

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

P. A. Cleary et al.

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The reviewer takes issue with our basic conclusions that this data set informs us about the average alkyl nitrate and O₃ yield of the VOC mix in the Sacramento Urban plume. As stated in our response to Reviewer #1, this paper develops several strategies for assessing the relative production of O₃ and ANs and the coupled HO_x/NO_x chemistry at this site. Our paper presents 4 quasi-independent lines of evidence that the coupled production of ozone and ANs (alkyl and multifunctional nitrates) in the Sacramento Urban plume 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 HO_x catalytic cycles to between 4.7 and 6.3. Reviewer #2 has misinter-

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preted the similarities and differences between the previous manuscripts from our two research groups and this current manuscript, perhaps because we have not been clear enough in the manuscript about the patterns of emissions and winds in the region. In a revised manuscript we will add information that clarifies the points described below. Our previous papers that the reviewer refers to addressed the photochemistry at the UC Blodgett Forest Research Station (UC-BFRS), a site several hours downwind of Granite Bay. Between Granite Bay and the UC BFRS lies a large band of oak trees which are a major source of biogenic emissions and does as the reviewer points out contribute to the largely biogenic signature of the VOC observed at Blodgett Forest. Granite Bay, however, lies at the edge of the suburban sprawl of Sacramento, CA, downwind of the urban centre for a significant proportion of daylight hours but upwind of this band of oaks. The biogenic and anthropogenic VOC observed at Granite Bay are directly related to Sacramento urban emissions, from the trees and shrubs mixed into the urban landscaping and from mobile transportation.

To address the specific comments of reviewer #2:

Paragraph 2: The reviewer takes issue with our statement that the concentrations of PNs, ANs, HNO₃ and O₃ vary with sunlight. He/she suggests that they instead vary with the diurnal wind patterns. This is not the case. As can be seen in Figure 7a, which represents the typical wind pattern at the site, concentrations of these species begin to decrease before the change in wind direction occurs at 16:00h. Furthermore, in the hours immediately following the change in wind direction we are seeing essentially the same air that passed over the site earlier aged by a few hours. That is not to say that the concentrations are independent of wind direction as can be seen in Figures 7b and c. However, we stand by our statement that daytime patterns are largely correlated with sunlight.

Paragraph 3: By strong, we mean to say that the production of ANs is constrained to better than a factor of two. In Figure 5 there is a marked difference between the group of observations that correspond to 09:00-12:00h local time and the group that

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correspond to 14:00-18:00h. We recognize that we have not been quantitative about what we mean by strong and that this is a subjective interpretation.

Paragraphs 4 and 5: The reviewer makes three separate points in paragraph 4 and 5. First, he or she suggests that the fact that isoprene is a major source of ANs invalidates our statement that “ANs are a photoproduct of urban hydrocarbon mixtures” The reviewer’s argument seems to be that biogenic compounds are by definition not urban, confusing the terms ‘urban’ and ‘anthropogenic’ at least as we are using them. Many urban plumes in the U.S. have high VOC reactivity due to isoprene, a fact identified by Chameides et al (1988) in their classic paper. The isoprene that we observe is a critical component of the reactivity of the Sacramento urban plume and is not merely added outside that plume. Second, the reviewer suggests that many of the compounds we discuss were not measured but were estimated. We did estimate the abundance of a wide variety of compounds—such an estimate is implicit in every paper or scientific analysis that attempts to describe the temporal behaviour of O₃ on the continents. Here we made the assumptions explicit. In our opinion that allows the reader to make clearer judgements about the accuracy of our analysis. However, we argue that those judgements should be made based on consideration of our estimates in detail and not wholesale dismissing our arguments because we make our assumptions explicit. In our response to reviewer #1, we describe the results of a calculation omitting all of the compounds we made estimates for except CO and CH₄. That calculation does not lead to a different conclusion or expanded uncertainty. Third, the reviewer comments that our previous papers describe the chemistry of this plume 5 hours downwind and that those papers emphasize the role of biogenics that are added to the plume during 5 hours of travel on the way to the UC Blodgett Forest Research Station. We agree, but what happens downwind is not responsible for the behaviour we see at the Granite Bay site. As described above, the major sources of biogenic emissions that we see at Granite Bay are upwind of the site. In fact, observations near downtown Sacramento have isoprene concentrations that are typically 1/3 of what we observe at Granite Bay (Murphy, 2005). In that the biogenic and anthropogenic VOC sources are co-located

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in the Sacramento urban and suburban area, we cannot differentiate specific spatial and temporal profiles of these two ‘disparate’ sources, which is why we therefore use a mean morning VOC distribution. The biogenic and anthropogenic signatures of the VOC change more as a function of time of day (rush-hour/sunlight hours) than as a function of wind direction (see above).

In paragraph 6, the reviewer makes specific objections to the estimates of VOC at the site, in particular noting that we used measurements from Tennessee to estimate some of the higher aldehydes. We believe that the sources of aldehydes in Tennessee and in Sacramento have much in common and likely are biogenic. We provide the reader enough information to make a different estimate and to evaluate its impact on our conclusions.

In paragraph 7, the reviewer argues we should’ve acknowledged uncertainty in the isoprene nitrate yield earlier in the manuscript than we do. The uncertainty is prominently noted in our text (line 25, page 4817) and its effect is evaluated explicitly (line 4, page 4818). The reviewer is correct that the source of our hydroxycarbonyl estimate (Sprengnether, et al., 2002) observed a nitrate branching ration near 12% while we adopt the 4.4% value of Chen et al. (1998) as a reference. Sprengnether et al. give a particularly complete description of the products of the oxidation mechanism of isoprene and we found it useful. So long as we include an estimate of hydroxycarbonyl production (and do not implicitly assume zero), we believe we are getting a reasonably accurate picture of the VOC mix and its nitrate and O₃ yields and this same logic applies to the other species we have estimated. To make it simpler for the reader to evaluate the consequences of our estimates, in a revised manuscript we will include a sentence at the end of section 6 of the paper that gives an explicit calculation of O₃ and AN production rates and the AN yield based on a VOC mix that includes only the observed species and estimates of CO and CH₄. The motivation for providing Figure 6 was to highlight the outliers in the analysis that O₃ and ANs both rise in the morning for all days in the campaign, which is clearly not the case. In a revised manuscript, we

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will describe the increase in Ox and ANs along with a standard deviation to replace the fit to data shown in Figure 6.

References:

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