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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.

R. Sommariva et al.

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We thank the referees for his constructive and detailed comments.

> My major concern is that it is difficult to find out what is the original analysis of this paper in this special issue with many related papers (e.g. Smith et al. 2006, Fleming et al. 2006, Bitter et al. in preparation), which include nighttime analysis of the radicals at least as their parts. This point needs clarification.

The papers from Saiz-Lopez et al. (2005), Smith et al. (2006) and Fleming et al. (2006) were manly concerned with the description and analysis of the respective measurements. The paper from Bitter et al. will discuss the NO3 and N2O5 measurements by CRDS and also use a model to try to resolve the DOAS/CRDS differences. This paper and Fleming et al. (2006) are complementary papers. While Fleming et al. used

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the model results to compare with HO2+RO2 measurements, this paper also discusses model-measurements comparisons with HO2, NO3 and N2O5 and uses the model to study the connections between HOx and the NO3/N2O5 system. The differences between all these related papers will be made clearer in the introduction.

> 2.page 7719, line 15. It is mentioned that the NMHCs data were linearly interpolated to 15 min. The original frequency of the NMHC measurements (40 min? from Heard et al. (2006)) should be included here.

The time resolution of the NMHCs measurements was 40 minutes, as reported in Lewis et al. (2005) and Heard et al. (2006). This will be added to the paper.

> 3.page 7720, lines 10-19. It is not clear whether the observed boundary layer height is used in the model to calculated deposition rates.

A boundary layer (BL) height of 400 m, based on the wind profiler measurements (Norton et al., 2006), was used for the modelled nights. However, sensitivity tests showed that it was not a significant parameter. This will be specified in the text.

> 4.page 7721, lines 2-4, 6, 11, and 15. Integration time and signal-to-noise ratio with which the detection limits of OH, HO2, HO2+RO2, and NO3 are calculated should be given. 5. In section 2, the times of sunset and sunrise should be specified for the campaign period to define nighttime.

This information is in the corresponding papers (Saiz-Lopez et al. 2005, Smith et al. 2006, Fleming et al. 2006, Bitter et al.). It will be added to the text.

> 6.page 7722, line 5. Nighttime OH was below the detection limit (6x10ˆ4 molecule cm-3). It seems from the inset graph of Figure 1a that modeled OH (fulloxy) sometimes reaches 1x10ˆ5 molecule cm-3. Does this suggest model's overprediction of OH? Can the authors discuss nighttime OH levels with averaging intervals longer than 15 min? 7.page 7722, lines 9-10. E. the presence of an OH source unaccounted for or underestimated by the model "at sunrise", such as HONO. How do the authors explain the

model’s overestimation at sunset?

Modelled OH was above the instrumental detection limit only for the first couple of hours after sunset on the night 31 August-1 September. The model is known to have a tendency to overestimate OH concentrations at sunset (see Sommariva et al., 2004 for example). The cause of this overestimation has not been determined.

> 8.page 7722, line 17. Is the uncertainty of the model calculated for the nighttime of the NAMBLEX campaign?

The cited model uncertainty is an estimate calculated using a simple inorganic-CO-CH4 model similar to the ‘‘clean” model used in this work (Sommariva et al., 2004). The uncertainty is similar during the day and during the night. However it should be taken as a lower limit due to the influence of NMHCs. Given the importance of alkenes as a night-time radical source and the fact that the O3 + alkene chemistry (including the radical yields) is less well understood than is ozone photolysis, the overall model uncertainty will be higher at night-time.

> 9.page 7722, lines 26-28. Fleming et al. (2006) suggests that the peroxy radical in-crease with NOx is suggestive of NO3 reacting with hydrocarbons to form peroxy radical. However, this study shows that the increase in [HO2+RO2] with NOx increase is not reproduced by the model including NO3 chemistry. Are the model results completely different if constrained by observed NO3? Or is this positive correlation between NOx and HO2+RO2 attributable to unknown production of HO2+RO2 rather than NO3 chemistry? In Figure 1a and 1b, both observed HO2 and HO2+RO2 show peaks at around 22:00 - 23:00 when NO2 shows a maximum (Figure 7), while the modeled HO2 and HO2+RO2 do not show any peaks. These features could also suggest unknown production of HO2 or HO2+RO2.

The model does not seem to be able to reproduce the observed HO2+RO2 concentration during some night-time NOx events. We do not have an explanation for this, even though it is possible that some unknown chemistry (like unmeasured hydrocarbons) was going on. It must also be stressed that Fleming et al. used the DOAS measurements, which the model underestimated, for their analysis.

