

General comments

This paper presents peroxy radical measurements made by PERCA (HO₂+RO₂) and LIF (HO₂) at a coastal site in Spain that was influenced by a variety of air-masses under varying meteorological and chemical conditions. The dataset presented is novel and includes measurements of nocturnal peroxy radical concentrations alongside NO₃ concentrations (such measurements are rare in the literature) in air-masses (such as the industrial plume) that are understudied. The paper itself is rather confusing to follow, however, it isn't well planned and in places poorly written. Many of the figures fail to show any significant radical trend or features that are noteworthy and there are few conclusions drawn. There is potential to gain new knowledge on atmospheric chemistry processes from this dataset, however, revisions are required to the manuscript before this can be achieved. Some suggestions for improvements are provided below:

Specific comments

Section 3.1 rather than give the general peroxy radical features during the campaign as indicated by the title to this section instead provides an overview of the meteorological conditions and air-mass sectors encountered. It is difficult to gauge how important a role meteorology vs air-mass type plays in controlling radical concentrations, maybe it is difficult/impossible to separate the two influences? Maybe they are unimportant? Providing some average radical concentrations encountered in each air-mass identified in the text would benefit this section.

General features of peroxy radicals during the campaign are summarised in Fig.2 using the 23.11.2008 as example. Both the degree of cloudiness as proxy for radiation and temperature are the meteorological variables which play a role in the peroxy radical features. The structure and content of section 3 has been modified in order to address the comments of the referee. The analysis of the relative importance of those meteorological parameters is emphasised now in the text.

As the radical mixing ratios present very significant diurnal variations, providing an average radical concentration for each air mass is not very informative without considering other influencing variables (cloudiness, time of the day, etc)

Figure 3 is quite confusing; it would help if the different air-mass sectors were added to all wind-roses presented throughout the manuscript so the reader could identify which wind direction was associated with which air-mass. Also, rather than colour in accordance to date it would be more useful to colour according to meteorological conditions.

The figure has been improved and the air mass sectors have been included to gain in clarity.

Why are the 2nd, 6th and 7th Dec identified separately in Figure 3 but not Figure 4? These dates are not highlighted as significant in the text.

The day 2 was highlighted for being the only sunny day in the last period of the campaign, the others for being of marine origin. As they are not further discussed in the text, these are not extra highlighted in the new figures.

Section 3.2 discusses daytime radical trends, and the potential of biogenic precursors, such as isoprene, to increase radical concentrations. Mono-terpene concentrations are given for one day when high radicals were observed but not for another day; the concentrations of mono-terpenes for both days should be included to aid discussion.

Sections 3.1 and 3.2 have been extensively modified. The comment of the referee has been incorporated by modifying the corresponding part of the text as follows:

“Furthermore the measured monoterpenes comprising alpha-pinene, limonene, 1, 8-cineole and camphor did not generally show any clear diel cycle. However, on the 24 November the mean mixing ratio of the sum of monoterpenes was 37 ± 25 pptv, in contrast to 23 ± 13 pptv measured on the 23 November. This is about twice the level measured on all other clear days (Song et al., 2012).

Concerning b) RO_2^* and isoprene diel variations agreed reasonably, and nocturnal maxima were often accompanied by α -pinene peak concentrations as on the 24 November at midnight. These nighttime maxima suggest the release of monoterpenes from the storage pool of the needles from the pine and eucalyptus forest into a shallow nocturnal boundary layer.”

The impact of NO on radical concentrations should also be discussed. One of the most revealing plots in the paper is Figure 6 which highlights that when NO is low and OH reactivity is high, RO2 radicals are also high and perhaps demonstrates that there is not a clear radical signature associated with specific air-masses instead it is the chemistry that is important and it would benefit the paper if further discussion on the chemistry controlling radicals were included.

In such a complex environment we do not expect to get a clear radical signature associated with specific air masses. VOC originating from different sources may provide different mixtures of peroxy radical precursors which will be involved in the in situ production of the peroxy radical measured. However, it is expected that the known chemistry is still identifiable, i.e., that NO and RO_2^* can hardly coexist since they react with each other, and that the high OH reactivity is indication of processing of the high organic load present, which in turn provides organic radicals.

