

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 Referee #2

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 and denoted by ‘***’. 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: “I note that is listed as part of a special issue dealing with the MILAGRO project; I presume that is in error, it is intended to be part of an issue dealing

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with INTEX-B?”

**1. We have been informed that this issue will be expanded to include INTEX-B (indeed other INTEX-B related papers have since been submitted to this issue).

“The TD-CIMS technique has some advantages over the more established method of GC/ECD including the fact that it enables a better speciation of APNs, but the paper does not go very far in making use of this added value. Almost all interpretation is limited to PAN and PPN data that could be obtained by the much simpler GC/ECD method. A missed opportunity, or is chemical modeling exercise envisaged (which might be mentioned)?”

**2. While more attention is paid to PPN and PAN than to the remaining APNs, primarily due to their higher abundance, we do make great use of the MPAN, APAN and PiBN/PnBN measurements. Figures 5 and 6 detail the use of such measurements for characterizing the different types of air masses impacting MBO, particularly the difference between mixed-boundary layer and free tropospheric air, and the relative degree of anthropogenic influence (see also our response to Referee 1). Unfortunately, further interpretation of the less-abundant APNs is somewhat limited by a lack of VOC precursor measurements, but we do envisage a future modeling study of broader questions regarding whether models would predict the levels of MPAN and PiBn/PnBN observed given that what we report are believed to be lower limits.

“The distribution of the PAN data is clearly skewed by a couple of ill defined episodes (a discussion of which is deemed outside the scope of the paper). The authors should use either the median or the geometric mean throughout the paper (starting with Table 2).”

**3. The referee raises a valid point, and indeed we are aware that the APN species are log-normally distributed. We primarily rely on the median values, particularly in our trajectory analysis; we also provide median values when comparing our results to other campaigns (Table 3). A note about the skewed nature of our data has been added in

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the text when Table 2 is introduced. We also note that although APNs are log-normally distributed, APN/PAN ratios are normally distributed.

Minor Comments: P9140/L13 “highest levels” gives wrong impression because it is influenced by those ill defined episodes. Say “FT levels of ≈ 1.5 are in general substantially higher than BL levels”

**4. P9140/L13: This sentence has been modified accordingly.

"P9142/L1 the sentence here could be interpreted as stating that the non-attainment of US EPA standards is due only to this Asian pollution. This is of course not true, it results from a combination of enhanced background levels (where the enhancement is possibly due to all sorts of hemispheric impacts, including Asian pollution), and local US pollution sources. Given political sensitivities the text should be modified."

**5. P9142/L1: Agreed. We have modified the sentence to reflect the multiple causes of local O₃ non-attainment episodes.

"P9142/L23 transport of NO_x"

**6. P9142/L23: Fixed.

"P9144/L17 Hg and scattering data are not used for analysis of the APN data, and their mentioning should be deleted (see also below)"

**7. P9144/L17: Although we do not use scattering to characterize the average spring-time behavior, we do utilize it to characterize some of the pollution events mentioned in the text, and a new Figure (Fig. 4d) that shows PAN vs scattering has been added as a result of Referee 1's comments. For comments on the use of Hg measurements, see response 21 below.

"P9147/L4 while discussing the sensitivities, the fact that the PPN sensitivity changes in comparison with PAN due to H₂O content should be discussed in this section, not later in the paper (P9157/L2)"

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**8. P9147/L4: Agreed. That discussion has been moved up.

"P9147/L13 re the background noise test. Destructing APNs this way, a commonly used method to determine background levels in GC/ECD analysis for APNs, is of course similar how the TD-CIMS method works in the first place. So the key here is to show that the RCO3 has reacted away. In fact, would it be possible that the background count rates reflect remaining RCO3?"

**9. P9147/L13: It is certainly possible that a small amount of RCO3 radicals escape our zeroing apparatus; however, the background count rates observed by this method are the same as the observed background when UHP Nitrogen is pulled through our sampling orifice, indicating that this is an internal background.

"P9150/L6 this statement is rather confusing in the context of this paper (LRT tends to lower the PPN/PAN ratio, but here it is usually at the high end); may rethink how to formulate this, or at least mention that in what follows this is not necessarily the case"

**10. P9150/L6: We have modified this sentence to give the reader a more clear indication of the results to be presented later in the manuscript.

"P9150/L24 a decrease of mean (7%) and standard deviation (17%) is not "minimal" (previous line) but granted, it has little impact on the discussion. In any case, a prime argument for using instead the geometric mean"

**11. P9150/L24: We have altered this sentence to remove the "minimal" statement. See also response 3 above.

"P9153/L2 as with the PAN-CO relationship, mention that this is a log-linear plot"

**12. P9153/L2: Done.

"P9153/L3 are there periods when the PAN vs ozone correlation was negative?"

**13. P9153/L3: While we have not looked closely at the chemical characteristics of all enhancement episodes, there do not appear to be any significant cases of negative

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PAN-O3 correlation within the time series of Fig. 2. It is certainly conceivable that such a correlation could occur with a stratospheric intrusion or during an event where strong PAN decomposition leads to ozone production, although additional NO_y measurements (particularly NO_x or HNO₃) would be necessary to positively identify either case.

"P9156/L26 indicate what the r² value represents. Is it the correlation between the trends, taking the phase shift into account?"

