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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Alkyl nitrate production and persistence in the Mexico City Plume" *by* A. E. Perring et al.

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ACPD Response to reviewer #3

Comment: While the data presented here is unique and very interesting, I have significant problems with the data analysis. Not only in much of the analysis based on a large number of assumptions and approximations, which introduce substantial uncertainties, but it is also fundamentally problematic. I will try to examine two of the major findings below. 1. Analysis of the observed correlations between ANs and Ox and comparison with expected values: Most of the red data points were likely taken during the MC fly-bys of the NASA DC-8. These occurred during comparably short time periods (i.e. less than 30 minutes each) during mid-day or in the afternoon. It is therefore likely that a fraction of the observed variation in the red points (young air masses) is due

to varying degrees of dilution with background air as opposed to varying degrees of photochemical processing (i.e. production of Ox and AN).

The average value of 600ppb (table 1) for example illustrates that significant dilution has taken place, as the average values observed at T-0 are typically 1-1.5ppm. As a result, the observed Ox v. ANs slope of 17 will be a lower limit to the true ratio of photochemical production rates because increasing dilution with the background air (containing around 50ppb of O3 and very little AN, as suggested by the authors) will lower the observed slope by biasing the points with lower ozone and AN into the direction of higher ozone to ANs ratios.

Response: Our response is more or less the same as the one published by Reviewer #1 in their response to reviewer #3. While there is no question that the concentrations we use in our analysis are lower than observed at T0, we do not believe that fact causes any problems for our analysis. Dilution of the plume by background air that has $\sim$50ppb Ox and no appreciable ANs would make the slope of the Ox-ANs correlation lower, not higher as reviewer #3 suggest. Further, our view is that the origin of the lines shown in figure 6 all converge to the same point which can be used to estimate the background. In the absence of chemistry, mixing with this background doesn't change the slope of the correlation at all, it only moves the points along the line. The only way that dilution could make the slope higher is if the plume were mixing with background air with fewer ANs and more Ox than are observed in the plume.

We also note that the most visible variations of the points referred to here are at O3 values of 120-150ppb. We do not believe these values are significantly affected by dilution. However, we note that excluding those points substantially improves the R2 of the fitted line and decreases the slope.

Comment: Conversely, I believe that the calculated "expected" Ox/AN slope is an upper limit to the true production rate. This is because the observed NMHC values during the fly-bys are being used to calculate this ratio. Corroborated by the large amount

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of HCHO and CH3CHO shown in Table 1, this hydrocarbon mix has experienced considerable photochemical processing prior to observation. Photochemical processing will deplete the fast-reacting compounds (which tend to produce relatively more AN) to a much higher degree than the slower reacting compounds (which typically produce lower AN yields). In addition, at least the initial photochemical processing increases the fraction of HCHO, Acetaldehyde and other secondary VOC, which produce only Ox but no AN (in fact, the data in table 1 shows that nearly 25% of the Ox are produced by HCHO and CH3CHO alone).

Response: We agree (as indicated in our paper) that there has been significant photochemical processing during the first 5 hours of plume evolution. The reviewer's assumptions that our calculated ratio of ozone to AN production rates is an upper limit are not generally agreed upon. We would welcome a thorough analysis of these points in the literature and hope this paper inspires someone to do that work. We note that alkenes as a class of "fast-reacting" compounds have generally lower AN yields than their slower reacting alkane counterparts, that yields of aromatics and their daughters are not well documented.

While the reviewer is correct that at a hypothetical origin where zero oxidation had taken place there would be zero secondary aldehydes, and that at this hypothetical location ozone production would have a lower yield and AN production a higher one per unit OH reaction with a VOC. However, early in plume evolution, there is relatively less OH reaction with VOC because of the extremely high NOx. We believe that using median values from the observations over the range of photochemical lifetimes observed by the DC-8, at least approximately, represents the oxidative environment experienced over the early plume evolution. Thus the value of 60 we calculate for the slope is not an upper limit, but our best estimate based on current information. Nonetheless, the paper includes details of our assumptions making it possible for those who might want to pursue a different analysis to do so with full knowledge of what we have done.