> 11.page 7724, lines 20-22. How large is the uncertainty in the CRDS measurements of NO3? Can it be included in Figure 3a as error bars?

The CRDS uncertainty was +/-4 ppt before midnight and +/-1.5 ppt after midnight on 1-2 August. These numbers will be added to the caption of Figure 3.

> 12.page 7725, line 17. Only effect on modeled [NO3+N2O5] (not [NO3]) can be seen in Figure 3a. Is heterogeneous loss of N2O5 with gamma = 0.016 - 0.032 slower than its gaseous reactions with H2O assumed in the model?

This was a typo in the text. The CRDS measured [NO3+N2O5], as shown in the figure. In the base models (gamma N2O5 = 0.032) gas-phase hydrolysis and heterogeneous uptake of N2O5 were comparable. However, with gamma N2O5 = 0.016 gas-phase hydrolysis became the main sink for N2O5.

> 14.page 7726. In addition to NO and DMS, can I2, measured up to 90 pptv in nighttime during the campaign, provide significant sink of NO3 by the reaction between them with a rate coefficient of 1.5x10ˆ-12 cm-3 molec-1 s-1 (Chambers et al. 1992)?

While I2 was sometimes observed at concentrations as high as 90 ppt, during the night it was typically much lower (10-20 ppt, see Saiz-Lopez et al. 2006). Since the rate coefficient of I2 with NO3 is about 20 times slower than the the reaction between NO and NO3. Under these conditions I2 is unlikely to be a significant NO3 sink.

> 15.page 7726, last paragraph. Can a vertical gradient of NO, which is possibly present when considering its emission from soil, also affect the vertical NO3 gradient?

This is likely to be the case. The final paragraph of this section will be modified to take the vertical gradient of NO into account.

> 17.page 7728, line 5. The authors mention that propene, c-2-butene, t-2-butene,

c- 2-pentene, and t-2-pentene are important to produce radicals from O3 + alkene reac-tions. In addition to propene concentrations specified in Table 2, the levels of the other alkene concentrations should be listed. The radical production rate from ozonolysis of propene is calculated to be only <2x10ˆ3 molecule cm-3 s-1, if using ozone and propene concentrations listed in Table 2, the rate coefficient 1.2x10ˆ-17 cm3 molec-1 s-1, and the OH yield of 0.33. This is only <20% of the decomposition rate of Criegee intermediates (1-2x10ˆ4 molecule cm-3 s-1) shown in Figure 5a, suggesting the importance of the other alkenes. Are the other alkenes emitted from anthropogenic activity? Is marine source important for propene?

The average concentrations of these alkenes will be added to Table 2. A discussion of their sources is, however, beyond the scope of this paper.

> 18.page 7728, lines 17-18 and Figure 6a. It seems from Figure 6a that the main destruction of NO3 takes place by the NO3+NO reaction, not by the NO3+ NO2 reaction. 19.page 7729, lines 15-16. It is misleading to mention that NO2 was produced from NO, through its reactions with CH3O2 and HO2 and not to mention NO2 production from NO + O3 reaction.

These are errors and/or typos and will be corrected.

> 20.page 7729, lines 25-27. The ozone decrease by about 30% (or by 10 ppb) cannot be fully attributed to the NO2 + O3 reaction. It is more likely that O3 is titrated by NO during the air mass travel from source region. The NO decrease is influenced by a larger degree by changes in emission and titration, rather than the change in the rate of NO3 + NO reaction.

We agree. The text will be modified accordingly.

> 21.Figure 8. The flux of the CH3O2 + NO reaction should be specified. It is questionable that the HO2 and HO2NO2 are not well balanced at 23:00 (with flux of +12.5), when NO2 concentration did not show a rapid change. Do the CH3SCH2O2 radical

and other peroxy radicals produced from NO3 reactions produce HO2 by their reactions with NO? Is this more important "coupling" between NO3 and HOx chemistry rather than the shown ones?

The flux of CH3O2+NO will be added to Figure 8. CH3SCH2O2 does not produce HO2 in the mechanism used in this work. HO2NO2 was not in balance at 23:00 because at that time the concentration of NO2 was lower than the spike's maximum value (which occurred around 22:30, Figure 7), so HO2NO2 was decomposing to reach a new equilibrium. A sentence explaining this will be added to the text.

$>$ 22.page 7730, line 25. It is unclear to what HO2 and CH3O2 are important.

HO2 and CH3O2 are "important" in the sense that they were the two radicals with the highest contribution to the total peroxy radicals concentration. It will be made clearer in the text.

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