Atmospheric
Chemistry
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Discussions

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 #2

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Review of "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 S. Kundu et al.

The paper describes the measurement of peroxy radicals (HO_2, RO_2) with two different techniques. The LIF-FAGE technique by Indiana University was originally designed to measure solely HO_2 radicals by chemical conversion with NO to OH, which is then

detected by LIF. However, different experimental studies (including a study by authors of this paper) have shown that the technique is also sensitive to specific RO2 radicals with different sensitivities when the instrument is tuned for maximum HO2-to-OH conversion efficiency. The measured quantity is called HO2*. The new ECHAMP technique, a chemical amplifier using ethane instead of CO, is designed to measure the sum of HO2 and all RO2 species. Due to different amplifier chain lengths for different radical species, the resulting quantity XO2 is a proxy for the total peroxy radical concentration. Comparing the measurements by the two techniques sounds like comparing apples with oranges. The present paper demonstrates that such a comparison can be done in a meaningful way, if the instruments are carefully characterized and additional information about the peroxy radical speciation is available (here from box model calculations constrained by measured trace gases). The direct comparison of the conceptually different calibration methods (photolysis of water vapor vs. photolysis of acetone) and the field comparison show that the measurement techniques yield consistent data within the specified experimental uncertainties. These findings suggest that the two described methods can also be used for meaningful tests of atmospheric chemistry models, if the measured peroxy radicals (HO2*, XO2) are appropriately simulated by the model by taking RO2-specific weighting factors of the instruments into account. This requirement should be explicitly stated in the conclusions. Furthermore, recent progress in the measurement of HO2 by LIF-FAGE instruments should be mentioned. It has been shown that the interference by RO2 can be avoided by reducing the concentration of NO that is used for conversion to OH (e.g. Fuchs et al., 2011; Whalley et al., 2013; Feiner et al., 2016; Tan et al., 2017).

Overall, the paper is thoroughly and well written. It is suitable for ACP, but could have been submitted to AMT as well. The authors and editor should consider whether the paper should appear as a "Technical note" in ACP. I recommend publication after the following minor comments have been addressed.

Minor comments

(1) Introduction: as the topic of the paper is an instrumental intercomparison, I suggest to provide a more complete list of previous intercomparisons. For instance, Mount et al. (JGR vol.102, no.D5, p6437, 1997), Zenker et al. (JGR vol 103, no Dll, p13,615, 1998), Ren et al. (JGR vol 108, no D19, 4605, 2003), Fuchs et al. (AMT 5, 1611–1626, 2012), Onel et al. (AMT 10, 4877–4894, 2017), Sanchez et al. (Atmos. Env. 174, 227–236, 2018).

(2) In the experimental section, the authors point out that the use of ethane instead of CO offers advantages. Safer operation is obviously a plus. However, I don't understand why the choice of ethane reduces the sensitivity on relative humidity. Is this due to the reduced chain length? Is there evidence for water influence on the OH+CO reaction? To my knowledge, the water effect has been attributed to the reaction HO2+NO (e.g., Mihele et al. 1999, Butkovskaya et al., 2007). Why is the amplification factor lower, if ethane is used? Another advantage of ethane could be mentioned, although it is probably not relevant in a forest environment. Ethane avoids possible interferences from ClOx, which can lead to amplification in CO/NO systems (Perner et al., J. Atmos. Chem. 34, 9, 1999).

(3) Page 9: "For this project, [O3] was instead quantified by the ECHAMP CAPS NO2 sensors after conversion to NO2 by reaction with excess NO". A few details should be explained: is the flow in the calibrator laminar or turbulent? Where is the NO added (upstream, downstream of the calibrator)? Is the NO2 measured after it has been passed through the FAGE cell or is it measured in the air that bypasses the inlet of the FAGE cell? How much NO is added and how large is the resulting NO2 mixing ratio?

(4) Page 9, line 18: is the water vapor correction based on laboratory characterization of the LIF-FAGE instrument, or on theoretical calculations using published data for the OH fluorescence lifetime and cross sections for quenching?

(5) Model constraints: was atmospheric CO measured? Which formaldehyde data were used (GC-FID or DNPH)? I see large gaps in the measured time series of NO

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in the first half of the campaign. Was NO (when available) used as a constraint, or was NO calculated by the model using NO2 as a constraint? The box model was constrained with 30 minute average mixing ratios. As peroxy radicals show a strong non-linear dependence on NO, using 30 minute average values as constraint can lead to systematic bias in the model results. I would like to see the model results that are averaged to 30 minutes after the model has been run at the much higher time resolution of the NOx measurements.

(6) Figure 4 - 6: Is it meaningful to adjust the result of the linear regression for the calibration difference (section 3.1)? This would only make sense, if the calibration would be done for the same peroxy radical speciation as encountered during the measurement days in the field.

(7) Figure 1: what is the scale of the map?

(8) Figure 3: what is causing the noise and spikes on the NO data? Is it measurement precision or atmospheric variability from nearby NO sources?

(9) Figure 3 and 4: vertical dotted lines = midnight ?

(10) Figure 5: the shown error bars (1sigma precisions) seem too large compared to the variability of the shown data.

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