The text in section 3 has been modified in order to further highlight this idea:

“No definite air mass dependence is expected in such a complex environment. VOC originating from different sources may provide different mixtures of precursors leading to the in situ production of the RO_2^* measured. However, general patterns related to known chemistry (e.g. anti-correlation of NO with RO_2^* due to their common reaction, high RO_2^* at high organic loads accompanied by high OH reactivities, etc) are expected to be identifiable. In that context, two features can be highlighted during DOMINO (Fig.4)

Two features can be highlighted during DOMINO:

- a) highest daylight mixing ratios were associated with air masses within the continental sector, which in turn were linked to clear sky conditions, i.e., most favouring photochemical radical production, like at the beginning of the campaign, and,
- b) enhanced nocturnal RO_2^* were observed mainly when the site was impacted with air masses coming from the urban sector transporting emissions of the industrial area of Huelva.

Concerning a) the RO_2^* maximum was considerably higher on the 23 and 24 November (47 ± 10 and 35 ± 10 pptv respectively) which reached the highest temperatures of the campaign ($T_{\text{max}} 22^\circ\text{C}$ and 18°C respectively). This apparent positive relation with the temperature has been interpreted in previous work as an indirect temperature effect in the formation of

radicals, driven by variations in the emission of radical precursors of biogenic origin with the temperature. On the 23 November isoprene increased steadily to 120 pptv in the afternoon (16:00 UTC), a value about a factor 10 higher than the average during the whole measurement period. Song et al. (2012) interpret the delay in the isoprene maximum respect to the temperature maximum as an indication of isoprene not being emitted from the local forest but transported from other more distant forests and orange groves in the NE direction.

Furthermore, the measured monoterpenes comprising α -pinene, limonene, 1, 8-cineole and camphor did generally not show any clear diel cycle. However, on the 24 November the mean mixing ratio of the sum of monoterpenes was 37 ± 25 pptv, in contrast to 23 ± 13 pptv measured on the 23 November. This is about twice the level measured on all other clear days (Song et al., 2012).

Concerning b) RO_2^* and isoprene diel variations agreed reasonably, and nocturnal maxima were often accompanied by α -pinene peak concentrations as on the 24 November at midnight. These nighttime maxima suggest the release of monoterpenes from the storage pool of the needles from the pine and eucalyptus forest into a shallow nocturnal boundary layer. “

When calculating [RO2] from the deviation from photostationary state a number of reasons for disagreement are stated but there is limited discussion past this. How closely were the PERCA and NO_x instruments located? There seems to be a difference in the [RO2]_{calc.} / [RO2]_{obs.} ratio depending on clear sky vs other conditions. Could the PERCA have a lower sensitivity for different RO2 types that may have been more prevalent in air masses experienced under non-clear sky conditions? Could the NO₂ measurement suffer from an interference from NO_y species that could artificially increase the calculated RO2?

The inlets for the DUALER and the NO/NO_x and J_{NO₂} instruments were very close together at the same height, on top of the measurement platform, so that the disagreement cannot be attributed to differences in the air mass sampled.

There is no indication of interferences in the NO₂ measurement. As described in Crowley et al, 2010, 2011):

“NO and NO₂ measurements were made with a modified commercial chemiluminescence detector (CLD 790 SR) originally manufactured by ECO Physics (Duernten, Switzerland). The quantitative detection of NO₂ is based on its photolytic conversion (Blue Light Converter, Droplet Measurement Technologies, Boulder, Co, USA) to NO, which was subsequently detected in the CLD (Kley and McFarland, 1980). The detection limits for the NO and NO₂ measurements were 6 pptv and 8 ppt, respectively for an integration period of 1 s. The total uncertainties for the measurements of NO, NO₂ were determined both to be 10 %, based on the reproducibility of in-field background measurements, calibrations, the uncertainties of the standards and the conversion efficiency of the photolytic converter.”

