

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.

R. Sommariva et al.

Received and published: 27 January 2009

We would like to thank the referees for their insightful comments. We will soon prepare a new version of the manuscript, which will take into account all their suggestions and corrections. Our reply to some of the comments:

REFeree #1 ———

Comment: There should be some clarification of the model timing, discussed on p16649. The timing is constrained by the GC-MS measurements, which refer to 5 minute sampling periods every 30 mins. Do the calculated radical concentrations refer to these 5 minute periods? Were the concentrations of other species averaged over these periods (line 12 is ambiguous). Were the simulations continued for period that

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was long enough to ensure that the transient changes in the radical concentrations, associated with the changes in constrained concentrations, were complete?

Reply: The concentration of the measured species and parameters was averaged over 5 minutes every 30 minutes, so that each model input had the same frequency (that of the GC-MS data). The calculated radical concentrations were not averaged. This point will be clarified in the text of the final manuscript. A 30 minutes interval between two consecutive inputs is enough to allow the radical concentrations to reach a steady state during the day. For the longer lived night-time species, such as NO₃ and N₂O₅, a 30 minutes interval between two consecutive inputs might not always be enough, although we think that most of the time this was not an issue in the present work (as shown by the good agreement between the model and the steady state calculation, see also the following comment and the reply to the comments of Referee #2).

Comment: Two issues are raised in the discussion of the steady state on p 16655: the validity of the steady state approximation (ssa) itself and the contribution to the sink terms of purely calculated species, such as peroxy radicals. The former issue can be assessed by calculating the error in the ssa, using the methodology outlined by Turanyi et al (J Phys Chem, 1993, 97, 163). Only the first order term needs to be considered. Such an analysis would be more convincing than the final sentence in section 4.1.

Reply: We appreciate the reviewer's comment regarding quantification of the errors associated with the steady state approximation. Indeed, the statement at the end of section 4.1 is somewhat vague in this regard. The suggested method of Turanyi et al. [1993] is similar to analysis that we have carried out previously to assess the uncertainty associated with the steady state approximation, which involves comparison of steady state lifetimes calculated with a box model to those predicted from sink rate coefficients for NO₃ and N₂O₅. We will perform this analysis for typical conditions of the NEAQS 2004 dataset and modify the statement at the end of this section to include an estimate of the time needed to approach steady state and of the error at steady state.

Comment: There is extensive discussion of the contributions of different sinks. It would be helped by a figure showing the fractional contributions to the total pseudo first order NO₃ sink rate constant from kNO₃ and kN₂O₅.Keq in eq 4. This could be restricted to the filtered periods discussed on line 21 p16656.

Reply: We will add this information to the final version of the paper.

Comment: The time profiles in Fig 12 (which is inadequately labelled – needs to say which night is which) vary greatly, e.g. there is a decrease in RO₂ in the first figure and an increase in the last. There are substantial dips in the third profile. Can these be rationalised.

Reply: The large decrease in RO₂ concentrations in the first profile is due to a large NO plume, which is shown in the figure, as explained in the text. We will add some detail about the other profiles.

Comment: There is extensive discussion of RO₂ + NO₃ reactions, but their consequences are only hinted at.

Reply: In the final version of the manuscript we will elaborate more on the impact of these reactions on the oxidative capacity of the atmosphere, particularly on their role in the formation of night-time OH, as also requested from referee #2, and on how they can affect the nitrogen budget.

Comment: Some comments on the transit times from the emitting regions would help the reader to understand the processing occurring – e.g. for isoprene and anthropogenic NMHCs on July 16. Minor point: the english needs some attention in this section, e.g. missing definite articles, use twice as abundant rather than twice more abundant etc.

Reply: These points will be addressed in the final version of the manuscript.

REFeree #2 ———

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Comment: 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.

