Atmos. Chem. Phys. Discuss., 9, C9459–C9462, 2010
www.atmos-chem-phys-discuss.net/9/C9459/2010/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #3

Received and published: 8 January 2010

The paper describes findings derived from measurements of the sum of the alkyl nitrates (AN) and the impact of their formation on ozone production in the Mexico City (MC) plume. Major conclusions are an unexpectedly large AN production rate, implying a significant reduction of the ozone production in the MC outflow.

While the data presented here is unique and very interesting, I have significant problems with the data analysis. Not only is 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 AN 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 600 ppb CO (table 1) for example illustrates that significant dilution has taken place, as the average values observed at T-0 are typically in the range of 1-1.5 ppm. As a result, the observed Ox vs. AN slope of 17 will be a lower limit to the true ratio of photochemical production rates because increasing dilution with background air (containing around 50 ppb of Ozone 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 AN ratios. Conversely, I believe that the calculated "expected" Ox/AN slope of 60 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 amounts 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).

At this point, we are comparing a lower limit of $\sim$17 with an upper limit of $\sim$60.

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. A similar (if not larger) uncertainty can be attributed to the calculated "expected" production ratio as most of the critical branching ratios have not been mea-

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sured 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.

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. 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. 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, ACP/D 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.

Based on the above, I cannot recommend this paper for publication. The data presented is interesting, however, and therefore should be published. I encourage the authors to resubmit a data paper – containing some data analysis, which should be taken only as far as can be supported with measured data (like for example the comparison of the sum of AN with the individually measured, simple C1-C5 alkyl nitrates).

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

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