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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection" *by* E. V. Fischer et al.

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Response to Reviewer 2 Document

Title: Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection

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We thank all four anonymous reviewers for their thorough evaluation and constructive recommendations for improving this manuscript. Their comments and our responses are listed below. All authors listed on the manuscript concur with submission of the

manuscript in its revised form. We have uploaded a pdf version of this text with our responses in italics.

Anonymous Referee #2 General Comments: This paper presents 3 successive years of measurement of spring time PANs at Mountain Bachelor Observatory (MBO) using Gas-Chromatography with Electron Capture Detector (GC/ECD), and then lists a few factors that might have impacts on the year to year variations, finally discusses the requirements to detect a trend within the range predicted in a previous model run. The data is valuable, and it is scientifically important to sort out the possible causes of observed variation and determine the requirement for trend detection. This paper shows a good effort of doing so, though the analysis is still coarse. I think it is publishable if the authors use some work to make the discussion deeper. For example, besides saying the listed factors can have an impact and 2009's observation might be able to be explained, it will be better to estimate the size of the effects, even an order of magnitude estimation will help. It is argued that 2008 has more fires (by how much? And how much variation in PAN?), and in 2009 the long range transportation spent more time at cold region thus thermal dissociation was reduced (again, by how much?), so in 2009 still more PAN was observed, but there is no detailed analysis.

We have clarified many of these sections and added further details as specifically suggested by the other 3 reviewers. Without the use of a chemical transport model, which Reviewer 1 points out would be associated with substantial uncertainty, it is not possible to separate the relative impact of changes in emissions and transport on the observed interannual variability at MBO. The best we can do is point out factors that are consistent (or inconsistent) with the observations. However, there is still value in presenting these analyses because they provide important context for the data.

In fact, if the meteorology condition can suppress the "big" variation in the source (and how does this bio mass burning variation compare to the change in the anthropogenic inventory?), then the PAN trend story would be much more complicate and I believe it is.

We agree with the reviewer that the future PAN story will be very complicated due to the likely competing effects of changes to emissions and climate. We have changed the discussion to put the previously published GEOS-Chem chemical transport model results, used only as a general guide for our calculations, in a more limited role.

The ozone measurement is mentioned in the title and there are 3 paragraphs in the introduction talking about O3 concentration, but no O3 data is shown in the paper. It would be nice to be included.

O3 data is shown in Figure 5, and it is included in the calculations presented in Table 1. The emphasis here is on the PAN data because this is a new and unique dataset.

Some specific comments: P4114 Line24-25: the campaign mean does not have much meaning here, given that if C-130 had couple more flights to chase plumes, the upper limits would be larger than 240pptv. It is not clear what these lower and upper limits are going to tell us.

We agree with the reviewer. Various sampling strategies lead to variability in reported PAN mixing ratios, and this is a key point of this figure and the discussion of it. In response to this comment and a later comment by Reviewer 3 we have added further discussion of the differences in these datasets and we have modified the emphasis to focus on the lower relative standard deviation apparent in the 2008-2010 MBO data compared to the compilation of previous PAN observations in this region. We also added a discussion of the C-130 and DC-8 data following the reviewers comment.

P4115 Line18-22: Need some explanation on the inset map, why this region is chosen, is all the grid cell equally weighted in the fire counting? If so, is it a fair assumption?

In response to suggestions by Reviewer 3 and 4 to shorten the manuscript, we have removed this Figure and added some additional discussion and clarification of this section. See response to following comment.

P4116-P4115, section 4.1: How does the fire counts in figure 3 link with the observed

PAN variation? There are more fires in 2008, but lower average PAN mixing ratio?

We agree that too much is implied here, so we have added additional discussion to this section:

"Though the impact of the Russian fires is evident in several plumes of elevated PAN (Fischer et al., 2010), mean PAN mixing ratios at MBO during spring 2008 were lower than the following two years. Mean CO mixing ratios at MBO for 1 April – 20 May were 135, 133, and 159 ppbv for 2008, 2009, and 2010 respectively. Thus the extreme fire year in southeastern Russia also did not produce anomalously high mean springtime CO at MBO. This is in contrast to previous work showing a strong link between seasonal mean CO at MBO and anomalously strong biomass burning in Southeast Asia (Reidmiller et al., 2009b). Calculations presented later in the paper (Section 5) implicitly assume that the three years of PAN data from MBO represent the true variability in this species. The observation period at MBO did coincide with an extreme fire season in southeastern Russia. Unless relatively weak transpacific transport during spring 2008 acted to reduce the impact of these fires on western North America, the MBO PAN observations do not underestimate this driver of variability."

P4115 Line 2-3: Can not find MBO 2006 data in this paper.

The mean PAN mixing ratio presented by Wolfe et al., was 340 ppbv. This value is higher than the upper limit of the vertical scale used in Figure 2 and we have added an additional sentence to Figure 2 to make that clear.

As discussed above in response to Reviewer 1, a motivation for our analysis is to determine whether a trend in PAN due to rising Asian NOx emissions would be detected sooner than a trend in O3. In Section 5, we use observations of both species, to show that PAN is more variable than O3, so a larger trend in PAN could take longer to detect. PAN measurements are more challenging and laborious than O3 measurements, so unless a trend could be detected in that species more quickly, it may not be a good use of community resources to target PAN over O3 from a trend-detection perspective.

