

Interactive comment on “Ozone production in remote oceanic and industrial areas derived from ship based measurements of peroxy radicals during TexAQS 2006” by R. Sommariva et al.

Anonymous Referee #2

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This is an interesting paper in which the PERCA method, deployed on a ship, is used to measure the sum of peroxy radicals in a range of environments, from clean(ish) marine to heavily polluted (Houston Ship canal). At times very high levels of total peroxy radicals are seen, despite a very high NO_x environment, but there are very high levels of VOCs to fuel the production radical oxidation. The measured total peroxy radicals and other parameters were used to calculate the net rate of ozone production, and compared with measurements of O₃ and other species.

Specific points

Does the PERCA instrument respond to halogenated species, for example high levels

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of CINO₂ were observed in this region, and halogen species can oxidise NO to NO₂ and generate a response.

Was the chain length determined for HO₂, which is expected to make up a significant amount of the total HO₂+RO₂? (50% is mentioned later in the paper)

I didn't see any values of the chain length (CL) actually given – please provide for the species for which calibration was undertaken.

Perhaps surprising is that the data collected did not require a correction for relative humidity given the previous literature on this and the corrections for humidity that have been published for PERCA previously. These corrections in the past have been quite large, and this is a humid environment. The other instrument mentioned (Andres-Hernandez et al reference) was aboard an aircraft, where the calibration and relative humidity dependence might be expected to be very different (sampling mode, temperatures and pressures). I am pleased that there is a humidity correction for the Scintrex. I think more discussion is required here, as there is a great deal of confusion in the literature about the humidity correction (or not) of PERCA instruments. The main argument given here is that the zero air chain length for CH₃O₂ and the ambient (high humidity) chain length for CH₃COO₂ are the same and so no humidity dependence is necessary. I am not sure that this is a valid and logical conclusion. Could it be the case that the CLs are different for dry air for the two species, and that it happens that the CL for humid CH₃OCO just matches that for dry air CH₃O₂? Was the instrument calibrated as a function of humidity for CH₃COO₂ and CH₃O₂? Or can laboratory (or field) calibrations for these two species from previous studies as a function of humidity be used to estimate the dependence. I am surprised that the CL for CH₃CO would have no humidity dependence. Although not determined here, the HO₂ CL would also be expected to have a humidity dependence (and later this is assumed to be 50% of the total species measured). It is appreciated that these are difficult things to measure, but given the humid environment of this study, it is important to be as detailed as possible.

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The dual channel instrument helps to mitigate against varying background levels of NO₂ and O₃ which give a response in the PERCA instrument. In the very polluted periods, what was the relative change in NO₂ signal observed in the Scintrex between radical measuring and background measuring modes (i.e. dynamic range of the modulations, which will depend on the CL, and concentrations of NO_x, O₃ and radicals).

The nighttime levels of 134 ppt are interesting, and are considered in the paper to be likely related to night-time oxidation of O₃ or NO₃ in the entrance to the Houston Ship canal. What was the level of NO in the ship canal at night – one might expect this to be quite high due to local fresh sources of NO_x emissions (were there any), and this may keep NO₃ levels down due to the NO₃+NO reaction? I think a table showing the typical levels (of e.g. NO) could be a useful addition – as well as that of supporting data (e.g. NO₃ if measured). The very high HO₂+RO₂ levels at night are very interesting but there is insufficient data or information presented to get much insight into the chemistry responsible for this.

Page 23122, line 25, rather than “atomic oxygen” it would be better to say O(3P) ground-state atomic oxygen, as O(1D) is also atomic oxygen.

Page 23123. HO₂ was measured at the La Porte site, and so in line 13 something could be said about an experimental value of the HO₂/(HO₂+sum RO₂) ratio. This could be used rather than relying solely on a model calculation for this ratio? OH was also calculated in the model, but again, this was measured at the La Porte site and so some reference to actual values rather than just model values could be discussed.

Page 23124. Line 4 and up to section 4.2, the MCM has a lot more detail than just a general rate constant for RO₂+NO. It is true that for RO₂ where k is not known, a generic value is used, but for those R where a value is known, it is present in the MCM. How different are k for RO₂ where k is known? The approach here seems too simplistic given that k data do exist for a number of RO₂ species. Especially given that the value of N(O₃) is sensitive to the rate constant for RO₂+NO.

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Page 23128, what is the source of isoprene. Biogenics are listed, but is there an anthropogenic source of isoprene, particularly given the very rich mixture of VOCs at high levels that were observed? High correlations of 1-3 butadiene and isoprene have been observed in the past. Page 23129. Line 15. Measurements at La Porte in 2000 are compared with the measurements from this paper, but there is no reference given, e.g. for the HO₂ measurements. Wasn't OH measured as well?

I would like to see more discussion of the assumption of HO₂ being approximately 50% of the total HO₂+sum(RO₂). HO₂ and the sum HO₂+RO₂ have been measured at quite a few other urban areas, and so there is further information that can be used to support this or otherwise.

Also, Figure 10 displays a large range of modelled and measured values (not explicitly said which measurements agree very well with the model presumably this statement means for all four parameters in the 4 panels?), and the conclusion that there is very good agreement (line 25 on page 23129) is not obviously supported by this figure. Plots of modelled versus measured would enable this statement to be made with more confidence, and the current discussion is very inadequate. What is meant by very good agreement? Ratios need to be given, and the errors in the measurement and the model considered in order to be quantitative about what very good agreement means. This would enable the conclusions given in section 5 to be made with more confidence.

Page 23129, line 29, a reference needs to be given for the P(O₃) calculation from HO₂ measured in the 2000 campaign, or is this done in this paper?

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