 1, would the true profile be the retrieved profile?

*The “true profile” is the actual atmospheric profile. We have updated the caption and text to indicate this.*

P2 L106-107: “As discussed in Payne et al. (2014), the TES PAN retrievals do not provide information on the vertical variation of PAN”. This does not make sense. PAN is retrieved at several vertical levels and the AKs will provide information on the vertical sensitivity. P2 L107-109: IF a DOF < 1 means a retrieval is heavily influenced by the a priori then why do the authors often use the criteria of the DOF > 0.6?

*This threshold value of DOF > 0.6 was chosen to be consistent with a signal to noise ratio (SNR) greater than 1 (Payne et al. 2014), and this criteria has been used in all the papers that have presented TES PAN data thus far. We have added these sentences to the manuscript to clarify this choice. It is also worth noting that the shape of the retrieved profile is always heavily influenced by the shape of the a priori profile for these measurements (see response to next comment).*

P3 L128-129: The authors state TES has sensitivity to enhanced PBL PAN, but the concentrations are much lower than that of the aircraft?

*For nadir retrievals of molecules with weak spectral signatures where the DOFS < 1.0, the shape of the retrieved profile is heavily influenced by the shape of the prior. Since the prior profile for this case peaks in the mid-troposphere, the retrieved profile will also peak in the mid-troposphere. A large enhancement in boundary layer PAN shows up in the TES radiances as a small enhancement in the PAN signal. A small enhancement in the mid-troposphere would also show up in the TES radiances as a small enhancement in the PAN signal. The nature of the measurement is such that it is not possible to distinguish between these two scenarios in the TES radiances. An example is provided in Figure 2 in Payne et al. (2014). Therefore, although we demonstrate for this case that TES has some sensitivity to elevated PAN in the boundary layer, for the more general case where we do not have co-located in-situ profile measurements, we would only be able to say that there is some enhancement in PAN somewhere in the column.*

*We have added this discussion to the second to last paragraph of section 2.1. This now reads:*

*“The peak sensitivity for PAN is generally between 400 – 800 hPa (Payne et al., 2014), but a comparison between TES PAN transect observations coincident with Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) observations (Figure 2) show that TES can have some degree of sensitivity to PAN in the boundary layer when boundary layer PAN is elevated. As an example, Figure 3 presents in situ observations from a flight during FRAPPÉ made with a thermal dissociation chemical ionization mass*

spectrometer (TD-CIMS) (Zheng et al., 2011). Mean PAN observed by the C-130 below 3 km during the field campaign was 481 pptv (Zaragoza et al., 2017). This particular day (29 July) was one of the four days identified by Zaragoza et al. (2017) with the highest surface PAN mixing ratios observed at the Boulder Atmospheric Observatory. The overlaid TES data in Figure 3a (parallelograms) show an enhancement in the TES PAN (as shown by the TES observation highlighted by a black square) in the vicinity of aircraft measurements of highly elevated PAN values in the boundary layer indicating that in this case TES is weakly sensitive to the elevated boundary layer values despite the presence of high clouds (dashed line Figure 3c). Figure 3 also shows red and blue lines corresponding to application of the averaging kernel for this case to hypothetical “true” profiles with and without the enhancement in the boundary layer. The red and blue lines show that TES has some sensitivity to PAN below 800 hPa, but the retrieval places the additional PAN higher up in the atmosphere. While the difference between the red and the blue solid lines in Figure 3d is small, it is non-zero indicating that TES has some sensitivity to the boundary layer enhancement in this case.”

P3 L127-128: Add tropospheric column definition to the Figure 2 caption.

*This information was added. Figure 2 is now Figure 3.*

P4 L 153-154: Please explain “i.e. matching based only on UTC day” more clearly.

*Matching by UTC day is explained in the following sentences, but we added on additional one for clarification. This now reads: “We matched all TES PAN retrievals based on UTC day. This means that overnight retrievals are paired with the plume from the prior day. As discussed in Brey et al. (2017), most of the large wildfire plumes occurring in July over the western U.S. are very large and last several days. So we would expect that pairing the overnight retrievals with the plume from the prior day (i.e. matching based only on UTC day) is not likely to change our results, and that to be the case. We have repeated all our calculations using only the daytime retrievals, and the choice to use all the retrievals does not change the results.”*

P4 L178: Do the authors mean Supplementary Figure (SF) 2 not SF1? Also, why is the red axis (number of attempts) over the Pacific Ocean? This needs to be explained more clearly?

*Yes, we mean Supplementary Figure 2. This typo has been corrected. The second comment is also the product of a typo in the caption for Supplementary Figure 2. This sentence is supposed to point readers to a comparable figure in Zhu et al. (2017), but that reference is missing. Similar data for the Pacific Ocean is presented there for the same set of months. This has been fixed.*

P4 L180: Figure 3c instead of 3a?

