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Atmospheric Chemistry and Physics Discussions



# *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.

**Anonymous Referee #2**

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Perez et al. have performed a box modelling study investigating the chemical evolution of the Sacramento urban plume, and compared their modelling results with measurements of this plume. Their particular emphasis has been examination of the speciation of organic nitrate compounds. Their most interesting result is that newly proposed reaction pathways for isoprene nitrates, when added to their model, degrade its ability to simulate the observations of this Sacramento plume. The authors suggest that hitherto unknown deficiencies in the understanding of alkyl nitrate (AN) chemistry could be to blame for this reduced ability of their model to simulate the observed AN loading when these new pathways are introduced. In particular, the authors suggest that reaction of AN with the OH radical should not form $NO_2$ and carbonyl products, as currently



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assumed in modern photochemical oxidation mechanisms, but should rather produce very high yields of multifunctional nitrates.

I am not able to recommend this paper for publication in ACP at the present time, for the reasons outlined below. I encourage the authors to resubmit their manuscript after they have addressed the following concerns about the appropriateness of the chemical mechanism used in the study.

In particular I am concerned that their use of a highly simplified photochemical oxidation mechanism may be at least partially to blame for the model-measurement disagreement reported by the authors. The chemical mechanism used by Perez et al. is supposedly based on the MCM, but their mechanism, as presented in their Appendix A, has actually been heavily simplified. In particular, almost all of the chemistry of the oxidation products of VOC other than isoprene and MBO has been removed; these VOC basically form lumped $RO_2$ immediately in their model, which removes the representation of the many different possible AN based on the various generations of intermediate oxidation products. If the authors wish to make conclusions from their model about the speciation of AN, then in my opinion they should employ a model which actually includes a representation of this speciation. I would recommend using the full MCM, rather than the present simplified version.

This simplification of the chemical mechanism also severely impacts the representation of peroxy nitrate (PN) species in the model, in particular the ability of the model to form PAN, by removing important sources of peroxy acetyl (PA) radicals, both directly from degradation of the omitted VOC oxidation intermediates as well as from acetaldehyde formed by other similarly omitted intermediates. The effects of this are noted on page 27112 of the manuscript where is is acknowledged that acetaldehyde concentrations are underestimated in the model by 100%. It appears that the model is only able to form PAN through the degradation of isoprene, even though the initial conditions of the model run (an urban area) include anthropogenic VOC and their intermediate oxidation products. This distortion of the chemistry can be expected to lead to less production of



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PAN, and indeed both the "reference" case as well as the case with an artificial source of PA radicals both heavily underestimate the observed PN concentrations.

It is mentioned on page 27111 that a compensating error for this underestimation of PAN production could be an overestimated production of unspeciated PN from the lumped aldehyde species, and when the model is tuned with the addition of various VOC oxidation intermediates, the agreement with the measurements is improved somewhat. Given the high degree of simplification and tuning present in the study it is, however, difficult to know how well the simulations correspond with reality. If the authors wish to make conclusions about the speciation of PN, then it would certainly help if these simulations were performed again without such a high degree of simplification. I recommend that the authors use the full MCM chemistry, or at least enough of it to be able to adequately represent the formation of PAN (and other PN) from all VOC which are present in the model run, and all of the oxidation intermediates of these VOC which can be expected to be present.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 27099, 2009.