

## ***Interactive comment on “Closing the peroxy acetyl (PA) radical budget: Observations of acyl peroxy nitrates (PAN, PPN, and MPAN) during BEARPEX 2007” by B. W. LaFranchi et al.***

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We would like to thank the referees for their useful critique and suggestions. We have tried to address the concerns of both referees, as described below.

Both referees felt that some summary of values used in the calculations would be helpful and would allow the reader to better understand how the major conclusions of the paper were reached. We have, therefore, included a new table (Table 3, included here as an attached supplement) that incorporates average concentrations for all the chemical species involved in the analysis. Averages are given for the entire campaign and separately for the warm and cold periods, as in the PA production summary table

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(formerly Table 2, now Table 4).

Referee 1 asks us to clarify whether our discussion referred to APN vs APN<sub>T</sub> lifetimes. It was our intent to discuss lifetimes solely in terms of APN<sub>T</sub> lifetime, not in terms of the thermal dissociation lifetime of APNs. We have clarified this distinction throughout the text by including the subscript “T” where necessary. The lifetimes given in the text in Sec. 5 (p. 9902) are APN<sub>T</sub> lifetimes, calculated as  $1/((1-\beta)k_2b+k_6[\text{OH}])$ , where  $k_2b$  is the APN thermal dissociation rate constant,  $k_6$  is the APN+OH rate constant, and  $\beta$  is defined in the manuscript in Eq. 4.

Referee 1 speculates that the APN<sub>T</sub> lifetime would decrease as temperature decreases even though the APN thermal dissociation lifetime increases. For this to be true, the NO<sub>2</sub> to NO+RO<sub>2</sub>+HO<sub>2</sub> ratio would need to decrease significantly with temperature. In fact, this ratio increases as temperature decreases – resulting from decreases in HO<sub>2</sub> and RO<sub>2</sub> with temperature. The MPAN<sub>T</sub> lifetime also increases as temperature decreases, since OH concentrations are highest at the highest temperatures.

Referee 2 raises a number of additional concerns, which we have tried to address as follows (*referee comments in italics*):

*In reference to the discussion on the applicability of the steady-state model, the referee states: “I found this part hard to follow and would thus suggest to (i) streamline the text and (ii) include at the end of this section a Table which summarises the salient conclusions.”*

We have added a table (Table 2, included here as an attached supplement) that summarizes the conclusions from the comparison of time-dependent and steady-state models. While the discussion in this section remains quite dense, we feel that the table should make the section easier to follow without the need for altering the text.

*“Likewise difficult to follow is the analysis of overall uncertainty”*

We have tried to be more explicit in explaining how we have treated uncertainty in

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the analysis (see below for specifics). Further, we have included the instrumental uncertainties in Table 3 for each measured value and a conservative estimate of the uncertainty (100%, i.e. a factor of 2) for the inferred values ([NO], [MGLY], and [RO2]).

*“NO was not measured during the campaign. Instead, it was estimated from the photostationary state of NO<sub>x</sub> (PSS). This could constitute a significant source of error, as reaction with NO is one of the important loss processes for the peroxy radicals, and thus also determines the effective lifetime of the APNs. Several publications (e.g., Volz-Thomas et al., 2003) have discussed the fact that significant differences exist between observed NO/NO<sub>2</sub> ratios and their estimation from PSS.”*

Based on a prior analysis of the NO-NO<sub>2</sub>-O<sub>3</sub> PSS calculation at UC-BFRS, NO and NO<sub>2</sub> are found to be in approximate steady-state, and it is unlikely that our inferred value of [NO] is off by more than a factor of 2 (Day et al., 2009).

*“...a table summarising the individual contributions to the overall uncertainty of the radical budget etc. would be extremely helpful for the reader.”*

We have included the following text in Sec. 5 summarizing the contribution of various sources of error to the PA radical budget:

“The uncertainty in the absolute PA radical production rate is estimated to be 20-30%. Individual contributions to this uncertainty are largest for the MVK (10%) and acetaldehyde (9%) sources. Propagating this uncertainty through the calculation of the MPAN/PAN and PPN/PAN ratios (Eq. 7) gives an overall uncertainty of 40% in the predicted APN ratios.”

