The results from this study are very interesting and could have wide reaching implications, not only for the understanding of atmospheric oxidation mechanisms, but also for the OH measurement community. The authors state that the possible interference from ROOOH decomposition in the FAGE apparatus could account for high OH concentration measurements around the globe from multiple groups. I am keen to understand more about the experiments and hence have some questions.

* Could the authors clarify their idea for the mechanism (chemical and/or physical) of the decomposition of the ROOOH in the FAGE inlet?

The decomposition of ROOOH in the FAGE is not chemical; we suspect it to be a physical process probably due to decomposition caused by the fast variation of temperature within the shock wave during gas expansion, occurring when the mixture enters into the FAGE from high to low pressure. The ROOOH is stabilized by only around 120 kJ/mol with respect to \( \text{RO}_2 + \text{OH} \), the decomposition to \( \text{RO} + \text{HO}_2 \) is slightly less endothermic (115 kJ/mol, see Assaf et al., IJCK DOI: 10.1002/kin.21191 (2018)), so one could also expect decomposition into \( \text{HO}_2 \). However, this cannot be tested in our set up, and well-designed experiments (for example in simulation chambers) will be necessary to test the mechanism for more details.

* No two FAGE instruments are alike. Instruments where interference signals have been categorized have a range of different inlet lengths and inlet pinhole constructions (e.g. Faloona et al. (2004), Martinez et al. (2010) and Rickly and Stevens (2018)). Could the authors comment on the possible effects of FAGE instrument design on this interference?

Yes we agree, the effect will probably not be the same for all FAGE systems. It is similar to the RO2 interference on HO2 measurements: each FAGE system has to be tested. We think the best test would be that the concerned groups re-analyze their data from earlier field campaigns in remote environments that have shown unexpected high OH concentrations: the reaction of \( \text{RO}_2 + \text{OH} \) could be integrated into their models and they could check if the disagreement between modeled and measured OH concentration correlates with the modeled ROOOH concentration. A “sensitivity” for each FAGE could be estimated from these tests, even though it is clear that this can be only relative, as currently nothing is known about the removal rate of ROOOH, and thus the resulting steady-state concentration.

* Were there any experiments conducted with different inlet pinhole diameters and inlet lengths to try and elucidate the effect on the possible ROOOH decomposition?

No measurements were conducted using different pinholes. As explained above, it is expected that this interference is instrument / pinhole / pump-speed / etc., specific and needs to be tested for each configuration used in the field. We think it is now clear (or even was already clear before) that all FAGE measurements in low NO environments must be carried out with the scavenger method. Our finding can give a possible explanation for the earlier unexplained measurements, and perhaps an advantage can be taken from this interference to use it for investigating the chemistry of ROOOH, just as the RO2 problem in HO2 detection was turned into a kind of advantage for quantifying RO2 (see for example: Whalley LK, Stone D, Dunmore R, et al. Understanding in situ ozone production in the summertime through radical observations and modelling studies during the Clean air for London project (CleanFlO). *Atmos. Chem. Phys.* 2018;18:2547-2571).
* Could the authors comment on the losses of ROOOH in the system? Are there expected losses on surfaces (e.g. the FAGE inlet pinhole)? Also, Müller et al. (2016), hypothesised a loss pathway for the ROOOH species via the reaction with water dimer. Will this be important under the experimental conditions presented here?

No information on wall losses or reaction with the water dimer can be given due to the complexity of the production of the trioxide in our system. All we could do was to estimate by modeling what ROOOOH concentration had probably been reached the FAGE. As we discuss in the manuscript, we think the model gives an upper limit, and in reality we have less ROOOH entering the FAGE due to wall losses and also to a decreased formation due to diffusion within the cell. But this is very difficult (if not impossible) to quantify. Also, our photolysis laser (quadrupled YAG) does not have a very homogeneous profile, i.e. there are some hot-spots. And as ROOOH is the product of a radical-radical reaction, this can make some difference in the final ROOOH concentration. Anyway, the goal of this paper is not a precise quantification of the interference, but rather to propose a new idea to solve some old questions.

* The manuscript mentions the importance of OH scavenger experiments to determine whether there is a production of OH in the FAGE inlet (Novelli et al., 2014; Rickly and Stevens, 2018). Were similar experiments conducted here?

We do add scavenger all the time: the isoprene, butane or CH₄ are all added in such high concentrations that all initial OH has reacted after a few 100 ms and we measure the remaining signal.

The flow tube experiments were conducted at high relative humidity (12000 ppmv) and with low flow rates to promote the formation of ROOOOH over subsequent photolysis laser shots. I have a few questions about the chemistry and apparatus used. I think it would be useful information for the SOM for those in the FAGE community that might be interested:

* It has been hypothesized that RO₂ radicals generated in the OH initiated oxidation of unsaturated hydrocarbons could form complexes with H₂O molecules (Clark et al., 2010; Clark et al., 2008; Khan et al., 2015). Could the authors comment on the use of high [H₂O] concentrations during these experiments and the possible effects this might have on the, already complicated, isoprene + OH oxidation mechanism?