Adding the Wolfe et al. data to the analysis presented in Section 5 would only further the variability in PAN, so it would not change the conclusions of this analysis.

P4116 Line 3-6: Again the southeast Asian impact is mentioned but no real analysis.

This sentence cites a previous study. Note that this section has been substantially edited in response to other comments.

P4116 Line20-25: Authors firstly say "with such a small number of points the correlation coefficient is not significantly different from zero. " Then they make assertion that 2010's transportation is stronger than 2008 and 2009. Though the exact numbers are not given here, it still makes readers wonder how reliable the conclusion is.

We have added a more detailed discussion including the exact index values. We keep the LRT3 discussion because Reviewer 3 recommends using a climate index. However, we have added an additional sentence explaining that LRT3 was constructed using meteorological indices and output from a global chemical transport model. It is interesting that LRT3 is not a good predictor for CO at MBO. This is not expected, and should probably be investigated further. We do not have anything regarding LRT3 in the conclusions. We only discuss variations in transport temperature/altitude during spring 2009, because this is the only factor we can identify that is consistent with the higher PAN mixing ratios observed during this season.

P4117 Line8-14: What kind of message should we take from this paragraph? So the trajectory study says MBO is under the influence of different air between 2009 and 2010, what does that mean to the PAN observation?

We added the following sentence:

"Unlike the previous years, the highest observed PAN mixing ratio (543 pptv hourly average on 11 April) during spring 2010 was associated with transport from the U.S. boundary layer."

Reviewer 4 also asked for an additional sentence of interpretation in this paragraph.

We added the following in response to Reviewer 4's comments:

"Though the horizontal transport fields in Figure 3 appear to be fairly similar in spring 2008 and 2009, the mean PAN observed at MBO was different between these two years. In the following section we show that differences in temperature, rather than transport direction, are consistent with observed difference in PAN mixing ratios between 2008 and 2009."

P4119 Line25-27: How much is the spring time variation of isoprene emission? For all the variability and even trend discussion, without some estimation, it is just hard to make sense out of it.

There is not an adequate reference to answer this question. Papers that focus in interannual variability in isoprene (e.g. Palmer et al., JGR 2006) focus on May to September because this is when emissions are greatest. Palmer et al., (JGR 2006), which focuses on the United States rather than Asia or Europe, do not give a specific number for the month of May, but state that isoprene emissions vary by 27% percent for the month of June. We have added an additional reference to this section, and updated the Fiore et al., 2010 reference.

P4120 Line24-P4121 Line5: does Zhang's calculation include the variation in bio mass burning? If not, how would variation in the fires mentioned in section 4.1 impact the trend of PAN?

No, there was no change in biomass burning emissions in the Zhang calculation (Lin Zhang personal communication). Only Asian anthropogenic emissions were changed, and we have added this information to this section. We expect that natural sources of variability, such as biomass burning emissions, will impact PAN at MBO. This is one reason that we have presented a range of possible trends in PAN in Table 1. Warming in northern latitudes might cause an increasing trend in area burnt in Siberia and could lengthen or intensify the fire season (see Kasischke et al., Global Biogeochem Cycles 2005). This would certainly produce more PAN. However, warmer temperatures would also shorten the lifetime of PAN. Thus it is unclear how a climate-driven long term changes in fire emissions in this area would change PAN. There is a very new reference, published in March 2011, which estimates the interannual variability of fire activity in Russia for the period 2000 – 2008. (Vivchar, 2011). We have added this reference to Section 4.1. We have also pointed readers to the detailed discussion of emissions for 2000 and 2006 that is presented by Zhang et al., (2008).

P4121 Line 6: a reference for this assertion?

We changed this sentence in Response to Reviewer 1: Zhang et al., (2008) presents a very detailed discussion of the constraints on both the 2000 and 2006 Streets inventories. We have changed this sentence to point readers to the discussion in Zhang et al. The emissions used in global chemical transport models are highly uncertain. Our goal here is to highlight the uncertainties.

P4125 Line 25: "By incorporating the multi-year dataset, we include both synoptic scale and interannual variability in the calculation" : : : need more explanation here. I think this re-sampling is the core part that the authors acclaim the usage of the real data to determine the requirement for 4% trend detection. A single sentence like this is not very convincing, please list references.

This sentence was changed to: "By sampling average PAN from the multi-year MBO dataset, we are able to include both synoptic scale and interannual variability in the calculation. By incorporating the actual variability, regardless of whether we fully understand all the drivers, we can develop a reasonable expectation of when a trend may be detected (Weatherhead et al., 2002). "

Fig. 2 In Intex-B C130 and DC8 were sampling different air for most of the time; In fact, these two points can be any number depends on the flight plan, it is just confusing to put these points in the same figure without further filtering.

We agree with the reviewer. This is a key point of this figure so we have chosen not

to filter the data. Various sampling strategies lead to variability in reported PAN mixing ratios. However, we have added further discussion of the differences in these datasets and this section now emphasizes the lower RSD in the 2008-2010 MBO data compared to a aggregate of all available data.

Fig. 4 log10(hours) is hard to understand, my guess it means "occurrence of trajectory went through the gird cell (in log scale)"

We agree this scale is confusing and in Response to a comment by Reviewer 1, we added an additional paragraph explaining how this figure was created. We also changed the legend to make it easier to understand.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C3046/2011/acpd-11-C3046-2011-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4105, 2011.