

## ***Interactive comment on* “Influence of trans-Pacific pollution transport on acyl peroxy nitrate abundances and speciation at Mount Bachelor Observatory during INTEX-B” by G. M. Wolfe et al.**

### **Anonymous Referee #1**

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Review of the manuscript “Influence of trans-Pacific pollution transport on acyl peroxy nitrate abundance and speciation at Mt. Bachelor Observatory during INTEX-B” by G. M. Wolfe, J. A. Thornton, V. F. McNeill, D. A. Jaffe, D. Reidmiller, D. Chand, J. Smith, P. Swartzenruber, F. Flocke, and W. Zheng.

### General Comments:

This paper describes speciated measurements of peroxyacyl nitrates (PANs) from the Mount Bachelor Observatory (MBO) in the spring of 2006. The PANs were using a thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique. The observations are examined in terms of speciated PAN levels, contribution from the

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free troposphere and boundary layer, and compared to previous measurements in the region. An analysis of back trajectories from the HYSPLIT model is used to estimate the impact of Asian pollution at MBO.

The results presented here are appropriate for the scope of ACP. The title and abstract reflect the contents of the paper. The paper is clearly written. It is fairly well structured though the Results and Analysis sections could be combined into one Observations and Analysis section, since much of the discussion in section 3 is really analysis not a summary of observations. This paper attempts to build on a previous one, Weiss-Penzias et al. (2006), by introducing a new dataset of PANs observations. This is a suitable paper for publication with some revisions discussed below.

Specific Comments:

Introduction: The introduction a good job of supplying background and introducing the importance of PANs as NO<sub>x</sub> reservoirs, describing the thermal properties that allow PAN species to be transported, and citing previous work in this area.

Methods: Though the site is described in detail elsewhere, a map of the region and location of the MBO sampling station would be appropriate. Not many readers, especially European based, will be familiar with the Route 97 corridor. I think a map including MBO and the East Asian box source region described in section 2.4 would be very useful to the reader.

The references seem to indicate this is the first publication of data collected with this instrument. Therefore, an instrument schematic including orifice sizes and sampling inlet with calibration port and zeroing area would be appropriate, possibly as supplemental material, for comparison to the similar techniques cited.

I am concerned with the variability, approximately 50%, in sensitivity reported over the measurement period. What was the time scale of the variation? For example, interpolating between the sensitivity at calibration time A, 0.8 Hz pptv-1, and the sensitivity

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at calibration time B, 1.6 Hz pptv-1, 90 minutes later, both within the stated variability of the average sensitivity during the measurement period, introduces more uncertainty for that data then stated at the end of the section. Was the sensitivity a function of ambient water vapor? Equation (2) shows that I- is clustering with water and the cluster is reacting with the peroxy radicals. Since it is not mentioned that the ion-molecule reaction region was humidified, I suspect that some, if not most, of the variability in sensitivity comes from changes in the I-(H<sub>2</sub>O)<sub>n</sub> cluster size due to ambient water changes. Air mass changes can change the ambient water vapor on time scales faster than 45 minutes, the minimum calibration interval stated for this study.

I think the authors do a nice job of pointing out that the detection limit is a combination of counting statistics and the deviation between adjacent background measurements. Too often CIMS instruments ignore this fact and average data over longer time intervals to report unrealistic detection limits that are not supported by a closer examination of the data.

Results: The discussion in 3.1 refers greatly to Figure 2. However, Figure 2 is not very informative. By showing the data from the whole measurement period in hourly averages in one plot the x-axis is so compressed that it is difficult to differentiate between days and follow the discussion in the text. For example, it is difficult to see the correlation in PAN and ozone during the events on day 128 and 132, as discussed in the text. If an event is significant enough to be mentioned in the text, it should be easily discerned in the figure. Since CO is used as a tracer for long range transport in many of the previous works cited, why is it not included in Figure 2?

Page 9149 line 14 What is the criteria used to determine if an episodic increase in PAN is or is not associated with LRT from Asia?

Page 9152 line 13 ‘Such enhancements suggest a local but unidentified anthropogenic combustion or biomass burning source’ I don’t see that the CO and particle scattering data lead to this conclusion. LRT plumes with CO levels over 200 pbbv have been

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previously reported. Is it solely based on the APN levels? If so the levels should be mentioned and compared to the previous work to support the statement. What does the other data say about local vs distant sources for these plumes (Days 124 and 126), such as the PPN/PAN and CO/NO<sub>y</sub> ratios?

For section 3.3, what does the O<sub>3</sub>-CO relationship look like? Do the data from day 112 have the characteristic negative slope observed with stratospheric air?

There are three general weaknesses to this section. 1) Data from all the instruments listed in section 2.1 is not used to in interpreting the PAN observations. 2) None of the episodic events, in particular Day 132, are examined in detail. In fact, page 9150 lines 21-22 states a more detailed analysis of these events is beyond the scope of the study. However, it is the episodic events that bring high enough levels of the precursors to push O<sub>3</sub> levels over the EPA standards. If the episodic events are to be ignored then whatever metric is used to separate them from the continual mixing of pollutants into the background air needs to be clearly stated. 3) A big selling point of this TD-CIMS instrument is providing speciation information. Yet, nothing presented here suggests that speciated measurements are necessary at this site.

Analysis and Discussion: Page 9157 line 7, here I feel that a detailed instrument schematic would provide enough details about the instrument could strengthen this argument. As presented the instrument is a too much of a black box to the reader and that introduces doubt.

Page 9158 line 22-25: What types of petrochemical sources are in the region?

The color bar on Figure 7a I think is confusing because it indicates 0 hours is the dark purple when in fact 0 hours is white. I realize the picture caption states white is equivalent to 0 hours but that is the 3rd sentence. I suggest change the lower limit of the label to something like 0.1 hrs and add in parentheses next to Hours in Asian Box (white = 0 hrs).

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The discussion on page 9160 could be strengthened in a couple of ways. One is to add a third panel to plotting PAN and/or PPN to Figure 7. Though this duplicates a bit of Figure 2 it is much easier to see when the pollution events are captured by the ALERT index and when they are not. The second way is to include a trajectory map or a plot of trajectory altitude or temperature versus time back in the trajectory to show emphasize the point made on page 9160 line 24.

Minor Comments:

Page 9140 line 25: NO<sub>x</sub>, SO<sub>2</sub>, and CO are not written in words before the chemical formula is used, though this is done for HNO<sub>3</sub> (page 9141 line 7).

Page 9149 line 6: Since day of year and not date is used throughout, it seems more logical to put the dates in parentheses.

Page 9150 line 24: PAN and PPN by 7% and 17 %

Figure 3: Day 124 is plotted as an x not a cross. I realize the units for MPAN are going to be a lower limit but I think the MPAN y-axis should be labeled as such nonetheless.

Other figures as discussed above.

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