Reply: We think that the time between two consecutive inputs is generally enough to allow NO₃ to reach a steady-state. The comparison and the good correlation between the model and the steady-state calculation clearly suggests that this was the case most of the time during the cruise (see also our reply to the comments by Referee #1). However, we agree with the referee that part of the discrepancy between the model and the measurements could indeed be due to this fact and we will point it out more clearly in the text of the final version of the paper.

Comment: 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.

Reply: We agree with the referee that this is an important point. However, on the basis of the available data, it is very difficult to properly address this issue. The paper makes reference in section 5.2 to the measured boundary layers during NEAQS 2004, which were 100 m deep and generally invariant with time of day. We will add the following statement in section 4.1, following the reference to the vertically resolved work of Geyer et al., to clarify this point: "Vertical gradients within the marine boundary layer, which was observed to be 100 m deep and invariant with time of day, could lead

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to differences between the zero-dimensional model and the measured NO₃ and N₂O₅. The underlying assumption is that the air within this boundary layer is mixed on the time scale of transport and chemical transformation of the relevant species. We note only that such an approach has been successful in describing NO_x loss budgets and NO₃ and N₂O₅ sink budgets in previous analyses of field measurements from the same region (see Brown GRL 2004 and Aldener JGR 2006)."

Comment: 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 $J(NO_2)$. The authors also state that only comparison between ambient measurements of HO_x 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.

Reply: We agree with the referee that the box model should perform better for OH than the Ehhalt parameterization, and the section was not intended as a comparison between the two. Indeed, as we point out, there were no HO_x measurements that could be used to validate either model. The rationale behind this discussion was rather that the Ehhalt parametrization has been used by our group to interpret data from this and previous field campaigns in this region. Therefore, an assessment of the potential error associated with this calculation in an environment other than that for which it was designed (i.e. a forested region in central Europe) is useful: in the absence of measurements, a comparison with a more sophisticated model gives some measure of the reliability of the simpler Ehhalt parameterization.

Comment: 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 ?

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Reply: The most important source of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ in the model was the reaction of acetaldehyde with OH. This reaction is fairly well known, with an associated uncertainty of about 20% (according to the IUPAC evaluation), and the model was constrained to measured acetaldehyde. Other important sources were the reactions of several products of biogenic VOCs oxidation (mostly isoprene), such as methyl glyoxal and methacrolein. The number and the variability of sources of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ was quite large and depended on the conditions encountered during the cruise. A sentence will be added to section 3.2 to include this information.

Comment: P16657 I'm surprised that the rate coefficient for $\text{NO}_3 + \text{CH}_3\text{SCH}_3$ has an associated uncertainty of 40 percent. Does this uncertainty apply to 1bar and ambient temperatures ?

Reply: The uncertainty reported in the IUPAC evaluation is $\text{Dlog}_{10}(k) = 0.15$ meaning that k is uncertain to a factor of 1.41 at 298 K. The rate coefficient for the $\text{NO}_3 + \text{DMS}$ reaction is pressure-independent.

Comment: P16659 There is much discussion of the modeled sinks of N_2O_5 and of model versus measurement deviations. Why not show any N_2O_5 data to compare the model output with instead of just a model-model comparison (Figure 10)?

Reply: Section 5 explores the model sensitivity to the parametrization of N_2O_5 sinks in the model. The approach was to follow the discussion by plotting the models against the 'base' model rather than against the measurements, because the resulting plots are not complicated by the scatter and the outliers in the measurements (see Figure 7).

Comment: P16663 There is a strong interaction between organic peroxy radicals and NO_3 at night. Some of these interactions (especially $\text{CH}_3\text{O}_2 + \text{NO}_3$) lead to OH formation (initially via methoxy and then via $\text{HO}_2 + \text{NO}_3$). 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).

Reply: Although a detailed analysis of night-time OH production is beyond the scope of this paper, more discussion about the formation of OH from the interaction between peroxy radicals and NO₃ will be added to the final version of the paper.

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 ? 16649 L13 in-situ levels of their sources an sinks (replace levels with strengths ?)

These typos will be corrected in the final version of the manuscript.

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

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