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

Anonymous Referee #1

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GENERAL

This paper describes a measurement series of NO2, total peroxy nitrates, total alkyl nitrates, and HNO3, some VOC, CO2, ozone and met parameters, conducted in the CA central valley from July through September, 2001. A NO2 LIF instrument is used which utilizes an inlet with different heating stages to distinguish between the different groups of reactive nitrogen. The emphasis of data analysis is on the interpretation of the observed sum of all alkyl nitrates in the context of ozone formation and VOC reactivity.

The paper is well written and clearly structured. The underlying measurement effort

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and the data presented certainly justify its publication in ACP.

However, I have some major comments regarding the data interpretation. I believe that the paper over-interprets the measurements and that the stated errors and uncertainties are strongly underestimated.

SPECIFIC

1. Selection of data, photochemistry vs. transport The authors describe the local meteorology on page 4805 such that typically the wind direction changes continually between 800 and 1200 hours LT from south to southwest (the length of the 4h back trajectories are all about the same, does this mean that the wind speed is constant during the morning ? please clarify, if not). This, continuous, change means that the air masses arriving at 900 have seen considerably different emissions than air masses arriving at 1200. The former have seen mostly emissions from the greater central valley, but most recently from the nearby forest and maybe some urban emissions during the last hour before arriving at Granite Bay. The latter air masses will have picked up emissions from the city continuously during the last three hours. Much of the observed increase in photooxidants during the morning hours might therefore be attributed to transport rather than photochemistry. Furthermore, the assumptions of a constant VOC mix as well as a similar OH reactivity history of air masses encountered at Granite Bay seem very unrealistic. Much of the analysis presented in the paper, however, rests on these assumptions. Later, for the model calculations, a boundary layer height of 500m is assumed, with a constant OH mixing ratio of 5x10(6). I would think it is more realistic to assume a strong increase in both the BL height and OH during the course of the morning. I am not sure what a model run with such unrealistic assumptions is telling us. At least for the BL height there might be measurements available (met sondes?) to help constrain this a little better.

2. Estimated VOC mixing ratios and branching ratios for AN production Table 1 lists an impressive number of VOC and while it is nice to see that many species were measured

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at the site there is a large number of species for which mixing ratios were estimated. Many of the latter are species which contribute significantly to the total VOC reactivity at the site, which introduces large uncertainties into the data analysis. I am more concerned with the fact that the branching ratios for the alkyl nitrate production from most of the species shown are estimated. Some of the estimates also seem rather high such as 20% for the terpenes (Aschmann et al, JJGR 2002 estimates the branching ratio for alpha-pinene at 1%). The estimates for the aromatics also seem rather high. For many aromatics the abstraction reactions are only small percentages of the total OH reaction so the formation of nitrates should be scaled by this factor.

On the other hand, nitrocresols formed from aromatics would probably be measured as ANs in this instrument although they technically are not alkyl nitrates.

3. Ox vs. ANs plot The correlation between Ox-Ox(backgnd.) versus ANs-ANs(backgnd.) shown in Figure 6 is terrible. I do not understand how the stated error in the linear fit can only be plus or minus 5%.

In summary, the uncertainties in analytically derived numbers (i.e. from Fig. 6) combined with the uncertainties in the AN production from measured and unmeasured VOC do not allow for the extent of interpretation of the data as presented in the manuscript. The estimated alpha parameters in table 1, the unmeasured VOC, and the fit in figure 6 leave so much wiggle room that almost any desired result could be obtained. Similar arguments can be made with regard to the model runs presented in chapter 7. I strongly advise the authors to scale down the extent at which the data is interpreted or at least clearly state the huge uncertainties that are hidden in this analysis.

TECHNICAL

Figure 1: there should be ticks on the trajectories indicating transport time

Page 4818, caption 7 “The morning tiseĚ” should read “The morning riseĚ”

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

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