Anonymous Referee #3

Received and published: 29 September 2012

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.

As we know neither the mixture of alkenes nor their diurnal behaviour during the DOMINO campaign, the number of assumptions required for any simulation reduces the usefulness of the results obtained. In order to address the point made by the referee, a mixture of alkenes was considered on the basis of the data published by Leuchner et al (Atm Env 2010) of the plume from Houston as an example of emissions of industrial-petrochemical origin. Benzene measurements in Houston and DOMINO were used as reference and dimethylbutene, methylpentene and butadiene mixing ratios were normalized to the benzene measured ratios, on the basis of their relation to benzene in the Houston plume, i.e., 18%, 5% and 100% respectively. This implies that benzene and those olefins are assumed to have a common source and /or identical diurnal behaviour. The corresponding RO_2 steady state mixing ratios were calculated by using the O_3 measured during DOMINO and assuming two different radical-radical reaction rates: (a) 1.1×10^{-11} and (b) 7.1×10^{-12} cm^3 $molec^{-1}$ s^{-1}, representing a radical mixture dominated by HO_2+RO_2 (according to the parametrisation by Calvert et al., 2011) or by different RO_2+RO_2 (Sander et al., 2011). The RO_{2ss} calculated were compared with the RO_2^* measured. Except on the 23 November the RO_{2ss} calculated for the measured isoprene and α-pinene represents on average around 4% and 8% respectively of the total RO_{2ss} calculated for the alkene mixture assumed.

The results show that the RO_{2ss} calculated for a plume of these assumed alkene would account on average for 59%±19% and 68%±20% of the RO_2^* observed most of the nights for $k_{RO2+RO2}$ (a) and (b) respectively. Using the same $k_{RO2+RO2}$ the calculation of the $RO_{2\ ss}$ coming from NO_3 can on average account for 47%±16% and 54%±17% of the RO_2^* measured. On the 24 Dec. night both alkenes and NO_3 can only account for about 25% of the RO_2^* measured. These results and the corresponding graphs have been included in the text (sections 3.3.1 and 3.3.2; Fig. 8).

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling M. J., and Wallington T. J.,: The mechanisms of atmospheric oxidation of the oxygenates, Oxford University Press, New York, 2011.

Sander, S. P., Friedl, R. R., Barker, J.R., Golden, D.M., Kurylo, M. J, Wine, P. H, Abbatt, J.P.D., Burkholder, J.B., Kolb, C. E. Moortgat, G. K., Huie, R. E., Orkin, V. L.,: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 17, JPL publication 10-6, Jet Propulsion Laboratory, 2011.

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,

The present work focuses rather on the identification of high nocturnal concentrations of peroxyradicals than on the quantitative comparison of diurnal and nocturnal levels. As stated by the referee (and in the paper) the nocturnal dates are of less accuracy as the detection limit and the total uncertainty increase with the relative humidity which was generally higher in the night than during the day. This has an effect in the noise of the nocturnal signals but it does not significantly affect the main findings of the work as the nocturnal peroxy radicals levels measured during DOMINO were generally well above the detection limit of the instrument.

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),

The text and the figures have been accordingly modified and improved.

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

This part of the text has been removed

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.

The comments of the referee have been taking into account in the revision of the manuscript.

Specific comments:

1. page 19532, line 8. Add an apostrophe

It has been done

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

It has been replaced

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

Yes. It has been added in the text: “the total 1σ uncertainty”

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

It has been done

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

Following text and references have been included:

“A detailed description of the HORUS instrument can be found in Martinez et al. (2010). HORUS is based on the ATHOS instrument, for which a detailed study of possible interferences was performed by Ren et al. (2004). Recently Fuchs et al. (2012) reported on an interference for HO_2 measurements by laser induced fluorescence (LIF), which was calculated to be to at least 30% in conditions with very high VOC and low NO_x. The HO_2 data should thus be considered an upper limit for $HO_2^{”}$.

