

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 #1

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This paper reports a detailed modelling study of OH, peroxy and nitrate radicals during the 2004 NEAQS campaign; emphasis is placed on NO₃. The modelling is based on a detailed box model, with the chemistry drawn from the master chemical mechanism, MCMv3.1. The paper provides good insights into radical sources, sinks and interactions and should be published. The authors should give some consideration, though, to the following issues that, in the opinion of the reviewer, would clarify some aspects of the analysis.

1. 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

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

2. 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.

3. 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.

4. The discussion in section 6 is interesting and demonstrates the range of chemical conditions encountered. Some issues could be examined further:

a) 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.

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

c) 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.

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d) 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.

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

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