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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 #1

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This paper deals with the chemistry within an urban plume as it is transported to rural areas, and is a useful application of the Master Chemical Mechanism. There is sufficient new material here to be worth publishing, however there are a number of general and specific issues that the authors need to consider.

General Comments; The authors state in the abstract and the introduction that most previous studies "focused on limiting cases of high NOx or of near zero NOx". This is simply not true. I invite the authors to read Liu et al., 1987, and some of the 521 articles that cite it. The Lagrangian plume model used in this work assumes mixing with the free trop. is the biggest dilution effect. However, mixing of PBL air also has to be

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important and that air most certainly has significant amounts of pollutants. We know that because the authors make the point, made many times previously too, that the circulation between the Sacramento urban area and Blodgett has a regular upslope-downslope pattern. That downslope portion returns processed urban air to the lower elevation PBL. This is a major limitation of the Lagrangian plume assumption and needs to be discussed here. Because plume model really has only two points (urban air and Blodgett air), and two adjustable parameters, (mixing rate and OH), it is a bit like fitting a straight line to two points. The authors may argue that the use of multiple HC makes it different, but those HC are all correlated, and would be somewhat correlated in the background PBL air mixing in. So all the time spent in the paper discussing the model measurement agreements in absolute numbers is not all that useful. The really new and interesting material here is how the relative abundances of the particular classes of NOy species, and the relative abundances among the PAN species, compare between the model and measurements. These parts should be emphasized and the material comparing the absolute numbers should be de-emphasized since those are dependent on the Lagrangian model that has the above-mentioned limitations.

Detailed Comments;

Measurements;

There is no measurement description given in the paper. If there were, it could be used to point out that while the NO_2 and ΣPNs measurements by this group appear reasonable, the ΣAN and HNO_3 measurements either have not been compared or the comparisons have not been very good. Also, previous work by this group [Perez et al., 2007] shows that the measurement labeled 'NOy' in this work would not include HONO, when it is there, and so is not really a true NOy measurement.

Model;

The MCM has a feature that drops compounds after they fall below a threshold percentage of carbon. Was this turned on in this study? If so, how would this affect the

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calculated nitrogen balances?

The MPAN + OH rate constant in the MCM 3.1, as written, is too low, as it is based on the work of Grosjean et al. 1993. The new value, 2.6 x10^{-11} reported by Orlando et al., 2002 is a fair bit higher and is more realistic. How would this affect this modeling study?

There seems to be some confusion regarding deposition velocities. The authors reference the work of Farmer and Cohen, but then proceed to quote downward deposition velocities for PANs and HNO_3. Farmer and Cohen observed upward fluxes of PAN and HNO_3 in their summertime measurements at Blodgett Forest. This issue needs an explanation; is the work of Farmer and Cohen no longer to be believed? Does the flux change from downward to upward at some point along the transport path? Aren't the numbers quoted in the paper really from the literature review presented in Farmer and Cohen?

In section 4.1 the authors spent some time discussing differences between measured and modelled NOy. These differences are likely small compared to the variability of NOy sources, just declare the agreement reasonable, given that variability, and move on.

References;

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