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

On the 23rd the NO mixing ratios were indeed very low during the day, reaching at the maximum 150 pptv. This is surely one of the factors enabling the measurement of high RO_2^* mixing ratios at the site as RO_2^* and NO are expected to be anticorrelated as result to their reaction forming NO_2. However, no clear correlation between HO_2/RO_2 or RO_2^* and NO was observed during the campaign indicating that the amount and nature of peroxy radical precursors on the air mass arriving at the site is dominating the peroxy radical levels reached.

The text on section 3.2 has been modified to address this point.

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

This figure is considered of interest by the other referee and has therefore not been removed. The text has been modified in order to better emphasise its importance in the discussion of results

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

This part of the text tried to deal with the point indicated by the referee. Although the levels of the pollutants measured (like NOx and HCHO) and the meteorological conditions did not change significantly except on the 27 and 28 November, the correlations between RO_2^* and $j(O^1D)$ varied considerably indicating the existence of a non photolytic source of radicals. However, we do agree that this part is quite descriptive and not closely related to any conclusion of the study and therefore it has been deleted as suggested.

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

This r^2 was obtained for the 23 November, as expected for a day with very clean conditions. This part of the text has however been deleted as suggested above.

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.

This limitation of the PSS calculation is mentioned in the text" "apart from uncertainties associated with the substraction of two terms of similar magnitude in Eq (1)"

The influence of the ratio $[NO]/NO_2]$ has been checked as suggested by the referee, by considering in the correlation only those measurements with $[NO]/NO_2]<10$. The correlation does not change significantly, as included now in the text and shown in the modified figure 8. This rules out this as the cause for discrepancies between RO_2^* measured and calculated.

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.

The anthropogenic influence is observable any time of the day when the wind direction comes from the industrial sector. As states in the text, "the NO and VOC profiles were plume like rather than having a structured reproducible diel pattern over the campaign". In order to emphasise this point the introductory paragraph has been moved to the beginning of section ***3. Results and discussion***.

Concerning RO_2^* temporal variations, as in our answer to the general comments, we agree with the referee in that RO_2^* uncertainty is larger in the nighttime. As stated in the section 2 (Experimental) the total RO_2^* uncertainty for 1 minute averages is about 60% for RH between 70 and 90% , which were relatively frequent during the campaign at night. This can have an influence in the variability of the RO_2^* measured, although not decisive for the determination of the nocturnal RO_2^* mixing ratios which are well above the corresponding detection limits.

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

It has been replaced

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.

The text in section 3.3 has been rephrased.

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.

Bey et al. (2001b) write in their paper "In other situations with lower NOx, ozonolysis reactions dominate the radical initiation. We found that, when a significant interconversion among HOx species appears at night, it is essentially driven by RO_2+ NO or RO_2+RO_2 reactions".

The sentence has been slightly modified for clarification: "Any significant interconversion among HO_x species (i.e., HO_2 and OH) at night is found to be driven by RO_2 +NO or RO_2 +RO_2 reactions."

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.

The results of these papers have been now considered in the text-and the new references have been included,

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

It has been replaced

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.

NO was measured, not assumed and was generally (but not always) lower than the detection limit of a few pptv. The NO measurements are described in more detail in Crowley et al. 2010.

The text has been extended: NO was measured and generally lower than the detection limit of a few pptv. The NO measurements are described in more detail in Crowley et al. 2010."

18, page 19542, line 17. Alkenes

It has been corrected

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.

We agree with the referee. The equation (4) and the left hand side of the equation (5) have been removed to gain in consistency and to only refer to the RO_2 production rate mentioned in the line above. In addition, the text has been extended for clarification:" α varied between ~ 0 (i.e. when NO was high and was responsible for NO_3 loss) to about 0.9 (when the NO_3 loss rates were dominated by reactions with largely non-measured organic trace gases). α was calculated for each time step and used to calculated the production rate of RO_2 for each time step assuming that loss of 1 NO_3 (with organics) leads to 1 RO_2. On average (but depending on which scenario was used for the N_2O_5 heterogeneous loss, see Crowley et al 2010) α was generally between 0.7 and 0.9."

