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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Night-time radical chemistry during the NAMBLEX campaign" *by* R. Sommariva et al.

R. Sommariva et al.

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We thank the editor and the second referee for their comments. Here is our reply:

COMMENT #1: Finally, from an editorial point of view, it is suggested that some improvements in clarity of the figures could be made. Some of the font sizes used for axis labels are quite small, and not easily read - not on a computer screen at least. The other issue is an unfortunate and irritating weakness of Excel that does not allow subscripts to be used in legend boxes. Normally one can get away with this, but the very extensive use of chemical formulae in legend boxes here - all without subscripts - spoils an otherwise professional appearance. I would recommend some alternative presentation of the legends. Finally one of the last figures has borders around the charts, whereas all of the others do not.

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REPLY to COMMENT #1: The font sizes in the figures will be increased. We regret that it is not feasible to use subscripts in figures from Excel spreadsheets, but we cannot see a clearer way of presenting the key to the rates of production and destruction in Figure 5 than the one we have adopted. To place them in the figure caption would mean that they were some way from the graph. The present location makes it easy to scan across from the key to the plots. It is not feasible, at this stage, to change to an alternative plotting package.

COMMENT #2: There are some additional pieces of information that should be included before publication, specifically providing defensible, rigorously propagated uncertainty estimates for all the measurements (esp. HOx) and model values before interpreting any differences. Some assertions are not fully supported, especially the methane-and-CO model result supporting the notion that ozone-alkene reactions can source HOx in agreement with the measurements. Given the general state of model uncertainty, and the HOx measurement comparisons that show very large disagreements between HOx instruments, more would need to be said to support this particular conclusion for it to stand on its own. My impression is that the disagreements suggesting ozone-alkene reactions are equally well explained by the error bars in the respective quantities being compared. Including more complete uncertainty estimates would help the reader decide whether this is a valid point.

REPLY to COMMENT #2: We refer to the experimental papers (Bitter et al. 2005, Saiz-Lopez et al. 2005, Smith et al. 2006, Fleming et al. 2006) for a proper discussion of the uncertainties in the measurements. As for the model uncertainties, the quoted numbers are estimates derived by a a simpler CO-CH4 model similar to the ‘‘clean” model used in this work. See Sommariva et al., ACP, 2004 for more details on the problems associated to the estimate of the uncertainty in a "full" model. The ozone+alkenes reactions have not been introduced in the discussion to explain the difference between modelled and measured HOx. The main reason for incorporating the ozone+alkenes reactions in the full models, was because they are based on measured concentrations of alkenes and on literature values for the radical yields from ozone+alkenes reactions. The results of this inclusion are (i) the model agrees better with the measured concentration; (ii) the reaction provides a night time source that offsets losses and provides an improved time dependence. The lack of agreement with the model was not the primary motive for inclusion of this source and so considerations of model uncertainty are not, in this context, the primary concern. The text has been changed to make this clearer.

COMMENT #3: Section 2. Models and measurements “The value of (gamma for N2O5) Eąwas 0.032Eą ”. Would a substantially smaller uptake coefficient help to reconcile the model-CRDS measurement differences? Recent work by Brown et al. (Science, 311, 67-70, 2006) has shown a lower, and highly variable, uptake coefficient for N2O5. The Brown study derives gamma values, using ambient measurements, ranging from 0.016 to less than 0.002, for the conditions they encountered. The sensitivity study in the current manuscript shows negligible dependence when their gamma is varied from 0.032 to 0.016, by a factor of two, but the Brown et al. results suggest that gamma could be much smaller yet for a neutralized aerosol. If uptake losses were actually smaller, N2O5 levels would be much higher, providing a source in the model for the elevated NO3 suggested by the CRDS measurements. The initial ACPD draft was probably submitted prior to publication of the Brown et al. results, but the primary author has been working with Dr. Brown for nearly a year and is aware of these results. I am curious if including a much lower gamma value helps reduce the discrepancies between the modeled and observed NO3. This inclusion would likely move the model values higher than currently calculated. This addition is up to the authors to include in the model for this manuscript, but might at least be mentioned in the text as a possible explanation.

REPLY to COMMENT #3: As explained in section 4, the model was rather unsensitive to changes in gamma(N2O5), because, under the conditions on 31 August - 1 September, the major loss process of N2O5 with the lower gamma(N2O5) was gas-phase hydrolysis. This point will be made clearer. Note that the approach used in this

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work to describe the uptake of gas-phase species on aerosol did not include information on the composition of aerosol, so that an analysis of the type carried out by Brown et al. was not feasible. It is clear, though, from the foregoing discussion that a quantitative discussion of the effects of a decrease in gamma (N2O5) are not significant in the present context.

COMMENT #4: Section 6 - A case-study night “The most probable explanation was a local source of NO2, Eą ”. This sounds highly unlikely. If true, this would warrant at least a citation to another work that can suggest a source of NO2 without NO. Far more likely is that the observed enhancement in NO2 was due to an upwind source of NO, which had been nearly completely converted to the observed NO2 by reaction with ambient ozone during transport to the measurement site. The fluxes presented in Figure 8 should be reconsidered as well. “NO2 was produced from NO, through its reactions with CH3O2 and HO2.” These are probably very small contributors to the observed NO2, relative to NO2 production via the NO + O3 reaction. The author’s description of the decrease in O3 by a factor of 30%, or from roughly 9 to about 6e11 molecules/cm3 (from the time series in Figure 7) is difficult to reconcile with the observed increase in NO, NO2, and NO3. Assuming an initial NO source (not NO2; see comment above) the decrease in O3 due to reaction with NO can only account for a small fraction of the change observed in O3. Summing the observed NO2 enhancements of ca. 0.2e11 (Fig. 7) and NO3 enhancements below 0.004e11 (fig. 3c) can only account for a decrease in O3 of less than 10% of that observed. There is simply not enough N in the measured species to account for the change in ozone as proposed by the authors. A better, alternate explanation of the case study data might be offered. The wind shift transported an air mass characterized by a slightly lower O3 background to the measurement site between 22:00 and 24:00. This air mass also must have passed over a local, but small, NO source, far enough back in time to permit the NO + O3 reaction to produce the observed NO2 and NO3 enhancements. This NO source and the resulting chemistry during transport caused the finer-scale structure in the observed species over time. This explanation assumes

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that all of the initial NO remains in the airmass as either NO, NO_2, or NO_3, and that N_2O_5 was not formed in any abundance and therefore no loss of N had taken place.

REPLY to COMMENT #4: We agree with and are grateful for this comment and the proposed explanation and we will modify the paper accordingly.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7715, 2006.