Comment: At this point we are comparing a lower limit of $\sim$17 to an upper limit of $\sim$60.

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Response: As noted above, we disagree with the reviewers claims that we compare a lower limit to an upper limit.

Comment: The paper completely lacks any kind of uncertainty analysis. Judging from the considerable scatter of the red points in figure 6, the uncertainty of the slope is likely about a factor of two.

Response: See our comments above about the scatter. Note also that the majority of the data does fall on a single line and that 3 points at 150 ppb O3 appear to be different.

Comment: A similar (if not larger) uncertainty can be attributed to the “expected” production ratio as most of the critical branching ratios have not been measured but are estimated from structure-reactivity relationships, which are very uncertain. Given these uncertainties and the fact that a lower limit is compared to an upper limit, there is no statistically significant difference between the observed and expected production rates.

Response: As noted above we disagree with the reviewer about the lower/upper limit claim. Also, while we include a number of estimated branching ratios for completeness, the fraction of AN and O3 production that is estimated is small (as can be verified from table 1) Using different numbers than these estimates amounts to saying that we should be using different branching ratios for these VOC. We make a weaker claim in the paper, saying only that we need additional AN sourcesâĂŤthose could be either higher yields for these VOC or additional high yield VOC.

Comment: 2. Reduction of ozone production owing to AN formation

The arguments above illustrate that the data does not support the derived average branching ratio of 9%. The use of the average “expected” branching ratio of 3% would dramatically lower the impact on ozone production. In addition to this, the analysis is highly uncertain and over-simplified.

Response: We note that Figure 7 shows our analysis of O3 and of the sum of C1-C5 hydrocarbons as compared to total ANs and that the analysis associated with this

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figure and presented in section 4.2 corroborates our conclusions about the need for higher yield compounds at early times in the plume.

Comment: Firstly, a major uncertainty is introduced by the use of average reaction rate constants for the RO2 reactions in equation 10. While this is probably OK for RO2+NO and maybe OK for RO2+HO2, the use of an average rate constant for RO2+RO2 is not. The measured rate constants for these reactions vary by 3-4 orders of magnitude. If the calculated RO2 radical concentration is indeed sensitive to the average rate constant used for RO2+RO2 (as stated in line 15 on page 23775), this analysis could have a huge uncertainty associated with it.

Response: We will add a sentence stating the explicit variation.

Comment: Secondly, the MC photochemistry is complicated (like it is in all heavily polluted areas) and cannot simply be described by the fate of RO2 radicals. For example, many of the papers in the MILAGRO special issue point out that much of the chemistry inside the MCMA is NOx inhibited (i.e., a NOx reduction would result in increase of the local ozone production; see Stephens et al., Shon et al., Tie et al., Song et al., ACPD MILAGRO special issue). As the formation of ANs removes NOx from the mix, an actual increase of the local ozone formation could be the result, not a reduction.

Response: We disagree: the rate of ozone production does more or less come down to the fate of HOx radicalsâĂŤif one specifies VOC, NOx and sunlight. Nowhere do we say that RO2 radicals are sufficient, rather we show that a model constrained by observed NOx and VOC can be used to assess the importance of AN chemistry. We know of no inconsistency with respect to this point between our results and those in these other papersâĂŤnone of which have a sufficiently detailed description of the role of ANs to evaluate whether they account for the chemistry we describe in this manuscript.

Comment: Based on the above, I cannot recommend this paper for publication. The data presented are interesting, however, and therefore should be published. I encourage the authors to resubmit a data paper – containing some data analysis, which

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should be taken only as far as can be supported with measured data (for example the comparison of the sum of AN with the individually measured, simple C1-C5 alkyl nitrates).

Response: We hope that the arguments presented above and in our responses to reviewers 1 and 2, persuade the reviewer that our revised paper should be published. However, we recognize that the reviewer may still be inclined to disagree. Still we hope he/she will recognize that we have attempted to present new ideas here about how to think about AN chemistry and that our paper contains sufficient information for a critic to pursue their own distinct analysis.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23755, 2009.