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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Diel peroxy radicals in a semi industrial coastal area: nighttime formation of free radicals" *by* M. D. Andrés-Hernández et al.

Anonymous Referee #3

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General comments: This paper describes the diurnal variations of the peroxy radical concentrations during the DOMINO campaign performed in Southern Spain in late autumn. The focus is on the high concentrations recorded during the nighttime. Basically I find that this result is new. The fact that the nighttime concentrations even exceeded the daytime concentrations is interesting. The interpretation is that the NO3 reactions with VOCs are important as RO2-producing processes, but they cannot fully explain the observed RO2* levels. The weak point of this analysis is that important VOCs (e.g., alkenes) are not fully measured; this disabled quantitative assessment of the importance of NO3 reactions in a box model simulation, together with the influence from ozonolysis reactions. The authors would be able to address this issue by assuming presence of several alkenes at reasonable concentrations, and this must be studied. Another concerns are that 1) the uncertainty in DUALER was increased to 60% during nighttime because of high RH, and this would perturb the comparisons of the radical concentrations in the daytime and nighttime, 2) in general impression, the manuscript is sometimes too descriptive, including information and figures which I think unnecessary with respect to the major conclusion (e.g., SO2 analysis in relation to Figure 7, and the last part discussing OH reactivity and Figure 14), 3) somewhat unreasonable analysis is included; e.g., we should not expect clear dependence of RO2* with respect to J(O1D) or its square root when pollution conditions (e.g., concentrations of NOx, HCHO etc.) and radical production rates from non-photolytic source show large variations, and 4) several figures are rough and need revision. The HO2/RO2* ratio analysis should be regarded as qualitative, because sensitivities of both DUALER and HORUS to several RO2 important under the conditions of this field campaign are unknown. Overall I request major revisions responding to the general comments above and specific points listed below before publication.

Specific comments:

1. page 19532, line 8. Add an apostrophe

2. page 19533, line 9. which (not what)

3. page 19533, line 20: the total uncertainty is 1-sigma?

4. page 19534, line 1. Numbers should be given for the title. (also for page 19542, line 3)

5. page 19534, line 5. Additional information of the HORUS instrument should be included. (for example, cell arrangement, potential artifacts etc)

6. page 19536, line 9. Can the low NO concentration be the most important factor resulting in the high RO2* concentrations on 23 November?

7. page 19537, line 8. Fig. 6 is not discussed. It is better removed.

8. page 19537, Discussion on the RO2* dependence on J(O1D) is not adequate be-

cause it is much perturbed by changeable pollution levels (e.g., concentrations of NOx, HCHO etc.) and the radical production rates from non-photolytic source. Fig. 7 is unnecessary; it just shows elevated SO2. Some sentences are descriptive here, and are left unrelated to the main conclusion of this study. Therefore I would recommend deleting this part.

9. page 19537, line 17. r**2 =0.9 is for which day?

10. page 19538. In equation (1), the RO2* concentration is determined by small difference between two large quantities. It is recommended to test [NO]/[NO2] ratio using the observed [RO2*] levels.

11. page 19539, lines 7-9. Is this strong anthropogenic influence a feature found only during nighttime? It seems that the temporal variations in the nighttime are larger than daytime. But they are partly due to the larger uncertainty in the nighttime [RO2*] measured with high RH.

12 .page 19540, lines 5 and 7. November, not December

13. page 19540, line 26. The sentence, starting with "If NO concentrations", describing RO2* loss, is not necessary here, because RO2* PRODUCTION is mainly discussed.

14. page 19541, line 9. How much of NO did the authors measure during nighttime, to make the RO2 + NO reaction active? Maybe the sentence, starting with "The interconversion", should be omitted.

15. page 19541, line 16. Ren et al. (Atmos. Environ., 40, S252–S263, 2006) and Kanaya et al., (J. Geophys. Res., 112, D21312, 2007) should be mentioned studying nighttime radical chemistry in the wintertime in New York city and Tokyo, using HOx observations and model calculations. Also, Kanaya et al. (J. Geophys. Res., 112, D11308, 2007) studied nighttime peroxy radical budget in fall at a clean marine site.

16. page 19542, line 1. Both studies are based. . .

17. page 19542. In the simulation of NO3 chemistry, it is critical that how much NO is assumed to be present in the nighttime (I guess it is below observational detection limit and thus assumed in the model), because the NO3 + NO reaction is fast. The authors mention OH radical source from HO2 (line 19). This also depends on the assumption. The concentration levels of nighttime NO in the model should be clearly mentioned.

18, page 19542, line 17. alkenes

19. page 19543, lines 16 and 18. Here RO2 loss is not included; thus del[RO2]/delt should be written in other way, such as P(RO2). It is better to mention typical values of alpha.

20. page 19544, line 8. Can the authors justify setting k(RO2+RO2) = 4 x 10**-12?

21. page 19544, line 10. What are "those nocturnal periods?" From summary and conclusions (page 19547, line 24), it seems they are all nighttime periods during this field campaign, but here it is unclear.

22. page 19544. The authors need to study how much of olefins, if added, can explain the observed RO2 levels by both NO3 and O3 reactions. If VOCs are added, steady state concentrations of NO3 could be reduced, and thereby the radical production rate, determined by k[NO3][VOC], may not be necessarily increased. The chemical situation is as such? If so, this may support the idea that ozonolysis is important.

23. Page 19546, line 2. What do the authors mean by "VOC controlled?"

24. page 19546, line 10. LIF instruments, with chemical conversion of HO2 to OH by adding NO, like HORUS. . .

25. page 19546, line 15. Measurement conditions (e.g., reaction time and NO concentration)

26. page 19546, line 22. chain length?

27. page 19547, lines 1-15. I do not think any conclusive results are described here. It

is recommended to shorten this part.

28. page 19548, line 24. This 62% is derived with the assumption that k(RO2+RO2) = 4 x 10**-12.

29. page 19548, lines 26-27. "the estimated NO3 production rates" should be "the estimated radical production from NO3 reactions"

30. page 19548, lines 6-10. The "HO2 proportion in the total", between 25% and 45%, seems to be inconsistent with the HO2/RO2* ratio measured to be 0.3-0.6.

31. page 19548, lines 11-12. The RO2 interference in the HO2 measurement is discussed in page 19546, but with parallel discussion of possible underestimation of RO2*. It is not fair that only RO2 interference in HO2 measurement is mentioned in conclusions.

32. The quality of figures should be improved. For example smaller circle symbols should be used in Figures 5, 9, 10, and 11. The top panels for Figure 9 are small and are not necessary.

33. Basically all rose diagrams are difficult to see. It is better to use averages for 8 wind sectors for example (0-45deg, 45-90 deg, etc).

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 19529, 2012.