In Hosaynali et al. (ACP, 2011) potential interfering species are discussed and summarized in Table 5:

Table 5. Absorption cross section of potentially interfering species.

	ASC at 390 nm	ASC at 395 nm	ASC at 400 nm	NO ₂ equivalent (7 pptv)
NO ₂	5.90×10^{-19}	6.10×10^{-19}	6.50×10^{-19}	–
BrONO ₂	2.90×10^{-20}	2.60×10^{-20}	2.30×10^{-20}	142
ClONO ₂	9.10×10^{-22}	7.60×10^{-22}	6.40×10^{-22}	4538
CINO	6.86×10^{-20}	5.97×10^{-20}	5.13×10^{-20}	60
CINO ₂	4.75×10^{-21}	–	3.27×10^{-21}	869
BrNO ₂	1.60×10^{-19}	1.50×10^{-19}	1.40×10^{-19}	26
HONO	2.40×10^{-20}	6.00×10^{-21}	–	172
PAN	–	–	–	–
HNO ₃	–	–	–	–
Methyl nitrate	–	–	–	–
Ethyl nitrate	–	–	–	–

Hosaynali Beygi, Z., Fischer, H., Harder, H. D., et al., Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state, *Atmos. Chem. Phys.*, 11, 8497–8513, 2011. doi:10.5194/acp-11-8497-2011

None of these species is expected to be in the concentrations required to cause a significant interference in the PSS calculations.

Concerning the PerCA, as discussed in section 3.4, although the response to a wide range of radicals has been proved to be very similar (Ashbourn et al., 1998), if the load of organic peroxy radicals having very reduced wall losses in the reactor compared to HO₂ is very high in the mixture sampled, RO₂^{*} can significantly be underestimated. However, this was not normally the case within the time periods selected for the PSS calculations.

Furthermore, the intercomparison of four J_{NO₂} filter radiometers at the site during DOMINO showed deviations related to their positioning as some of them were partially affected by artifacts due to trees shadowing or reflecting local surfaces. The J_{NO₂} sensor on top of the structure (used for the analysis of the present work) was recommended to be used as reference for radiation intensities at the top of the structure for short lived species. However, for species of several minutes lifetime, the use of albedo values derived from literature for an open pine forest with sand on the ground were recommended. The sensor was calibrated before and after the campaign.

The PSS assumption between species is only valid when O₃ and solar radiation levels assure that the NO-NO₂ conversion occurs with a time constant of a few minutes. The dependence observed under clear and non clear sky conditions is interpreted to be dependent on the uncertainty derived from J_{NO₂} short term variations in the calculation of the PSS radicals.

If only sunny days at the maximum irradiation time are considered, PSS calculated values remain generally lower than measured. This might be an indication that NO₂ photolysis over a large area did not vary as suggested by the J_{NO₂} values on the top of the structure. As indicated by Mannschreck et al., (2004), the NO₂ photolysis in the air masses transported within the forest canopy is substantially reduced due to reduced light penetration. The mixture of air parcels from within the forest and above might affect the PSS.

This part of the text of the manuscript has been accordingly extended.

Minor comments / queries / technical corrections:

Pg 19531, In 9: I don't think Whalley et al., 2011 is a relevant reference here

Whalley et al., 2011 reports on underestimation of OH sources in tropical forests in Borneo. The major uncertainties in the chemical models, which cannot simulate HO_x measurements without considering an additional source for OH different from isoprene oxidation accompanied by a HO₂ sink mechanisms are discussed in detail.

Therefore we consider this reference to be relevant in the introduction.

Pg 19532, In 18: R already defined earlier in the text

It has been removed.

Pg 19533, In 13: Remove 'and detector'

This refers to the fact that there are 2 detectors and each detector was calibrated twice per day

Pg 19536, section 3.2: Suggest additional sub-sections 'Clear-sky conditions' and 'Cloudy conditions'

The section 3 and corresponding subsections have been extensively modified to take into account diverse the comments of both referees.

Pg 19536, In 18: '(16:00 UTC)' does this refer to the time isoprene peaked? This should be made clear in the text.

