

Interactive comment on “Peroxy Radical Measurements by Ethane – Nitric Oxide Chemical Amplification and Laser-Induced Fluorescence/Fluorescence Assay by Gas Expansion during the IRRONIC field campaign in a Forest in Indiana” by Shuvashish Kundu et al.

Anonymous Referee #1

Received and published: 11 February 2019

This manuscript details the results of an intercomparison carried out in the field which compares total peroxy radicals using a chemical amplification system with HO₂* (which comprises HO₂ and a fraction of RO₂ radicals) measured by the FAGE technique. Although we may expect HO₂* and total RO₂ to be well correlated, the comparison presented here is the detected sum of ambient RO₂ by two instruments which do not measure different RO₂ radicals with the same efficiency, and so is a tricky undertaking. The authors have employed a variety of models with differing chemical mechanisms to

predict the composition of peroxy radicals present and from there predict the ratio of total RO₂ : HO₂* for comparison with the observations. I think on the whole, the approach taken to compare these two observations has led to a meaningful comparison and has demonstrated the performance of the new ECHAMP instrument in the field. I recommend publication once the following comments have been addressed:

Abstract: One concerning result is that the XO₂:HO₂* ratio is periodically less than one, which the authors themselves note is not possible and must indicate a problem with one or both instruments. A ratio of 0.8 is mentioned in the abstract, but no comment on this low ratio is given until the final pages of the manuscript. I suggest the authors are more upfront about this problem and comment on ratios <1 indicating instrumental issues in the abstract and conclusion.

Pg 3, line 18: 'Measurements of OH by laser-induced fluorescence technique can be affected by a sampling related interference which can exceed the actual concentration of OH.'. This interference is very much dependent on the FAGE instrument design. There are several FAGE instruments in operation that do not observe an OH interference and so this statement needs to be qualified to make this clear.

Pg 3, line 25: '~90%' is slightly misleading. In many of the FAGE instruments tested, α is not as high as 90% for the β -hydroxy peroxy radicals; α was as low as 17% in the cited 'Whalley et al., 2013' paper.

Pg 7, line 16: please provide the typical Li used for the ambient measurements. SI, section S3: Could the authors comment on whether the loss rate of radicals is solely dependent on residence time? Does the shape of the sampling cross and the PFA tees (the sampled air has to flow around corners) impact the loss rate? This could perhaps be determined if the transmitted radical signal was plotted against residence time in the 4 lengths of tube. An intercept would indicate additional losses in the cross piece.

Pg 7, line 23: The authors discuss the impact of alkyl nitrate and alkyl nitrite formation on the sensitivity of ECHAMP to individual RO₂ species, but could the authors also

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comment on the expected sensitivity of ECHAMP to RO₂ species which are generated from alkene + NO₃ reactions, so contain an NO₃-adduct? ROxLIF instruments are expected to have a low sensitivity to these types of RO₂ (Whalley et al. ACP, 2018). If a similarly low sensitivity for these RO₂ is expected in ECHAMP, could the authors discuss how this may influence the measured vs modelled ratio during the night?

Pg 8, line 20: Could the authors make it clear which conversion efficiencies were measured and which have been estimated.

Pg 8, line 22: The authors reference the Fuchs et al., 2011 work on RO₂ interferences in FAGE instruments. ' α ' is very much dependent upon the specific FAGE instrument and experimental conditions used, however. Using α determined using another FAGE instrument would likely bias the HO₂* model measurement comparison. The authors need to make it clear how α was estimated for the RO₂ species not experimentally tested with the IU-FAGE. Specifically, how was $\alpha = 0.7$ derived in equation 5 on page 14, line 21?

Pg 12, line 12, fig 3: Add the limit of detection of XO₂ to the figure. Also make it clear in the figure caption which instrument measured HO₂+RO₂

Pg 12, section 3.3: The authors acknowledge that comparing the 30 min averaged ECHAMP measurements to a single FAGE measurement made during the 30 minute bin is not ideal. I worry that this approach could introduce bias into the comparison, given that the peroxy radical concentrations will generally be increasing throughout the morning hours and then decreasing during the afternoon and evening. Are the FAGE HO₂* measurements made at the midpoint of each 30 minute bin? Does the gradient XO₂ vs HO₂* vary if the FAGE measurement falls at the start of a 30 minute bin? I think the authors need to explore the robustness of this averaging approach used for the ECHAMP data to satisfy the reader that the two measurements are comparable at the times they are taken.

Page 13, line 6 - 8: the authors report the highest XO₂:HO₂* ratio on days when

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isoprene and ethene concentrations were most elevated. This is unexpected, given the high sensitivity of FAGE to alkene-derived RO₂ species. Could the authors comment on this finding?

Page 13, line 10: The data in figure 5 has already been binned and then averaged over 9 days. Does the linear regression on the figure 5 data provide a reduced uncertainty relative to the data presented in figure 6? Errors on the fit should be included. I may have misunderstood, but don't both linear regressions use the same data (just one if further averaged into a diurnal)? Does the change in the regression slope as the data is averaged further suggest that the binning approach is biasing the correlation? Page 13, line 23: Although I appreciate that the authors do not know the reason why the measurements diverge on the 22nd, the possible explanation 'a transient interference in the HO₂^{*} measurement when sampling ambient air..' is rather vague. Could the authors elaborate on what they think this transient interference may be or what it may be related to?

Pg 13, line 25 –Pg 14, line 4: I suggest moving this paragraph to the start of section 3.3. It is important that the α of two instruments to different RO₂, and how the ratio is expected to change as ambient RO₂ types vary, is set out at the beginning of this section. Section 3.3: in general, there is a lot to consider when comparing HO₂^{*} and XO₂ measured and modelled. The ratio varies with RO₂ type present and calibration differences also need to be considered. A table detailing the measured HO₂^{*}, XO₂ and XO₂:HO₂^{*} and the 4 modelled HO₂^{*}, XO₂ and XO₂:HO₂^{*} on the individual days and campaign average would help to clarify the text.

Figure 4: The caption on the figure is obscuring the top x-axis

Figure 5: There does not seem to be a measured ratio for each 30 min point? Between the hours of 4 – 8, there are only 3 points?

Figure 4 – Figure 8: It is unclear whether the ECHAMP data has been corrected for the calibration comparison or not? This should be clear in each figure caption

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1359>, 2019.

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