*Yes, this should refer to 3c instead of 3a. This has been corrected.*

P7 L 259: Coloured dots? I can only see purple dots.

*Yes, this should say purple to be less confusing. This has been fixed by adding a more specific sentence.*

*“Figure 8 presents a histogram of PAN enhancement ratios in the subset of retrievals that overlap HMS smoke polygons and also are likely to have elevated PAN and CO in the free troposphere (TES CO > 150 hPa). The purple dots designate the two retrievals shown in Figure 7 that meet these strict criteria.”*

Figure 2b: Why is there such a large discrepancy between aircraft (blue) and TES (black) PAN?

*As discussed above, for nadir retrievals of molecules with weak spectral signatures where the DOFS < 1.0, the shape of the retrieved profile is heavily influenced by the shape of the prior. Since the prior profile for this case peaks in the mid-troposphere, the retrieved profile will also peak in the mid-troposphere. A large enhancement in boundary layer PAN shows up in the TES radiances as a small enhancement in the PAN*

signal. A small enhancement in the mid-troposphere would also show up in the TES radiances as a small enhancement in the PAN signal. The nature of the measurement is such that it is not possible to distinguish between these two scenarios in the TES radiances. An example is provided in Figure 2 in Payne et al. [2014]. Therefore, although we demonstrate for this case that TES has some sensitivity to elevated PAN in the boundary layer, for the more general case where we do not have co-located in-situ profile measurements, we would only be able to say that there is some enhancement in PAN somewhere in the column.

As discussed above, we have added more text to this section. We are not claiming good sensitivity to the boundary layer. This example provides the first direct evidence of any sensitivity to PAN in the boundary layer for TES.

Figure 2d: Worth adding equation in main text or caption how the AKs are applied.

*We have added substantial additional text and equations to Section 2.1 to address this comment.*

Figure 2d: The difference between the red and blue solid lines looks tiny, so how does this show TES has good sensitivity?

*We have not tried to claim “good” sensitivity. Rather this example shows that TES has some sensitivity. To make this clear, we have again added substantially more details to the latter part of Section 2.1, in particular, the updated paragraph now reads:*

*“The peak sensitivity for PAN is generally between 400 – 800 hPa (Payne et al., 2014), but a comparison between TES PAN transect observations coincident with Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) observations (Figure 2) show that TES can have some degree of sensitivity to PAN in the boundary layer when boundary layer PAN is elevated. As an example, Figure 3 presents in situ observations from a flight during FRAPPÉ made with a thermal dissociation chemical ionization mass spectrometer (TD-CIMS) (Zheng et al., 2011). Mean PAN observed by the C-130 below 3 km during the field campaign was 481 pptv (Zaragoza et al., 2017). This particular day (29 July) was one of the four days identified by Zaragoza et al. (2017) with the highest surface PAN mixing ratios observed at the Boulder Atmospheric Observatory. The overlaid TES data in Figure 3a (parallelograms) show an enhancement in the TES PAN (as shown by the TES observation highlighted by a black square) in the vicinity of aircraft measurements of highly elevated PAN values in the boundary layer indicating that in this case TES is weakly sensitive to the elevated boundary layer values despite the presence of high clouds (dashed line Figure 3c). Figure 3 also shows red and blue lines corresponding to application of the averaging kernel for this case to hypothetical “true” profiles with and without the enhancement in the boundary layer. The red and blue lines show that TES has some sensitivity to PAN below 800 hPa, but the retrieval places the additional PAN higher up in the atmosphere. While the difference between the red and the blue solid lines in Figure 3d is small, it is non-zero indicating that TES has some sensitivity to the boundary layer enhancement in this case.”*

Figure 6: Useful to add a CALIPSO track line to the top panel map. . . i.e. where did CALIPSO cross the domain?

*This was included in the figure already as a dashed line labeled “CALIPSO Overpass”.*

Figure 7: Where are the red lines/dots?

*We apologize for the labels on the original Figure 7. We changed the lines from red to black and color-coordinated the dots with the original Figure 6, and then it looks like only half of the caption for the original Figure 7 was updated. We have fixed this.*

Figure 8: State that the data is from ARCTAS.

*As suggested, we have changed the first sentence of the caption to also directly reference ARCTAS and not just Hecobian et al. (2011). This reads “Histogram of estimated PAN enhancement ratios based on in situ measurements of fire plumes described in Hecobian et al. (2011) from the ARCTAS campaign.”*

Figure S2: How do the authors define “elevated PAN”?

*We have removed this wording because it is confusing. TES has a high detection limit, and that is already stated in the methods. This word was not needed here.*

References:

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*All suggested references have been added.*