

Interactive comment on “Comparison of measurements of peroxyacyl nitrates and primary carbonaceous aerosol concentrations in Mexico City determined in 1997 and 2003” by N. A. Marley et al.

N. A. Marley et al.

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Authors Reply to Anonymous Referee Comments:

First we would like to thank the two reviewers for their comments and suggestions. Our response follows:

Anonymous Referee One:

Is it possible that some of the decrease in PAN levels due to the 2003 study being in April as compared to the February-March 1997 study as PAN levels are temperature dependent? Authors reply: The temperatures for the two periods were not substan-

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tially different. However, it should be noted that even if it was a bit warmer during the April period - the overall lifetime of PAN is really dependent upon the relative concentrations of NO and NO₂.¹ Since the PAN levels are formed after most of the NO is converted to NO₂ and the NO₂ concentrations are high relative to NO in Mexico City at that time, the back reaction to reform the PAN is relatively fast leading to no net thermal loss of PAN at elevated temperature. PAN thermal loss is important only when 1) NO₂ levels are low and NO is high (early morning in Mexico City) or 2) in areas where NO and NO₂ are very low and reaction of the peroxyacetyl radical with HO₂ can lead to loss when thermal decomposition occurs. This is the case in the remote troposphere where thermal decomposition of PAN is an important loss mechanism, but is not an important loss mechanism in the polluted environment of Mexico City from noon to late afternoon when NO has been converted to NO₂.

References: 1. Finlayson-Pitts, B.J. and J.N. Pitts, Jr., Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego, 2000, p. 219.

One Correction... is it 10-15 years? Authors reply: Yes, it should be 10 to 15 years (page 1423 line 9) and we will revise the manuscript to make that correction.

Paper was well written. Authors reply: Thanks, we try hard.

Anonymous Referee Two:

The formation of PAN and PAN type compounds requires the simultaneous presence of NO₂ and peroxy radicals. Figures 5 and 6 hint at something in that the PAN concentrations show maxima at or after noon, while in 2003, the PAN maxima are before noon. (By the way, this referee thinks that Figures 5 and 6 would actually work best if they were stacked one underneath the other with the same time scale shown in each so that the timing of the formation of high levels of NO₂ compared to the formation of high levels of peroxy radicals is mismatched in 2003 such that high levels of PAN are not seen as they were in 1997? For example, could the “rush hour” in Mexico City have shifted from 1997 to 2003 to earlier in the day, and as such, the maximum in the NO₂

concentration would occur before significant peroxy radical concentrations are built up? boundary layer dynamics are obviously involved in this as well. Could some proxy for peroxy radical concentrations be plotted along with the measurements in Figures 5 and 6? How about modeled values of peroxy radicals? Overall, further discussion of the timing of the chemistry in Mexico City is needed.

Authors reply: We would note that the conversion of NO to NO₂ is dependent on total peroxy radicals and their formation rates. NO₂ is not the primary NO_x species emitted from vehicular traffic, NO is the primary emitted NO_x species. Thus, peroxy radicals convert NO to NO₂. PAN is formed from the peroxyacetyl radical, specifically, and is in equilibrium with PAN and NO₂. The timing of the PAN formation depends upon a number of factors as the referee notes for secondary formation of peroxyacetyl radicals and NO₂, however, it is not likely that the timing of the “rush hour” was a major factor nor do we have any indication that has change significantly from 1997 to 2003. PAN is a proxy for peroxy acetyl radical concentrations due to the PAN equilibrium with the PA radical.

We will stack the graphs as suggested, and we have noted in re-examination of the figure that one of the figures has scaling problem in the graph. This will be corrected in the final revision.

Note for the two days shown in 2003, one day had an earlier PAN formation. This was not observed in many of the other days, nor do we see that it was significantly different timing. One should note that the time to reach relatively higher concentrations should be slightly longer (as it takes time to form the peroxy radicals and NO₂) and hence the timing should be a bit later for higher peak PAN levels to be produced, given high enough concentrations of precursors. The NO₂ concentrations overall in 2003 were lower than in 1997 as noted in the paper consistent with lower potential for formation of PAN and the lower PAN concentrations being observed. In our opinion the timing of the formation is similar for the two periods as noted in the discussion. On pages 1431 to 1432 we addressed the timing of the formation of the PAN, NO₂ and ozone, and

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we discussed the various processes in detail. We do not feel further discussion along these lines is warranted.

What about temperature?... Authors reply: See reply to first question (similar one) from Anonymous Referee one above.

Specific Comments: Pg. 1423 Line 9 1015 should be 10-15. Authors reply: Agreed. Will be corrected in revision.

Pg. 1424, line 5: It would be helpful to the unfamiliar reader to give some kind of a reference value to give perspective on how high 300 ppb of O3 is; for example the EPA or Mexican Government's threshold for O3 non-attainment could be included. Authors reply: We will add that in brackets in the revised manuscript. (EPA one hour standard is 125 ppb for ozone).

Pg. 1428, line 22: It should be explained why NO2 concentrations are estimated from NOx-NO-PAN; it is obvious to this referee, but may not be obvious to everyone. Authors reply: We will add a clause in front of sentence to clarify in revised manuscript. As the NOx analyzer in NO2 mode measures NO, NO2, and PAN, ...

Pg. 1429, line 7: A different technique was used to measure PAN.. Authors reply: We will add sentence.

Both instruments were compared in previous studies (Marley et al, 2004) and found to give good agreement using PAN standards with 10-15

Pg 1430 line 16: Figure 1 to Figure 5. diurnal variation. Authors reply: Will add in brackets (see Figure 5 for expansion of diurnal detail).

pg 1431 first paragraph: It is mentioned that traffic levels decrease during holidays in Mexico City; are there any numbers available to give a relative sense of the decrease in traffic during these times? Authors reply: no we do not have any definitive traffic counts for 1997. We were there and the traffic was "noticeably less" as very few cars on the road and all the pollutants were also lower, as noted in the paper.

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pg. 1431 line 9: *The maximum O3 concentration during the 2003 campaign reached higher than 135 ppb at the CENICA site (see Figure 6 in Dunlea et al, ACP, 6, 3163-3180, 2006). It is not clear which O3 data the authors used for this study in the 2003 campaign: this should be specified in the experiment and this reported maximum O3 concentration should be corrected.* Authors reply: Data was taken from RAMA network - CENICA station as one-hour averages and was reported as such in the Experimental Section. The data as noted higher than 135 ppb are one minute peak values. Hence the discrepancy. We used one hour averages to compare with the 1997 results and do not feel any changes are needed.

pg. 1431 line 11 *The authors noted that NO2 levels have decreased...* Authors Reply: We have found scaling factor mistake in Figure for NO2 levels and are correcting it for revised version.

pg. 1432, line 11: *The PAN levels in Fig. 6* Authors Reply: We note that the choice of line colors makes it difficult to differentiate BC from PAN. We will redo this graph. The point we made should be clearer with the revised figure, in that PAN starts to decline as BC peaks in both days.

pg. 1433, line 1: *Salcedo et al. comment.* Authors reply: That work and reported BC fraction was based on these same BC measurements, so they should agree for 2003. This is a comparison with 1997 with that same data.

pg. 1434 line 1: *It is mentioned that hydrocarbon levels have decreased substantially.* Authors reply: We will add the references suggested noting that the overall levels of VOCs and reactive precursors for PAN have been decreasing.

pg 1434 line 7; *“particularly...” to “including”...* Authors Reply: change will be made in revision.

Figures.... Authors reply: Revised version will have four figures stacked instead of eight individual.

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