**Atmospheric
Chemistry
and Physics
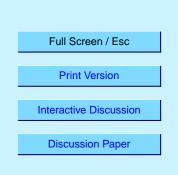Discussions**

Interactive
Comment

Interactive comment on "Observations of total alkyl nitrates within the Sacramento Urban Plume" *by* P. A. Cleary et al.

P. A. Cleary et al.

Received and published: 5 September 2005

Our paper presents 4 quasi-independent lines of reasoning (Sections 5-8) regarding the coupled production of ozone and ANs (alkyl and multifunctional nitrates) in the Sacramento Urban plume. All four of these approaches are consistent with a branching ratio for AN formation of order 4.2%. We conclude that a range of between 3.9 and 5.8% is consistent with the observations and also use the combined measurements of HNO3 and ANs to constrain the chain lengths for the HOx catalytic cycles to between 4.7 and 6.3.

In his or her comments, Referee #1 takes issue with some specific aspects of our analysis and argues we overstate the conclusions. We respond in detail below, but note at the outset, that the basic conclusions of our paper would be unchanged if we

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

adopted the referees approach to the analysis.

Specific comment #1:

The referee notes that the wind direction changes continually in the morning so that the air masses sampled at noon do not have a Lagrangian history that overlaps with air masses sampled at 09:00h. This is entirely true as we acknowledge in the paper. The referee points out the two air parcels have seen different emissions during their recent history. Our point is to use the 09:00h data as an initial condition. In that respect, we argue that the 09:00h data at Granite Bay are representative of the composition of air at 09:00h further west as it enters Sacramento from the South. Further, we observe little change in the reactivity during the course of the day and observations of VOC at downtown locations show that our measurements are reasonably representative of VOC at those locations.

The referee then suggests that the increase in Ox that we observe during the day might be due to transport rather than photochemistry. While we agree, and discuss briefly in the text that variations in the increase of Ox during the day is partly due to transport (including effects associated with the amount of time the air has been in contact with large NOx sources and the downward mixing of the residual layer in the early morning) the morning values of Ox at the surface are nearly constant over the region and mixing with the residual layer is expected to be relatively uniform over the region. We do explicitly consider the effects of this mixing in Section 7 of the manuscript.

The referee then challenges as unrealistic our assumption of a constant VOC mix and similar OH reactivity for the air masses arriving at Granite Bay. These assumptions are used in section 6 of our paper where we model the production of ANs using a large suite of VOC observations, and in Section 7 where we model the rise of Ox and ?ANs in the time window of 09:00-12:00h., the VOC reactivity changes very little (5%) over the time window of 09:00-12:00h. The referee would prefer we use more realistic conditions for our model where we assume 1) a boundary layer height of 500m and 2)

an OH of 5x10ˆ6. The boundary layer height is only used to estimate the importance of deposition to the budgets of Ox and ANs. The height we use is consistent with data in the region. Seaman et al 1995 (1995), describes measurements of the boundary layer height ranging from 400-800 m over the course of 1 day in August. Using 500 m, we estimate loss of ozone and ANs to deposition of 3.5%/hour. Even if the boundary layer height were an unreasonably low 150 m for the full 3 hours from 09:00-12:00h, that would only result in a deposition of 10%/hour (5 ppb/hour for 50 ppb Ox and 60 ppt/hour for 600 ppt ANs) compared to chemical production rates that average 12.5 ppb/hour and 0.24 ppb/hour). The referee is correct that losses to deposition are probably more important early on and chemical production probably faster later on during the three hour window. However, in our opinion this calculation shows the deposition is not important enough to worry about at that level of detail and the calculation justifies (at least to us) omitting the deposition terms from our subsequent calculations. The OH we use of 5 x 10ˆ6 is an average value for the appropriate time window derived from measurements of the ratio of NO2/HNO3 and PNs/NO2 at Granite Bay. We emphasize here and in our paper, that the absolute value of OH is most important for describing the timing of the rise of both Ox and AN. Because many of our conclusions depend only on the ratio of the production rates of Ox and ANs, our choice for absolute OH is unimportant for those conclusions. For the analyses that do depend on absolute OH, since we are only attempting to model the difference between 9 and noon and not the entire temporal profile, it makes no difference whether we use an average OH or one that increases over this time window.

