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Atmospheric Chemistry and Physics Discussions

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.

G. M. Wolfe et al.

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Response to Comments by Anonymous Referee #1

We thank the reviewer for taking the time and effort to provide a critical analysis of our manuscript. The reviewer's constructive comments have prompted a number of revisions to our manuscript that will make it more valuable and accessible to the greater scientific community. Responses to these comments are detailed below, denoted by a number and '**'. Note that only portions of Referee comments are included here, for the full set of comments please see those on the ACPD website.

General Comments: "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."

**1. As per the referee's suggestion, sections 3 and 4 have been combined into a single Observations and Analysis Section.

Specific Comments: 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."

**2. Maps of the Pacific Northwest and the "Asian Box" have been included as Supplemental Material.

"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."

**3. An instrument schematic has been added as part of Fig. 1.

"I am concerned with the variability, approximately 50%, in sensitivity reported over the measurement period. What was the time scale of the variation? Ĕ Was the sensitivity a function of ambient water vapor?"

**4. The median percent difference between adjacent sensitivities was 4.5% while the mean was 10%. The 50% variability was the standard deviation of all sensitivity measurements obtained over the entire campaign (not the point-to-point variation). We thank the reviewer for raising this issue and we have added a clarifying statement to the revised manuscript. On the short-term, the calibration factor is a function of variations in room temperature, ambient water vapor, and on the longer-term, it is a function of the loss of signal gain in our electron multiplier over the course of the campaign. As the referee points out and as has been shown previously by Slusher et al. (2004)

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(see reference in manuscript), the CIMS sensitivity is non-linearly dependent on water vapor. At MBO the water vapor content is largely controlled by the diurnal cycle of upslope and downslope flows. A comparison of PAN calibrations and water vapor data reveals that we were calibrating frequently enough to account for variations in water vapor. We have added a brief statement to this effect in the revised manuscript.

"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?"

**5. In regards to Figure 2, the referee raises a valid point. Grey highlighting has been added to Figure 2 for all events discussed in the text, and we have limited our discussion in this regard to a few high PAN events. Figure 2 and Figure 4 are also a bit more consistent in the events highlighted so that correlations can be discerned from either figure.

**6. We have included a time series of CO at the bottom of Fig. 2. We noted in the submitted manuscript that the 2006 CO measurements at MBO are significantly lower and less variable on average than previous years. While the causes for this year-to-year variation are still being considered, we agree with the reviewer that it makes sense to have CO 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?"

**7. As discussed later in the text, a measurement is assumed to be associated with Asian LRT if the ALRT index for that measurement is greater than 0, where the ALRT

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index is derived from ensemble HYSPLIT back trajectories. We agree that this specific sentence the reviewer points out is unclear, as our analysis is on the "bulk" data and we never discuss a more specific selection criterion for individual events; as such, the sentence has been removed.

"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 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/NOy ratios?"

**8. We have broadened our interpretation of this event in the text. The assertion that this could be a local event was based on 1) unique enhancements APAN and PiBN/PnBN, which are thought to have limited precursors (primarily 1,3-butadiene) and short lifetimes (the unsaturated bond in APAN is susceptible to O3 and OH), and 2) high particle scattering indicated that significant scavenging had not occurred in this plume. This event may also be a case of very rapid LRT, but there is inadequate data to test this assumption (e.g, NOy is unavailable and trajectories are inconclusive). As such we have qualified our original statement to include other possibilities. To better demonstrate the unique characteristics of events highlighted in the text, we have also added plots of CO vs O3 and aerosol scattering vs PAN in Fig. 4.

"For section 3.3, what does the O3-CO relationship look like? Do the data from day 112 have the characteristic negative slope observed with stratospheric air?"

**9. As mentioned in the text of this section, the CO measurements do not conclusively indicate whether the ozone enhancement of this event is due to a stratospheric intrusion or pollution, as CO is relatively flat during the strong increase of O3. While negative CO-O3 correlations are typically observed for relatively fresh stratospheric in-

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trusions, this correlation would likely degrade as the stratospheric air mass is mixed into the tropospheric background. Substantial mixing is likely to have occurred by the time such an air mass reaches MBO at 2.7 km. The absence of an increase in PAN, scatter, or Hg would seem to indicate that photochemical pollution did not play a role. Nevertheless, the referee raises a valid question, and we have included a plot of O3 vs. CO in Figure 4 to allow better interpretation.

"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 O3 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."

**10. Issue 1: We do use all of the measurements listed in section 2.1, to varying degrees, to guide our conclusions regarding the APNs measurements. The use of particle scattering was mentioned in the text and is now also expanded to be included in Fig. 4, and the Hg-CO enhancement ratio is used to help validate our trajectory analysis (P. 9161, L9-22). NOx and NOy measurements are not heavily used mainly because they are either sparse in the case of NOx, or unreliable due to drifting calibrations/zeros in the case of NOy, and so we have removed reference to them.

**11. Issue 2: While we do highlight individual events in the text, it is not our intention to focus on specific events for this manuscript but rather to 1) demonstrate the degree to which the average springtime composition is influenced by such episodic behavior and 2) to identify the main contributors to those APN episodes through a trajectory analysis. We certainly agree with the reviewer that the particular chemistry of spe-

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cific events is an important aspect of this data deserving further exploration. It is our opinion that such an event-based analysis is a separate endeavor to be done primarily in conjunction with models, given that a detailed observational analysis of individual transport events, in the context of our APN measurements, is limited by the paucity of supporting measurements (e.g. NOx, NOy and VOCs). For the revised manuscript we have limited the analysis to fewer individual events but expanded the relevant data presented for those events.

**12. Issue 3: Granted, at a remote location such as MBO, PAN and PPN are going to be the dominant APNs and thus the speciation ability of the TD-CIMS will not add significant information to the NOy budget. However, even though the other APNs were typically of low abundance we feel their measurements greatly added to our ability to characterize the air masses reaching MBO. In fact, the APN/PAN ratios shown Figures 5 and 6 provide important support to our conclusions regarding the differences between mixed-boundary layer and free tropospheric air (and indirectly air mass age) and the apparent anthropogenic contribution to ozone.

"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."

**13. Agreed. See response 3 above.

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

**14. MBO is not too far from an interstate highway and several towns; there is also a municipal airport in Redmond, to the NE of the site (see introduction). Thus, we believe the primary petrochemical sources are traffic related. It is conceivable that domestic fuel use (e.g. propane) is widespread, as much of the surrounding area is rural. Most major power plants operate with natural gas and are downwind or not within the typical flow intercepted at MBO. The closest major urban area likely to be upwind of

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MBO is Salem, OR. We have added a bit more information in this regard to the revised manuscript.

"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)."

**15. We agree. Figure 7 has been altered accordingly.

"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 ALRT 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."

**16. Two excellent suggestions. We have added PAN to Figure 7(b), and we have provided a new Figure (Fig. 8) that displays trajectories for several different transport events.

Responses to Minor Comments: 17. P9140,L25: We have added the full chemical names for NOx, SO2 and CO.

18. P9149,L6: Agreed; the dates are now in parentheses.

19. P9150,L24: The 7% and 17% are changes in the mean and standard deviation for PAN; changes in PPN after removing this event are not mentioned but are smaller than those for PAN.

20. The Fig. 3 caption has been changed to “x’s.” Units have been added to the MPAN axis.

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