**14. P9156/L26: The correlation coefficients are for the diurnal trends not accounting for any phase shift. We have added a clause to clarify this point.

"P9156/L28 the discussion here is rather confusing to say the least, in part because of the switching between mean and median. If the medians (or geometric means) are used for the PPN/PAN ratios, does the plot still look as in figure 5a, and is the trend as comparable with O₃ (also using the median or geometric mean)? Figure 5b shows that the mean diurnal variation in PPN and PAN is quite comparable, why would PPN correlate well with O₃, but PAN not?"

**15. P9156/L28: We agree that the use of means makes this section confusing, although we note that ozone, water vapor and PPN/PAN are normally distributed, and as such their diurnally averaged profiles are comparable for means vs medians. We have added a statement to this effect in the text, and we have removed the mean cycles for PAN and PPN from Fig. 5(b). The question of why PPN would correlate with ozone better than PAN is indeed an interesting one. We believe that this finding is because PPN (along with O₃) is slightly higher in the FT relative to PAN due to more anthropogenic VOC precursors, whereas PAN is formed from any number of VOC precursors and is thus less affected by the FT-BL diurnal cycle. Obviously this hypothesis deserves further testing.

"P9157/L23 Poor sentence; presumably should be "Medians for the total dataset, as well as the BL and FT subsets as derived above" (and by the way, PPN/PAN is not a chemical species)"

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**16. P9157/L23: The sentence has been modified as per the referee's suggestion.

"P9158/L4 the number 686 is somewhat curious (it implies that for all APNs there are a total of 6860 5-min data points which seems doubtful). I presume it results from taking only data points when there are valid data for all APNs (including BDLs), and then binning the data in 10 bins of equal number data points (presumably 686). The procedure should be described better"

**17. P9158/L4: We have removed the number 686, and instead we simply note that the bin widths are chosen so that they contain an equal number of points. This should prevent confusion or misinterpretation.

"P9158/L29 the fact that only the PPN/PAN ratio increases (correlates seems too strong a wording here) is somewhat curious and could use some additional discussion. Normally (as mentioned earlier in the paper) one would expect this ratio to decrease due to LRT etc, as reported by Singh and Salas"

**18. P9158/L29: We agree with the reviewer that initially we found the increase to be intriguing. In Singh and Salas (1989), it is noted that PPN/PAN should decrease from its typical urban values of 12 - 15% during transport due to dilution with PPN-free air, which we certainly agree with assuming urban VOC are the only sources of PPN. Our measured PPN/PAN ratio does increase in FT air relative to BL air, but it is not increasing to typical urban values, and indeed we believe it was likely higher (close to the source region) before the air was transported to MBO. In addition, dilution is expected to be less efficient when LRT occurs via the FT. We feel that the observed increase in PPN/PAN is more reflective of longer lifetimes of both PPN precursors and PPN in FT air. MPAN, APAN, PiBN, and their precursors are expected to have much shorter chemical lifetimes than simple alkanes (the dominant source of PPN), as such their contribution to total APN should be less in aged FT air.

"P9159/L4 delete the word initial (there is no follow up in this paper using a different method of analysis)"

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**19. P9159/L4: Done.

"P9159/L18 I doubt that Hysplit calculates ground level at MBO at 1.0-1.1 km. Change the wording into "ground level for the grid in which NBO is located is taken by Hysplit at 1.0 km" or something along these lines"

**20. P9159/L18: From the Description of HYSPLIT 4 Modeling System, which may be found on the HYSPLIT website: "The height of ground surface (Zg) is interpolated directly from the [temperature] profile if the ground level falls between input data levels. Otherwise the ground surface is estimated from the equation of state, $Zg = Z1 - Rd T01 \ln (P0/P1) g^{-1}$, where Rd is the gas constant for dry air (287.04 J kg⁻¹ K⁻¹), T01 is the average temperature between the two lowest data levels, and g is the acceleration of gravity." We have observed the ground level at any one location to change by +/- 50-100 m, depending on the meteorological input file and trajectory start time. We have modified our description in favor of the referee's comment given that "MBO" itself is not in the trajectory model.

"P9161/L9 This paragraph discussing Hg data should be removed since it is irrelevant to the topic of this paper. While maybe interesting, it does not add anything to the analysis of the APN data"

**21. P9151/L9: We respectfully disagree with the reviewer on this point. The Hg-CO enhancement ratio is becoming an established metric for identifying LRT from Asia (see references within the manuscript). We use this ratio to help validate our independent trajectory analysis and thus to support our conclusions about enhanced APN levels in ALRT air. While we do not use Hg directly in our APN analysis, the fact that the Hg-CO correlation for ALRT air agrees so well with expected values is certainly worthy of mention, being at the least a surprising coincidence and at best a justification for our use of back trajectories in a "bulk" analysis.

P9175/fig1 indicate the corresponding levels of the APNs (at a minimum for PAN and PPN)

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**21. P9175/fig1: Approximate levels for PAN and PPN have been added to the figure caption.

P9177/fig3b This figure needs some work: show the scale for the y-axis; there are no gray circles in my copy, but colored circles; with some effort I can only detect one cross in fig 3d only

**22. P9177/fig3b: We have modified the figure and caption to make the figure clearer.

P9179/fig5b indicate sunrise and sunset (as in fig 5a)

**23. P9179/fig5b: Done.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9139, 2007.

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