The sentence has been modified for clarification "isoprene increased steadily and reached a 120 pptv maximum in the afternoon at 16:00 UTC, a value.....".

Pg 19537, In 21, 22: what might have been affected by combustion emissions? [HCHO]or [RO2]? This section needs re-wording for clarity.

The combustion emissions of ships might have affected the composition of the air masses in terms of HCHO and this in turn could have caused the deterioration of the RO₂^{*} with J_{O1D} correlations although the level of measured carbonyl species did not increase substantially respect to the days where the correlations were reasonable. The observed SO₂ peaks on those days indicate/confirm the arrival of ship emissions to the measurement site.

However, this part of the text has been deleted following the suggestion of the Referee 3 (see comment 8)

Pg 19537, In 25: Fig.9 is referred to before Fig. 8 in the text.

All the plots in the text have been modified and the numbering of the new plots in the text has been checked.

Pg 19540, bullet points (a) and (b) need further detail: O3 alkene reactions are also a direct source of peroxy radicals. Only formaldehyde forms HO2 by reaction with NO3; longer-chain aldehydes form RO2 radicals. A description of reactions of O3 with alkenes is repeated on pg 19542 and should be removed to avoid repetition once the bullet points are improved.

The text has been re-structured to gain in clarity as suggested by the referee.

Pg 19541, In 8: NO₂ rather than NO_x?

In their paper Bey et al. (2001b) refer their simulations to NO_x levels rather than to NO₂ or to NO levels considered independently.

Pg 19541, In 23, 24: The factors controlling radical concentrations during the daytime during the PUMA campaign are not relevant for this section of the manuscript that is dealing with nighttime chemistry.

The sentence has been modified for clarification: “Heard et al. (2004) reported high OH and HO₂ radical levels in winter both during day and night. The corresponding modelling analysis of the radical budget (Emmerson et al., 2005) indicates that HO₂ and RO₂ formation at night involved primarily the reaction of O₃ with alkenes, whilst the termination of RO₂ was dominated by formation of peroxyacetyl nitrates.”

Pg 19542, In 1 and 2: Further discussion on the chemical regimes (e.g. NO_x levels) encountered during the different campaigns mentioned is needed to support the differences in radical nighttime production.

The text has been modified to address this and other comments of both referees:

“Only a few observations of nighttime peroxy radicals can be found in the literature and most of them have been measured in summer (Mihelcic et al., 1993; Kanaya et al., 2002; Platt et al., 2002; Martinez et al., 2003) or fall (Kanaya et al., 2007a). Furthermore, RO₂^{*} in winter has been mostly measured in remote areas (Carslaw et al., 1997; Penkett et al., 1999; Fleming et al., 2006a,b,) and some of those RO₂^{*} data are not corrected for the relative humidity interference reported by Mihele et al. (1998, 1999) and therefore not comparable with the present measurements. Within a seasonal study in an urban area (NO_x typically 10-30 ppbv) in England (Birmingham), Heard et al. (2004) reported high OH and HO₂ radical levels in winter both during day and night. The corresponding modelling analysis of the radical budget (Emmerson et al., 2005) indicates that HO₂ and RO₂ formation at night involved primarily the reaction of O₃ with alkenes, whilst the termination of RO₂ was dominated by formation of peroxyacetyl nitrates. In contrast, HO₂ mixing ratios measured in New York by Ren et al.(2006) were lower by a factor of ~15, with nocturnal values generally <0.3 pptv. NO_x/VOC ratios were higher in New York than in Birmingham with NO mostly 25-40 ppbv in the night. In addition the radical production was slowed down by the low temperatures in New York down to -25°C . Modelling studies underestimated both diurnal and nocturnal HO₂. HO_x budget analysis showed that HO_x production was dominated by the reaction of O₃ with alkenes in the night.

In contrast Geyer et al. (2003) attributed 77% and 53% of the RO₂ and HO₂ nighttime production to the reaction of NO₃ with terpenes, and 12% and 47% respectively to ozonolysis. This study is based on measurements from a semiurban atmosphere in summer with high nighttime levels of NO₂ and O₃ (5 -15 ppb and 60-10 ppb respectively).”

