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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 #2

Received and published: 24 August 2012

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

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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. 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. 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.

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. 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.

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

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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?

Minor comments / queries / technical corrections:

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

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

Pg 19533, ln 13: Remove 'and detector'

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

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

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

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

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.

Pg 19541, ln 8: NO₂ rather than NO_x?

Pg 19541, ln 23, 24: The factors controlling radical concentrations during the daytime

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during the PUMA campaign are not relevant for this section of the manuscript that is dealing with nighttime chemistry.

Pg 19542, ln 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.

Pg 19543, ln 7: 'determined' rather than 'calculated'?

Pg 19542, ln 17: 'alkenes'

Pg 19543, ln 5: define 'kloss'

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

Pg 19546, ln 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.

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

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

Pg 19548, ln 10: Remove 'though'

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

Figure 9: Wind roses are too small.

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

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