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Atmospheric
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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.

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Response to Referee #1:

The referee makes two major points in the overview comments.

First the reviewer points out that many papers have considered an intermediate regime between the remote atmosphere low NOx and VOC and high NOx urban chemistry. We don't disagree, however we stand by our statement that most of the literature has focused on those limiting cases and we believe it useful to remind the reader of the bias that has been introduced in the literature and to atmospheric chemistry textbooks. It is our opinion that high VOC low NOx chemistry that is the subject of this paper remains underexplored.

Second, the referee notes that the return flow of the Sacramento urban plume at night mixes into the plume and that as a result our strongest results are dependent on ratio and not absolute concentrations. While we agree, the effect of memory is relatively small (see Murphy et al. 2006). Also, because the mixing occurs as the PBL grows in the AM, it essentially affects the initial conditions of our calculations and is not relevant to evolution of the plume during midday when mixing with the free troposphere is essentially the only relevant parameter. That said, we do agree with the referee that the absolute values in our analysis are not as strong a constraint as ratios. We already draw our conclusions primarily from relative values, such as the total_ANs/NOx ratio or the NOx/NOy ratio, which are less sensitive to our treatment of plume mixing than are absolute values. In the revised manuscript, we will modify Section 4.1 to reduce the emphasis on model/observation comparison of absolute NOy concentrations.

The referee also argues in the overview comments that the hydrocarbon observations are all correlated. We acknowledge this issue and have done our best to bracket possible dilution constants by using two different sets of background concentrations (LOCALbk and GLOBALbk), producing two different mixing rates (see Appendix B and C). The plume average [OH] varies by about 10% in these two scenarios. In our opinion, the constraints on these terms are strong enough to be useful.

Detailed comments: The measurements used in this paper have been described in detail elsewhere in the literature. We have referenced these descriptions in the manuscript. We disagree with the reviewer's claim that comparison of our measurements of total alkyl nitrates and HNO3 to other measurements have not been very good. In every case where we have made such comparisons our measurements have been as accurate as other respected techniques. For total_ANs, Perring et al. (2009) is the only data set we are aware of where TD-LIF and an independent method were applied to simultaneous measurements of the classes of RONO2 molecules that we believe are the primary ones in ambient air. The measurements were in agreement to within 10%. At present, there is no example in the literature in which a direct quantitative comparison of the TD-LIF HNO3 measurement with other techniques is made. We are not aware of unpublished, direct examples showing our measurements are generally in error. However, it has been shown that the sum of NO (detected by chemiluminescence) + NOy compounds detected by TD-LIF (sum_NOy,i) compares favorably (within 15%) with total NOy (detected by catalysis-chemiluminescence) at UC-BFRS (Day et al., 2003). This indicates there is likely not a significant bias to any single contributor to sum_NOy,i including HNO3.

The reviewer notes that we do not measure NOy, but rather individual elements of NOy and that we do not measure HONO. We agree and thought we had carefully referred only to the sum of individual compounds. In the revised version we will correct any references to NOy, replacing them with sum_NOy,i. We have neglected HONO in the model because there is no accepted mechanism that would make it important to the daytime chemistry considered in this manuscriptâĂŤthus it could only be included in an ad hoc way that would be entirely dependent on unsubstantiated assumptions. Recent work (Ren et al, 2010) has found that HONO is not a significant component of NOy at UC-BFRS ($\sim$ 3%).

Also, we do not 'drop' compounds in the model, per se. Rather, we convert them into a single lumped oxygenate (to be referred to as 'oVOC' in revised manuscript) species. Anthropogenic VOCs are converted into a lumped species in the first generation of oxidation, isoprene and MBO are converted into a lumped species after three generations of oxidation, and terpenes (as alpha-pinene) are lumped after a single generation of oxidation.

The reviewer is correct that MCM v 3.1 uses an outdated MPAN+OH rate constant. In the revised version we will update this rate constant. The change, which amounts to an increase of about a factor of 10 in the rate constant (Orlando et al., 2002), has a negligible ($\sim$2%) effect on the overall model NOy budget and about a 4-5% effect on the total_PNs abundance . The modeled absolute MPAN concentration, however,

decreases by about 25% at UC-BFRS. All of the model scenarios were re-run with the revised rate constant; the values calculated in Table 1 in the revised manuscript reflect the model outputs using the updated rate constant.