Pg 19543, In 7: ‘determined’ rather than ‘calculated’?

The sentence has been rephrased to be more precise as:

“Calculated from the observed NO₃ concentration and its production term (k_{NO₂+O₃}[NO₂][O₃])”

Pg 19542, In 17: ‘alkenes’

It has been replaced

Pg 19543, In 5: define 'kloss'

The text has been extended:

“ k_{loss} is a first order term (s^{-1}) which includes all the losses of NO_3 except the gas reaction with organics, i.e., the direct reaction with NO , the indirect loss by aerosol uptake and dry deposition of N_2O_5 and the dry deposition of NO_3 .”

Pg 19543, equation 5: what is the value of alpha that was used?

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 calculate the production rate of RO_2 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 between 0.7 and 0.9”

Pg 19546, In 16, 17: The HO2 interference suffered by LIF instruments could, at most, explain a ratio of 1. Another explanation is required for ratio higher than this.

As stated in the text: “The effective chain length used for the calculation of the RO_2^* might change significantly with the set up as result of peroxy radical losses, especially HO_2 , before the amplification zone, which depend on the material and shape of the reactor. This can lead to an underestimation of the total sum of radicals. Laboratory experiments using different HO_2 + RO_2 mixtures indicated that for 50% HO_2 in the air mass, RO_2^* is 15% underestimated by the DUALER reactor used for DOMINO”

If the load of organic peroxy radicals (with low wall losses) is very high compared to HO_2 , RO_2^* can significantly be underestimated, and this underestimation, together with the artificially increased $[\text{HO}_2]$ by the LIF interference can occasionally lead to $[\text{HO}_2]/[\text{RO}_2^*]$ ratios higher than 1.

The text has been extended to clarify this point:

“There is no information available about the composition of the sampled peroxy radical mixture. Therefore, no correction was applied to the RO_2^* data. If the load of organic peroxy radicals with low wall losses is very high compared to HO_2 , RO_2^* can be significantly underestimated. This, together with the artificially increased $[\text{HO}_2]$ due to the LIF interference can occasionally lead to $[\text{HO}_2]/[\text{RO}_2^*]$ ratios higher than 1 in very polluted air masses. Overall the analysis of the $\text{HO}_2/\text{RO}_2^*$ ratio should therefore rather be considered as qualitative.”

Pg 19546, In 27, 28: Please clarify if a correction has been applied to the data to account for this.

No correction was applied as there is no available information about the proportion and composition of RO_2 in the total RO_2^* measured except from the comparison between DUALER and HORUS, which as mentioned seems to be problematic. This information is

therefore only added to be kept in mind when interpreting discrepancies. The text has been accordingly modified (see above).

Pg 19548, In 2: Why are there no nocturnal OH measurements? Was OH below the limit of detection of the instrument?

As previously discussed in another paper of this Special Issue (Sörgel et al., 2011), OH measurements during DOMINO showed an interference and should therefore be considered an upper limit of OH. During nighttime the OH signal was dominated by the interference.

Sörgel, M., E. Regelin, H. Bozem, J.-M. Diesch, F. Drewnick, H. Fischer, H. Harder, A. Held, Z. Hosaynali-Beygi, M. Martinez, and C. Zetzsch, Quantification of the unknown HONO daytime source and its relation to NO₂, Atmos. Chem. Phys. Discuss., 11, 15119–15155, 2011.

Pg 19548, In 10: Remove ‘though’

It has been removed

Figures 9 and 12: Y axes need to be re-scaled for j(O1D), RO2* and HO2/RO2* ratio

The scaling of these plots was justified because the maximum values are not important but the general comparison between days or wind directions. Scaling to the maximum doesn't add any information but prevents to see the order of magnitude of the smallest concentrations.

Most of the plots of the manuscript have been however modified to address the comments of both referees.

Figure 9: Wind roses are too small.

Most of the plots of the manuscript have been modified