

## ***Interactive comment on “Nitrogen oxide chemistry in an urban plume: investigation of the chemistry of peroxy and multifunctional organic nitrates with a Lagrangian model” by I. M. Pérez et al.***

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The paper by Perez et al. [ACPD, 9, 27099-27165, 2009] describes modeling of the Sacramento plume as a means to interpret measurements made at the Blodgett Forest Research Station (BFRS) of peroxy acyl nitrates and organic nitrates. The model uses a version of the Leeds Master Chemical Mechanism to describe processing of the plume in the 3-5 hour transit between Sacramento and BFRS.

One of the major findings of the paper is that concentrations of peroxy acetyl nitrate (PAN) are underestimated at BFRS, while non-speciated (lumped) peroxyacyl nitrates (PNs) are overpredicted. The authors conclude that the yield of PNs from large and

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multifunctional aldehydes is close to zero, and that an increase in PAN precursors is required.

However, the mechanism as it is presented in the paper is set up to favor the formation of PNs at the expense of PAN. While the biogenic VOCs are treated in some detail, anthropogenic VOCs are lumped together in a form that is inconsistent with their known chemistry. So, while many small alkanes (e.g. butane and isopentane) are known to give acetaldehyde as a major product [1,2], in the model their oxidation leads to the formation of a lumped aldehyde, the oxidation of which forms an unspeciated PN. A similar consideration applies to toluene and the xylenes, which form methyl glyoxal, another source of acetyl radicals. Since the model is initialized with several hundred ppt of these moderately long-lived anthropogenic hydrocarbons, acetaldehyde production will continue along the plume, reducing the need for additional sources.

On the other hand, long chain alkanes (such as pentane and hexane) give rise to the formation of ketones/hydroxyketones, which do not oxidize to form PNs very efficiently. However, in the model, they all lead to the production of the generic aldehyde (and hence potentially to PN molecules).

Thus, from the information given in the paper, it is not surprising that PAN concentrations are underpredicted, since many of its known sources are ignored, and PNs are overpredicted. This weakens the conclusions of the paper, since the inclusion of known chemistry in the model might change the interpretation considerably.

1. Atkinson, R. Rate constants for the atmospheric reactions of alkoxy radicals: An updated estimation method, *Atmos. Environ.* 41, 8468-8485, 2007. 2. Orlando, J. J., G. S. Tyndall, and T. J. Wallington, The atmospheric chemistry of alkoxy radicals, *Chem. Rev.*, 103, 4657-4689, 2003.

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