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

In order to address the comment of the referee, literature values for $k_{RO2+ RO2}$ available in the JPL data base (Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation Number 17, 2011) and by Orlando and Tyndall, 2012, have been now considered .

Based on this and as stated above, the RO_2 potentially produced by a supposed mixture of alkenes have been calculated for two different radical-radical reaction rates: (a) $1.1x\ 10^{-11}$ and (b) $7.1x10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, what intends to represent a radical mixture dominated by HO_2+RO_2 or by RO_2+RO_2. The results obtained for NO_3 and the alkenes considered when using $k_{RO2+ RO2} = 7.1x10^{-12}$ cm^3 $molec^{-1}$ s^{-1} have been considered an upper limit estimation (see section 3.3.1 and 3.3.2).

Orlando, J.J., and Tyndall, G. S.,: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, Critical Review, Chem Soc. Rev, 41, 6294-6317, 2012

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.

This actually only refers -as written in the text- to "those nocturnal periods with available NO_3 data". We cannot make any calculation in nocturnal periods without NO_3 measurements.

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.

In the calculation used in this work, the RO_2 radical production rate does not depend on the stationary state level of NO_3. The NO_3 concentration does not appear in the equation (6). The question of the referee may be answered by thinking about what concentration of reactive organics would reduce the NO_3 lifetime to that observed. This is covered in Crowley et al, and we state a few ppb, if they react with a rate coefficient of ~10^{-13} cm^3 $molecule^{-1}$ s^{-1} (like butadiene).

In Crowley et al 2010, it says:

"Hydrocarbon emissions related to the petrochemical industry, including unsaturated VOC such as 1,3-butadiene (Roberts et al., 2003) which are reactive towards NO_3 could then be responsible for the short NO_3 lifetimes. In this scenario, the source of the peroxy radicals observed on this night would be reaction of unsaturated hydrocarbons with either NO_3 or O_3. In this context note that NO_3 reacts at least a factor 10 more slowly with unsaturated, petrochemical-related hydrocarbons (e.g. the rate coefficient for NO_3 with 1,3-butadiene is 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) than with RSC (reduced sulphur compounds) so that mixing ratios of several tens of ppbv of the alkene would be necessary to explain the short NO_3 lifetimes."

In the case of ozonolysis we do not have the advantage of a chemical O_3 lifetime with respect to reaction with olefins and the rates of olefins with O_3 are very variable. Therefore a simple calculation (like for NO_3) is not possible. However, the effect of a potential mixture of alkenes have been investigated (see comments above)

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

As the NO values are close to the detection limit most of the nights, the factors controlling radical abundances depend on the sources of VOC precursors and their chemistry. The use of VOC controlled can lead to confusion as it is often used in the situation in which VOC are in much lower concentrations than NO. The sentence has been rephrased for clarity:

"It can be concluded that the radical chemistry was mainly determined by the abundance, nature and chemistry of the VOC acting as peroxy radical precursors in the air mass."

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

It has been added

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

It has been modified

26. page 19546, line 22. chain length?

It has been corrected

27. page 19547, lines 1-15. I do not think any conclusive results are described here. It is recommended to shorten this part.

The text has been modified.

28. page 19548 (it is actually on page 19547), ***line 24. This 62% is derived with the assumption that k(RO2+RO2) =4 x 10**-12.***

The text has been modified with the new $k_{RO2+RO2}$ considered (see comments above)

29. page 19548 (actually is 19547), ***lines 26-27. "the estimated NO3 production rates" should be "the estimated radical production from NO3 reactions"***

It has been changed

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.

There was some confusion between the values given in the section 3.4 and in the conclusions. The corresponding text has been corrected.

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.

The text of the abstract and conclusions have been modified to consider the comment of the referee.

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.

Most of the figures of the manuscript have been modified in the revised version in order to address the comments of both referees.

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).

Most of the figures of the manuscript have been modified in the revised version in order to address the comments of both referees.