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Atmospheric
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Discussions

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

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One set of reviewer’s comments became available during the official eight-week period for “open discussion”. The authors have already responded to these comments as shown on this web site, and they have prepared a revised version of their original manuscript. This revised version is not available to view the ACPD web pages; only the originally submitted version is shown here.

A second set of reviewers comments have since become available, from a second and independent referee. It is the journal policy to make all efforts to obtain at least two independent reviews of all submitted papers. These new comments refer to both the original manuscript, and to the revised one. The second referee makes some important points, and these should be addressed by the authors in a further revision. In particular, attention should be given to the claimed primary NO2 source referred to in the paper, and the discussion of attribution of the observed decline in ozone. The second referee, incidentally, was complimentary about the present amendments made to the paper in response to the first referees comments.

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.

Once these issues have been addressed, further consideration can be given to the publication status of the paper.

Review of Sommariva et al., Night-time radical chemistry during the NAMBLEX campaign, manuscript no. acpd-2006-0124: anonymous referee #2.

In general this is a well-done, and well-explained, model study. 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. However, there is value in the paper as presented, and this work deserves to be published. I think this will make a good contribution to the literature once two specific issues are addressed, as clarified below.

Section 2. Models and measurements “The value of (gamma for N2O5) Ěwas 0.032Ě”. 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.

Section 6 - A case-study night “The most probable explanation was a local source of NO2, Ě”. 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. Subsequent reaction of the ozone (in large excess at 9e11 molecules/cm3) also gave rise to NO3 enhancements observed during this period. I am not aware of any direct source of NO2 that could reasonably be invoked to support the author's hypothesis. Most sources of NOx (bacterial soil emissions, combustion, etc.) emit primarily NO, with NO2 emissions typically less than 10% of the total NOx. Without further support, the observed changes in NO, NO2, O3, and NO3 must be reconsidered as due to an upwind source of NO. 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 that all of the initial NO remains in the airmass as either NO, NO2, or NO3, and that N2O5 was not formed in any abundance and therefore no loss of N had taken place.

Another, but perhaps less likely, explanation invokes a larger NO source, sufficient to titrate the ozone by 30% from 9 to 6e11. However, to account for the imbalance between the increase in N species compared to the decrease in O3, this would require substantial N2O5 formation and subsequent loss via heterogeneous hydrolysis prior to arrival at the measurement site. Though the transport time is unspecified from NO source to measurement, there may not have been sufficient time to build up appreciable levels of N2O5, and unrealistically large N2O5 uptake coefficients (see earlier comments) would be necessary to make this explanation work.

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