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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.

Anonymous Referee #1

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General Comments

This paper describes multi-year measurements of PAN at Mount Bachelor Observatory a high altitude site in the NW U.S. These data are of interest and form a potentially useful addition to the literature. The paper has numerous problems, which are serious enough that it is not publishable without significant modifications. The authors seem to REALLY want to be the first to detect an increasing trend in PAN, and they have decided it will be 4%. So narrow is their focus that they leave out another data set from MBO taken in 2006 [Wolfe et al., 2007] (curiously since the senior author is a co-author on that paper), and do not mention the work of Parrish et al., [2004] who discuss a

trend in Eastern Pacific PAN measurements (again curious since the senior author is a co-author on that work as well). Paradoxically, they include a mention of the results of Murphy et al., from the foothills of the Sierra Nevada, which incorporated influences from California urban areas, and in any case, will have different transport patterns than MBO. The connection between PAN, and O3 formation is emphasized several places and the possible Asian influence on both was discussed. Why not include O3 in this analysis? The relationship between PAN and O3 is quite complex and may have several features that could result in something other than the simple expected increases that the authors seem to want to focus on. The authors' note that PAN decomposition to NO2 and subsequent NOx-drive chemistry can produce O3 in transported plumes. So one could imagine a scenario in which higher Asian NOx sources coupled with a warmer troposphere, or lower altitude transport, over the next decade compared to previous years, could result in a larger positive O3 trend and a negative PAN trend. As has been noted (and will be repeated below) vertical transport is a particular weak point of global models, and GEOS-CHEM is no exception. I think we should prefer to let the atmosphere show us what it is doing and then hope to see if we can capture that with numerical models. With that said, it is useful to see if a trend has been detected and to assess what kind of time-scale would be needed to observe a given trend. I would like to see the paper recast to reflect that the measurements come first, and modeled results should be treated with some skepticism for the afore-mentioned reasons.

Specific Comments

The abstract is too long and contains too much detail.

Pg 4108, line 23, PAN is formed from many VOC precursors, not just acetaldehyde +OH. Indeed, the isoprene => PAN mechanism goes through intermediates such as methylglyoxal.

Pg 4109 line 18 The authors are saying increases in PAN and O3 with are expected because of increasing Asian NOx. Elsewhere they say that PAN decomposition produces

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Interactive Comment

O3. Aren't these statements contradictory? See above general point.

The authors did not mention the work of Parrish et al., 2004, which is puzzling since the senior author on this paper is also on that paper.

The first consistent multi-year measurements – why did Wolfe et al., measurements from MBO during 2006 get left out of this? They included the same time period.

4110 – Lines 3-4, these statements are either not true, or are at best misleading.

4111 – Uncertainties seem low. The overall uncertainty should be reported differently. Clearly the overall uncertainty in a measurement that is close to detection limit is larger than 8.2%. The authors did not measure the PAN efficiency of their photo-source, but instead use a literature value, what is the uncertainty in that? How would one even put a number on that?

4113 – Line 10 Is this 3-4 days periodicity apparent in the autocorrelation spectrum? Line 16 What is an "event-like" structure? Line 20 You don't mention what the 1-20 May 2008 average was. Line 23 06:00pm should be 6:00pm

4114 – Wolfe et al. measurements were AT MBO, and spanned the time of year being analyzed in this paper, why is that data not included in this analysis?

4116 – Line 24 I don't understand what this sentence means. Do you mean that both 2008 and 2009 had weaker transpacific transport than all the years shown in Fig. 2, except for 2002? The sentence is ambiguous as written.

4117 – Lines 8-10 This is really unclear, when the author say "the number of hourly trajectory points within a given radius of the latitude and longitude points." What lat and long points are they referring to? The MBO coordinates? Or have they summed all the trajectory points within a given radius of each lat and long in the hemisphere? (which seems more likely) Line 11-14 I see the difference in Northerly origin, I don't see the SW aspect. Looking at the color scale, which is in thousands of hours, I realize, I don't have any idea what Figure 4 is showing, how did the authors get a number in hours?

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Is that hours in back-trajectory time, or number of hours out of all the trajectory times? In which case what are the total number of hours?

Lines 15- 21 How can a paper published in 1996 confirm differences in years 2008-2010? If the author mean that the re-analysis method described in the 1996 publication was used, then say that, and describe where the data came from.

4118- Lines 5- 9 I give up. I have no idea what the authors are talking about. What do 22 spatial degrees of freedom mean and how can that be used to derive the confidence limits? Please show your work.

4120 – Lines 1-9 This argument is just plain wrong. The variability in the amount of vertical transport out of East Asia has a huge effect on the amount of PAN that can reach the Eastern Pacific and therefore MBO. This has been shown by previous aircraft studies both in the Eastern Pacific (Nowak et al., 2004, Roberts et al., 2004) and along the continental margin of East Asia (Russo, et al., 2003). It should also be noted that it is precisely this stochastic vertical transport that models, and GEOS-CHEM is no exception, have the hardest time simulating. Assuming that transport is constant is precisely that kind of bias that leads one to believe a modeled result rather to look objectively at the ambient data to see what it actually is.

4121 - Line 6 Do the authors have any evidence to back up the statement 'The Streets et al. (2003) emissions inventory for 2000 underestimated NOx emissions'? Lines 20-21 The auto-correlation numbers presented here mean nothing to me, what would be considered significant? Lines 24-29 There is something wrong here, how does randomly sampling points from the 3 years give a trend with time. It looks like the authors have skipped a step in their explanation, wherein they describe that they mixed in a 4%/year increasing trend. How was this done?

4123- Lines 22-24 The statement 'There are even fewer observations of PAN, though a trend in this species is expected to be larger and would be significantly easier to attribute.' seems counter to the conclusion given just above that both O3 and PAN

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trends would require about the same time to detect, because PAN is more variable than O3.

Figure 4. It is completely unclear how this figure was generated, and what the unit 'hours' refers to.

Figure 5. The labels are different between the middle and bottom panels, but caption says they are the same. One is 'amgl' the other says 'amsl'. What do those mean?

References;

Parrish, D.D., et al,. Changes in the photochemical environment of the temperate North Pacific troposphere in response to increasing Asian emissions, J. Geophys. Res., 109, 10.1029/2003JD004978, 2004.

Russo, et al., Chemical composition of Asian continental outflow over the western Pacific: Results from Transport and Chemical Evolution of the Pacific (TRACE-P), J. Geophys. Res., 108, 8804, doi:10.1029/2002JD003184., 2003.

Wolfe, et al., Influence of trans-Pacific pollution transport on acyl peroxy nitrate abundances and speciation at Mount Bachelor Observatory during INTEX-B, Atmos. Chem. Phys., 7, 5309-5325, 2007

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