The reviewer notes that Farmer and Cohen observed net upward fluxes of some N species. The deposition velocities used in the model are taken from the winter-time observations of Farmer and Cohen (2007). These values represent deposition velocities associated with physical processes for NOy species. The only standing explanations for upward summertime fluxes indicate that within canopy chemistry affects the fluxes (c.f. Farmer and Cohen, 2007; Wolfe et al., 2009; Holzinger et al., 2006; Kurpius et al., 2003). While new methods applied to fluxes do find additional evidence for the idea of chemical fluxes (e.g Wolfe at al. 2009), the magnitude is different from that reported by Farmer and Cohen (2007). We do not have an adequate model for those effects and we do not know the extent to which they depend on ambient concentrations over the forest or the extent to which they are uniform over the different ecosystems along transect from Sacramento to Blodgett forest. This model is capable of explaining relative concentrations as they evolve along the urban plume without invoking that additional chemical flux term indicating the net effect of such upward fluxes is likely small or that it is unimportant to the average (e.g. upward fluxes might be more important for special conditions). The reviewer objects to the sentence in section 4.1 where we list possible explanations for model observation difference in total NOy using the argument that the source NOy variability is large enough to explain the difference. We argue in the text that this variability is not large enough to explain the difference. We don't think the one sentence is overly distracting or contains any statements that are incorrect.

Response to referee #2 and G.S. Tyndall: Both referee #2 and commenter G.S. Tyndall are concerned with the simplified treatment of VOCs in the model, in which all compounds, with the exception of MBO and isoprene, are lumped into an unspeciated peroxy radical (RO2) upon oxidation. The conversion of this lumped peroxy radical to a stable product results in a lumped unspeciated class of oxygenated VOCs. In the submitted manuscript we referred to this lumped species as a class of aldehydes. As Tyndall correctly points out, many of the hydrocarbons that feed into this class do not form aldehydes exclusively. Referee #2 suggests that our conclusions regarding alkyl nitrates may be affected by this over-simplification of anthropogenic VOCs. This assumed lumping could affect any of the NOy species discussed in the manuscript. In the revised manuscript we will make two changes. First, we will refer to this lumped class as a class of oVOCs rather than as aldehydes, to more accurately reflect how we treat the chemistry of this class.

Second, and more important, we will include a discussion of the effects of this lumping on our conclusions by describing some sensitivity studies that confirm our intuition about the effects of this lumping scheme. Specifically, we find that the abundance of the unspeciated class of RO2 is too small to have an impact on the total_ANs/NOx ratio. To bracket the possibilities, we performed calculations with an AN branching ratio for unspeciated RO2 of 20%, 7 times larger than in the Reference case. We find that the total_ANs/NOx ratio changes by $\sim$1-3%, that the unspeciated class of ANs increases from about 3% to 8% of total_ANs at UC-BFRS, but there is little impact on the overall NOy speciation.

For total_PNs, the issues are more complex. First, by not treating all hydrocarbons explicitly through one or more generations of oxidation, we have removed the sources of a number of potentially important PA radical precursors such as acetaldehyde and methyl glyoxal. This is supported by predictions of acetaldehyde that are lower in the model than observations at UC-BFRS. We attempted to address this by adding an artificial source of acetaldehyde and biacetyl in the model. However, we neglected to point out that our model may likely be adding to the lumped pool at the expense of acetaldehyde. For example, oxidation of ethanol, which leads to acetaldehyde production, is lumped into the unspeciated oVOC class. We have clarified this point in the revised manuscript. Second, by assuming that all of the lumped oVOC can form PNs with the same efficiency, we neglected the fact that a significant portion of these

compounds are likely not aldehydes, but, rather, ketones or other oxygenates. The MCM prescribed chemistry does not permit direct acyl peroxy radical production from these non-aldehydic species. As a result, there is a bias in the model to production of unspeciated PNs.

To assess the extent of this bias we did a rough estimate of the identity of the lumped RC(O)O2, which is the direct precursor to the unspeciated PNs. Approximately 40% of this class is produced directly from speciated aldehydes, of which, about 75% comes from oxidation of glycoaldehyde. The remaining 60% of the RC(O)O2 production results from the oxidation of the lumped oVOC class, which is predicted to be a complex mixture of oxygenated compounds including ketones, acids, alcohols, peroxides, and aldehydes. These compounds result from the oxidation of compounds such as C2-C7 alkanes, alkenes and dienes, aromatics, and terpenes. Additionally, a subset of HO2 + RO2 reactions also contributes to the oVOC class (as peroxides). Based on a semi-quantitative analysis of the major production channels, we estimate that the lumped oVOC class is at least 10-20% aldehydes (some of which is acetaldehyde), meaning that about 50- 60% of the production of our lumped RC(O)O2 species results from MCM-prescribed chemistry. So, at most, about 40-50% of the unspeciated PNs in the Reference model are the result of bias introduced by our imposed oVOC lumping.

Although adding detail to the chemistry of this lumped class would be desirable, the current calculations are sufficient to identify the need for speciation of the lumped oVOCs to more accurately make predictions of PNs without the artificial biacetyl and acetaldehyde sources we implement here. We plan to add this chemistry to future versions of the model.

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