

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.

Anonymous Referee #1

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Closing the PA radical budget LaFranchi et al.

The paper presents an interesting discussion of the formation of peroxyacyl radicals in the urban plume incident on Blodgett Forest, subject to both anthropogenic and biogenic emissions, via observations of three acylperoxy nitrates. The work builds on earlier analyses, particularly by Cleary et al. (2007) and Roberts et al. (2007 (references given in paper)). The analysis shows the origins of the peroxyacetyl radical and presents evidence that acetaldehyde is but one source and 4 additional sources are identified. The conclusions are drawn on the basis of analytic steady state and time dependent expressions that are solved iteratively.

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The total concentration of PA(peroxyacyl) + APN(nitrate) is expressed as the sum, APNT, for each of the three nitrates examined. There is some ambiguity in the discussion of the lifetime of APNT. E.g. on page 9888 it is stated, that the lifetime depends on the rate coefficient for dissociation, which regenerates PA. If we make, for the present, the simplifying assumption that PA and APN equilibrate on the timescales of the reactions removing APNT from the system, then the pseudo first order rate coefficient for removal of APNT is $k = (k_{PA}/K + k_{APN})/(1+K)$, where k_{PA} and k_{APN} are the pseudo first order rate coefficients for removal of PA and APN respectively and K is the PA, APN equilibrium constant and includes $[NO_2]$. The lifetime of APNT is the reciprocal of k . If PA, APN are not equilibrated, the analysis is a little more complex and gives a time dependent lifetime. The effective lifetime, though, is longer than $1/k$, becoming equal to it as the rate coefficient for APN dissociation gets large and equal to the APN lifetime as the dissociation rate coefficient tends to zero.

Much of the interesting discussion (section 5 – 7) is confusing because this distinction is not made clear. The lifetimes given seem to be the dissociation lifetimes, rather than the lifetimes of APNT, except in the case of MPANT, which reacts quickly with OH. I suspect, though cannot confirm this, because I do not have the data available, that the lifetime of APNT decreases as T falls, although the dissociation lifetime of APN increases. This section of the discussion should be clarified.

It is also very difficult to try and reinterpret the data, because so little information is given. It would be helpful to have information on the values of the concentrations of OH, HO₂, RO₂, NO and NO₂ that are used in the analysis of and interpretation of Figures 5-7, even when these values are inferred, rather than measured. Values of the lifetimes of the three APNT systems would also be helpful.

These issues should be resolved – either refuted or discussed more fully – before final publication in ACP. The results and analysis are potentially of considerable interest.