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Atmospheric
Chemistry
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Discussions

Interactive comment on "Radicals in the marine boundary layer during NEAQS 2004: a model study of day-time and night-time sources and sinks" *by* R. Sommariva et al.

Anonymous Referee #2

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General Using a box modeling approach with a highly detailed chemical mechanism this paper examines contributions to radical production and loss during NEAQS 2004. The use of the master chemical mechanism has provided insight into the complexities of NO3 loss processes and highlights the role of organic peroxy radicals (e.g. from the NO3 initiated oxidation of CH3SCH3) as sinks for NO3 at night. Indeed, one important aspect of the study is the prediction of significantly larger concentrations of organic peroxy radicals at night compared to the day. Simultaneous measurements of NO3, organics (such as CH3SCH3) and RO2 would be useful to confirm this prediction. Further, the improved performance of the model at low CH3SCH3 compared to high CH3SCH3 mixing ratios was highlighted and suggested to be evidence for uncer-

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tainties in the parameterisation of the CH3SCH3 oxidation mechanism. Overall, the application of the MCM to the nocturnal dataset has provided some interesting results and should be published. Some comments below should be addressed.

The use of a box model constrained by local measurements of radical precursors and J-values is appropriate for the fast photochemistry describing daytime HOx chemistry, but how suitable is it for nighttime chemistry given that the build up of NO3 during the night is controlled by the slow reaction of NO2 + O3. Could part of the discrepancy between the modeled and measured NO3 mixing ratios be a result of initialization of the model with local NO2 and O3 mixing ratios rather than those prevalent when the air mass was younger. Could this also help explain the fact that the model performed better when photochemically young air masses were encountered ? More information about the approximate age of the air masses sampled on the RB would be useful. In addition, a model without vertical resolution will not be able to reproduce the large variability in NO3 due to its strong vertical gradients in the boundary layer. The authors allude to this by citing Geyer et al, but do not really address this problem sufficiently.

P16650 I'm not sure what is gained from the comparison with the Ehhalt method of calculating OH which, as the authors point out, must perform worse than a box model constrained with the same input J(O(1D)) and J(NO2). The authors also state that only comparison between ambient measurements of HOx and model / Ehhalt expression are useful. Nevertheless, the agreement between the model and the Ehhalt expression was excellent on some days (e.g. 13th-15th) and much worse on others. It appears that good agreement is only achieved when modeled OH follows J(O(1D)) closely. Perhaps the authors could comment on this.

P16652 The most important sources of methylperoxy were OH + CH4 and acetylperoxy reaction with NO. Can the authors identify the major source of acetyl radicals in the model (acetaldehyde ?) and give an idea of the uncertainty associated with their formation rate ?

P16654 On average, the box model overestimated the NO3 mixing ratio by 30-50

P16657 I'm surprised that the rate coefficient for NO3 + CH3SCH3 has an associated uncertainty of 40 percent. Does this uncertainty apply to 1bar and ambient temperatures ?

P16659 There is much discussion of the modeled sinks of N2O5 and of model versus measurement deviations. Why not show any N2O5 data to compare the model output with instead of just a model-model comparison (Figure 10)?

P16663 There is a strong interaction between organic peroxy radicals and NO3 at night. Some of these interactions (especially CH3O2 + NO3) lead to OH formation (initially via methoxy and then via HO2 + NO3). Can the authors indicate what the nighttime OH production rate was and if this is significant (there is already some text on page 16666 which mentions this and which can be expanded).

Typos

P16644, L9 8230;.generally overestimated the measurements by 30-50

P16647 L11 check spelling of Sutugin (also in references)

P16649 L8 quantum yield spectra = wavelength dependent quantum yields ?

P16649 L13 in-situ levels of their sources an sinks (replace levels with strengths ?)

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16643, 2008.

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