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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 4 Document

Title: Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection Date: May 9, 2011

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 as a supplement.

Anonymous Referee #4 Review of "Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection, by Fischer, Jaffe, and Weatherhead The authors report springtime PAN measurements from 3 consecutive years made at an elevated ground site in Oregon (MBO) and attempt to relate PAN and its variability to (a) Russian fires, (b) transport and its variability, (c) vertical transport and its variability. The arguments are all quite plausible and common-sensical, but really not overwhelmingly convincing from a quantitative point of view. The data are valuable and merit publication. I suggest minimizing much of the discussion unless a more rigorous attempt is made at quantitative analysis. For example, how is the variability in Russian fires, plotted in Fig.3, related to PAN at MBO? I see little in the way of quantitative argument for this connection. Why is this figure in the paper? Perhaps this can be removed, and the paper can more purely focus on the data itself as part of long-term record that will become much more valuable if it can be continued for a decade more. Also, the connections with transport are not thoroughly demonstrated. Overall I find the data to be extremely valuable but the analysis of variability rather cursory. I recommend publication with either (1) a significant reduction in length, or (2) a more rigorous and thorough analysis of PAN variability and its causes.

We agree with that Section 5 is the most important and most rigorous portion of this paper. We did consider submitting a manuscript to a short-format journal such as GRL. However, as all reviewers have pointed out, this data is rare, valuable and likely to be used by others. For this reason, we decided to publish our analysis of the potential causes of variability. This will provide future users with a basic overview of the year-to-year variability in parameters that could have impacted the observed PAN mixing ratios. We have chosen to shorten certain sections, increase clarity where requested by a reviewer, and frame the discussion of fires, temperature and transport as contextual information. In response to the specific mention of Figure 3, this Figure was removed but the discussion was strengthened.

Specific comments: p.4109, line 3: "The lifetime of PAN" – need to clarify which lifetime this is. I think it's merely dissociative lifetime. As made clear later, this is not "real" lifetime, as dissociation is reversible.

We added the word "dissociative" here to clarify.

p.4111, line 14: Seems an unsafe assumption to assume 93% conversion to PAN as this can depend on intensity of light source, and this can vary from lamp to lamp, and with lamp age, and with lamp operating temperature.

As discussed above in response to Reviewer 1, there are several points to note here.

Briefly, in February 2008 we sampled the calibrator outflow using a two-channel chemiluminescence NOx instrument (see Reidmiller et al., ACP 2009 for a description of the NOx instrument.) This instrument has 5-minute NO and NO2 detection limits of 4 and 10 pptv respectively. There was no detectable NOx in the calibrator outflow.

A new Jelight Hg Pen-lamp (285 nm) was purchased and installed in the calibrator prior to spring 2010. Keeping all other settings identical, the PAN produced using the two lamps was injected into the GC. There was no significant change in the size of the PAN peak. This indicates that there was not likely to have been a change in the efficiency of the photo-source over time. Thus we have confidence in the relative differences in PAN from sample-to-sample.

One final point here, our lamp is cooled with a fan.

p.4111, line 18: Calibrations only every two weeks seems too infrequent. However, if cals shows stability, then may be fine. Is this dominant contributor to the quoted uncertainty?

The short story is that the calibrations are remarkably stable. The Shimadzu Mini-2 is a great ECD detector. Here are the details: Prior to the initial deployment in spring 2008 (2/12/2008 – 2/18/2008), the stability of the system was tested. We did calibrations every hour for 12 hours, then we did 2 calibrations a day for 4 days, then we did another calibration a week later. The standard deviation was within the expected

precision of the calibrator. Calibrations were done more frequently during the first deployment of the instrument in spring 2008. During this season, one-point calibrations were done weekly and multi-point calibrations were done biweekly. The room at MBO is temperature controlled to 20C, the instrument is also controlled to 20C, and the ECD is controlled to 40C. Thus the detector is not exposed to rapid temperature or pressure fluctuations. We switched to bi-weekly multipoint calibrations in spring 2009 once we had confidence in the system.

Here is a side note for those contemplating PAN measurements. Before switching to the Shimazdu Mini-2 ECD, we tested the Valco PD-ECD (Model D2). The PD-ECD was not used in the final version of the instrument because the PAN sensitivities changed significantly over short time periods. This was not the case with the Shimadzu Mini-2. We would not recommend a Valco PD-ECD for long-term PAN measurements. The main advantage of this new ECD is that it is not radioactive; however, it is very unstable.

p.4114, line 14: The value of aircraft measurements is modestly marginalized with the comment that aircraft sampling is not random. What measurements are? Making measurements as single ground site does not provide a random sample of the atmosphere.

We did not intend to marginalize the aircraft measurements! These types of observations are critical to understanding the evolution of individual plumes, something that is note easily done using only data from a surface site like MBO. We have changed the wording here slightly to improve the tone. However, we think that "random" is the right word here. We considered "reproducible," but no environmental measurement is reproducible.

p.4115, line 3: INTEX-B/C. Was there an INTEX-C?

Thanks for noting this typo.

p.4115, line 19: I don't understand "average number of fires in each grid cell in the region". Assuming there are a number of cells in the region, there should be multiple averages at each point in time, one for each grid cell. I'm missing something.

This plot was removed in response to comments by other reviewers to shorten the paper. The discussion was strengthened.

p.4115-6: It is plausible that fires are connected to PAN variability at MBO, but I don't see a connection made in section 4.1.

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

"Though the impact of the 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. 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 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. 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. "

pp.4116: In reading section 4.2 I'm puzzled by the fact that the point is being made that 2008 and 2009 had weak long-range transport from Asia, while 2010 had strong transport. In my mind I contrast this with the mean data if Fig. 1 which show high PAN in 2009 and 2010, and low PAN in 2008. Why is PAN high in 2009 when transport is weak? However, the authors do not explicitly address this unexpected result. This reader was left wanting some discussion of this point.

See response to next comment.

P.4118: I now see my quandary (just above) is addressed. Would have useful to acknowledge it in section where first arose.

As suggested, we have acknowledged the unexpected result in Section 4.2 by adding the following sentences to the end of this section.

"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. "

p.4118, line 15: I doubt that mean temperature is really a good measure of PAN loss. Two means could be the same, but one path might see greater extremes (high and low) and so could experience far greater PAN dissociation. Using the mean is a crude simplification.

We do agree this is crude, but it is not obvious how to improve it. We have added qualifying statements to ensure this is not misleading to readers.

p.4118, line 19: What is being called a "correction"? If it's the use of NO/NO2 ratio in calculating PAN lifetime, I would not call that a correction. Rather it is simply the proper way to calculate the meaningful lifetime.

We agree with the reviewer. Using the NO/NO2 ratio in calculating PAN lifetime is essential because of recycling and it is the proper way to do this. We have changed the word "correction" to "adjustment." (We note that the "correction" terminology is what is commonly used in textbooks (see Brasseur, Atmospheric Chemistry and Global Change).)

p.4120, line 7: The authors rely on a published quote to argue for lack of variability in transport out of Asia: "pool of Asian pollution in the western Pacific" is constantly replenished. But is it replenished to the same degree? Is it the the claim that there is not, say, factor-of-2 variability in the the replenishment, thereby leading to significant variability in PAN seen at MBO? This seems a very weak and non-quantitative argument – more just a plausibility argument.

We have changed this section in response to similar comment made by Reviewer 1.

p.4134, fig.1: Can barely see the x's or the small squares in my printed copy.

Thanks for noting that. We have more than doubled the size of the x's and the squares in the revised version.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C3058/2011/acpd-11-C3058-2011-supplement.pdf

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