*“From the information provided in the manuscript, I cannot verify the uncertainty of 40 percent stated for the measurement of MPAN.”*

We state that the uncertainty of the MPAN measurement is 31% ±3 pptv. The referee is referred to Wolfe et al. (2009), The following is a direct quote from the appendix in that paper (section A2):

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“In CIMS, calibration constants are typically assumed to be similar between a family of compounds, and previous work has shown this to be true for most APNs with the exception of MPAN (Slusher et al., 2004). Post-campaign calibrations done at NOAA-ESRL confirmed that our TD-CIMS is equally sensitive to PAN, PPN and APAN, but less sensitive to MPAN by a factor of 4.3. Thus, the PAN sensitivity was applied to all raw APN signals to yield concentrations, and the MPAN signal was further corrected for reduced sensitivity. . . . Total uncertainties for single-point concentration measurements are estimated as ±(21%+3 pptv) for PAN and PPN and ±(31%+3 pptv) for MPAN.”

*“The analysis seems to ignore the potential influence of transport and mixing. This should be discussed more explicitly.”*

Sub-section 3.3.3 has been added which discusses the effects of transport and mixing on our analysis. An important point of this section is that previous researchers (Perez, 2008; Dillon et al., 2002) have developed a Lagrangian model that accurately describes transport and oxidation of both biogenic and anthropogenic species from Sacramento and the Central Valley to Blodgett Forest, which is consistent with the assumptions that the simple time-dependent model described in Sec. 3 is an accurate description of the upwind behavior of the relevant oVOCs. We also admit that different entrainment or mixing rates for the different APNs or oVOCs into background air may exist (due to different background concentrations). However, we calculate that these mixing rates are slow ( $\tau_{mix} \sim 4$ -5 hours) compared to the  $APN_T$  chemical lifetimes at the high temperatures ( $\tau_{chem} < 1$  hour). Likewise, for the oVOCs used in the analysis, the mixing lifetime is estimated to be much longer than the chemical lifetime (e.g. for acetaldehyde,  $\tau_{mix} \sim 5$ -10 hours and  $\tau_{OH} \sim 1.5$  hours at the highest temperatures) Thus we assume that this effect is insignificant for this analysis. Similar assumptions have been made to previous analyses of APNs (cf. Roberts et al., 2006).

*“The abstract contains very little quantitative information. The first seven lines read like an introduction and should be moved to this section. The conclusions contain some of*

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*the information missing in the abstract. This should be rearranged.”*

The abstract has been edited such that the conclusions are summarized in a more quantitative way. Additionally, the beginning of the abstract has been edited to read less like an Introduction.

*“The section entitled “Measurements“ starts with a general review of the prevailing meteorological conditions mainly reviewing literature from prior campaigns. I would recommend moving this material into a section entitled meteorological situation, which should then put more emphasis on the conditions encountered in 2007 in the context of what had been observed in prior years.”*

We have changed the title of Sec. 2 to “Experimental”, and now include subsections entitled “Site Description” (in which the typical meteorology and wind patterns are described) and “Measurements”. We mention the most important point about the different meteorological conditions experienced in September 2007 vs September of previous years, namely that it was cooler and wetter, on average. Additional details, we feel, are not particularly relevant to our analysis.

References:

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Wolfe, G., Yatavelli, R. L. N., Thornton, J. A., McKay, M., Goldstein, A. H., LaFranchi, B. W., Min, K.-E. and Cohen, R. C.: Eddy covariance fluxes of acyl peroxy nitrates above a Ponderosa pine forest, Atmos. Chem. Phys., 9, 615-634, 2009.

Please also note the Supplement to this comment.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9879, 2009.

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