Specific Comment #2:

The referee notes that a large number of the VOC were estimated, that they are important to the reactivity and that branching ratios for nitrate formation for many species are not well known. We agree, however, we acknowledged these limitations in the text and attempted to bracket the uncertainties introduced by these estimates by explicitly considering some of the most important ones. Specifically we evaluated the uncer-

tainty introduced by the range of values in the literature for isoprene nitrate formation and in our estimates of the H2CO concentration. We also evaluated the consequences of halving or doubling the branching ratio to nitrate for all species for which we made an estimate of the branching. As another example, (one we will include in a revised manuscript), if we use only the measured VOC and estimates of CO and CH4 we calculate a branching ratio for AN formation of 3.7 or 6.2% depending on whether the isoprene nitrate branching ratio is 4.4 or 12%. The absolute rates for Ox and AN production are reduced to 72% and 68% respectively compared to the values in shown Table 1 and 2 of our manuscript. These do not change our conclusions to the respective average observed branching ratio.

The referee makes specific note of the branching ratio for terpenes. The 20% value that we adopt is consistent with the comment in the reference cited by the referee (Aschmann, et al., 2002) that the likely reason for their low value 1% compared to Noziere et al. (1999) 18% was loss of hydroxynitrates to the walls of their reaction vessel. Also, 20% is more consistent with structure reactivity relationships and is the same value as calculated for use in the Master Chemical mechanism of by Jenkins and co-workers (Saunders, et al., 2003). The referee also questions our estimate of the branching ratio for nitrate formation from aromatics of 10% as too high. Aromatics represent 8% of the ?AN production, none of our conclusions are substantially affected if, within reason, their branching ratios are higher or lower than estimated. Our estimates are consistent with the rules for estimation given by Kwok and Atkinson (1995) and again are similar to those used in the MCM. In the final sentence of this specific comment the referee asks about nitrocresols. The bond energy of the C-N bond in nitrophenol is approximately 300 kJ mol-1, which implies a dissociation temperatures in excess of 700°C. We assume the thermodynamics of nitrocresols to be similar. Since the hottest temperature we use are 600C for HNO3 and 350C for ANs, we do not expect to have observed any signal from nitrocresols.

Specific Comment #3 The referee comments on the poor quality of the information

provided by Figure 6 and on the uncertainties for a fit to the data reported in the text. The error on the fitted line is not meaningful because of the low R2 (0.22) of the fit. We did not mean to give the impression that that error was meaningful, and will correct this with a clear statement in a revised manuscript. We did note in the text that the data was representative of a range of air mass histories. In a revised manuscript we will add text to clarify this point and we will identify with distinct symbols those points that represent air masses with typical trajectories and that that are atypical. In the manuscript, we did discuss some specific examples of diurnal variation along these lines using the examples in Figure 7. What we reported was that alkyl nitrates decrease over the course of the morning when the air parcels arrived at Granite Bay from north of Sacramento. Such data is included in Figure 5 but not amenable to analysis using any of the assumptions in our paper. We agree that the figure emphasizes variability over correlation but felt it was important to communicate the range of variability given the apparent higher correlation in Figure 5, a correlation that Figure 6 shows is created at least in part by synoptic variability and not exclusively by correlated daily increases.

Finally the referee summarizes by suggesting that we grossly overstate the confidence in our conclusions. We disagree. We note that the paper contains more than sufficient information for the reader to do his or her own calculations to assess the various assumptions we have made. We also note that we have explicitly described the effect of the major uncertainties in some detail in each of the sections of our analysis and that these uncertainties are taken into account in the range of branching ratios we report in the abstract. Finally again we note that we use 4 somewhat different approaches: 1) the observed ANs/O3 ratio in the atmosphere, 2) modeling the VOC mixture in the atmosphere to predict the observed ratio, 3) estimating the effects of mixing on the observed AN/Ox correlation by a simple box model and 4) calculating the chain lengths within the catalytic ozone production cycle, to reach our conclusions and all of those approaches lead us to a consistent picture of the coupled alkyl nitrate - O3 chemistry.

References:

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Aschmann, S. M., Atkinson, R., and Arey, J.: Products of reaction of OH radicals with alpha-pinene, Journal of Geophysical Research-Atmospheres, 107, art. no.-4191, 2002.

Kwok, E. S. C., and Atkinson, R.: Estimation of Hydroxyl Radical Reaction-Rate Constants For Gas- Phase Organic-Compounds Using a Structure-Reactivity Relationship - an Update, Atmospheric Environment, 29, 1685-1695, 1995.

Noziere, B., Barnes, I., and Becker, K. H.: Product study and mechanisms of the reactions of alpha-pinene and of pinonaldehyde with OH radicals, Journal of Geophysical Research-Atmospheres, 104, 23645-23656, 1999.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmospheric Chemistry and Physics, 3, 161-180, 2003.

Seaman, N. L., Stauffer, D. R., and Lariogibbs, A. M.: A Multiscale 4-Dimensional Data Assimilation System Applied in the San-Joaquin Valley During Sarmap .1. Modeling Design and Basic Performance-Characteristics, Journal of Applied Meteorology, 34, 1739-1761, 1995.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 4801, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU