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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 #2

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The paper describes ambient measurements of total alkylnitrates within the Sacramento urban plume and attempts to rationalize their concentrations by an examination of their potential precursors that where also measured at the site or, to a large extend, had to be estimated. Conclusions are drawn about the average alkylnitrate and O3 yields seen in the air masses downwind of the Sacramento urban area. However, these conclusions do not seem to be supported by the data presented here.

For example, the abstract claims that "the diurnal variation in ?PNs, ?ANs and HNO3 were strongly correlated with sunlight, indicating both that they are photochemically produced and that they have a lifetime of a few hours at this site". From the discussion of the transport pattern at this site that has been presented here and in previous

publications it seems more likely that the diurnal pattern of the trace gases is largely driven by the repetitive upslope-downslope circulation pattern at the foothills of the Sierra Nevada mountains and does not necessarily provide any insight in the lifetime of these trace gases.

The abstract continues “Odd-oxygen (OX=O3+NO2) and ?ANs were strongly correlated reflecting both the common chemical source terms and the similar lifetimes of both species”. This is not apparent in the poor correlations shown in Figs. 5 and 6.

In the conclusions the authors state that “Our observations show that ?ANs are a photoproduct of oxidation of urban hydrocarbon mixtures with approximately one alkyl nitrate produced for every 25 molecules of O3.” This sentence misses the point that according to the analysis that is summarized in Table 2., the majority of the ?ANs are estimated to be formed in the oxidation of biogenic precursors such as isoprene or the longer chain aldehydes that were not measured but estimated. The message from previous papers by this group describing the evolution of the Sacramento urban plume emphasized the interaction of urban NOx emissions with biogenic emissions downwind of the urban area.

The dynamic of the evolution of the Sacramento urban plume that brings the urban emissions into contact with biogenic emissions downwind of the urban area calls into question the hypothesis of the current analysis that is outlined on page 4812 of the manuscript “To a first approximation, the composition of ?ANs in the atmosphere should closely reflect their source distribution in the morning”. This does not make sense if the major VOC sources are biogenic emissions downwind of the anthropogenic source region.

Unfortunately, the analysis summarized in Table 1. relies to a large extend on estimates of important compounds that were not measured at this site and alkyl nitrate yields that for many of the species are not well known. Any such estimate of the ?ANs yield will be highly uncertain. For example, according to Table 1 the larger aldehydes appear

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to contribute significantly to the estimated ?ANs yield. These aldehyde concentrations were estimated according to measurements that were made in a forested region of Tennessee that hardly has the same biogenic emission pattern as the foothills of the Sierra Nevadas.

In the estimation of the yield of ?ANs formation in the oxidation of isoprene it should be mentioned upfront that measurements of the yield differ by more than a factor of 2. It is peculiar to see that the authors chose the alkyl nitrate yield from isoprene oxidation as .044 (Table 1.) according to the study by Chen et al. (1998). However, in Appendix A it is mentioned that the concentrations of hydroxycarbonyls, formed in the oxidation of isoprene, were estimated according to studies by Sprengnether et al. (2002), who determined the alkyl nitrate yield in the isoprene oxidation as .12.

Considering the large uncertainties in the hydrocarbon mix and the yields of the formation of alkyl nitrates formed in the oxidation of these hydrocarbons, as well as the poor correlations seen between the derived ?ANs values and ozone (Figs. 5 and 6) the conclusion given in the Abstract and the Conclusions do not seem supported by the measurements and the analysis presented in this manuscript.

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