With 12,000 ppm of H₂O we have a relative humidity of around 50% at 20°C: this is the highest humidity that we can currently reach with our set-up. The H₂O concentrations and relative humidity during the remote rainforest campaigns were certainly much higher. We have not carried out experiments under different H₂O concentrations, because we need as much H₂O as we can to make as many OH radicals as we can. Again, we think well-designed simulation chamber studies might be able to shine some light onto this question.

* Was the effect of varying the initial conditions of the experiment investigated (e.g. [H₂O]₀, [O₃]₀ and [OH]₀)? Was an alternative OH source used (without H₂O)? Did the authors try other unsaturated hydrocarbons/terpenes such as pinene, as in Rickly and Stevens (2018)?

As mentioned, we did not change H₂O because the way the experiments are carried out requires very high OH concentration in order to generate high RO₂ concentration in order to allow competition between VOC and RO₂ after a few laser shots. Therefore, we have added
the highest H₂O and O₃ possible. We have changed the VOC concentration in order to have 2 different conditions:

i) High VOC concentration: no competition happens between the reaction of OH with the VOC and RO₂: in this case nearly all OH is consumed by reaction with VOC and high RO₂ concentrations are still formed, including the product of self-and cross reactions

ii) Low VOC concentration: to have competition between the reaction of OH and the VOC leading to formation of trioxides

No other source of OH radicals was used. We have tested butane and methane because Assaf et al (2018) have measured the HO₂ yields for the reaction of these compounds with OH and have shown that the HO₂ yield in the case of methane is high, i.e. the expected ROOOH yield is low, while for butane the inverse is the case. Isoprene has been tested, because it is so important, even though nothing is known about the reaction of OH with the corresponding peroxy radical. Other VOCs are planned to be investigated in the future.

* Were more than two OH probe laser powers used in the determination of the absence of laser induced photolysis?

No, only 2 probe laser powers were tested: the highest possible, and a very low one, just high enough to get an exploitable S/N ratio. No energy in-between the two has been tested. To further test for a possible signal due to photolysis, we have also tested two different repetition rates of the excitation laser (see Figure S4)

* The flow experiments were conducted in a regime where the photolysis beam did not fill the entire diameter of the flow tube. Could the authors comment on the possible impact of diffusion in and out of the photolysis region during the 20 s residence time?

As explained above, diffusion has not been taken into account in the model, but would probably lead to a lower ROOH concentration: considering diffusion leads to a decrease in average RO₂ concentration, and therefore the next pulse of OH radicals will see less RO₂ and more VOC (because fresh VOC from outside the photolysis volume diffuses into the photolysis volume). As mentioned, the given ROOOH concentration is an upper limit. On the other hand knowing the exact ROOH concentration in the photolysis reactor is not very interesting or important to check for the possible interference in field campaigns, as the modeled ROOOH concentration directly depends on the removal rate of ROOOH in the atmosphere. And nothing is known about this number, i.e. an uncertainty range of a factor of 10 is certainly possible. The conclusion from the current work can only be that ROOOH is a very good candidate to explain the high OH concentrations observed in remote environments, but that’s it, we cannot extract any more detailed numbers from our experiment.

* It would be useful to see an OH decay trace with pre-photolysis signal to judge the increase in the background level signal. Is the observed rise in the ILIF plateau above the S/N (and limit of detection) of the background signal, for example? Does the ILIF plateau value extend to the subsequent OH probe pulse? Was a run without an organic completed, to show the ILIF plateau base case in the absence of RO₂ (and therefore ROOOH)?
The pre-photolysis signal is the final signal of the preceding laser pulse, i.e. the value at 400 ms of pulse 1 corresponds to the signal 100 ms before pulse 2. The change in background is not visible by the eye (see figure 1 of the manuscript). Remember, only $\approx 4 \times 10^{-4}$ of ROOOH decomposed to OH radicals in our FAGE, i.e. the increase with respect to the initial OH signal is very small. However, the increase is statistically significant. Carrying out a run without VOC will not be helpful, as the decay in zero air is too slow ($\approx 5 \text{ s}^{-1}$) to allow for a precise determination of the plateau, i.e. the LIF signal does not decay fast enough between two laser pulses. However, experiments with high VOC concentrations (see figure S5 and S7) clearly show that, when there is no competition for OH radicals between VOC and RO$_2$ anymore, the background does not increase, even though the concentrations of all other products from cross- and self-reactions remain more or less the same. This test is much more useful to show that in the absence of ROOOH the plateau does not increase.

Finally, I have a couple of comments about the conclusions:

* The contribution of ROOOH to [OH] measured with FAGE instruments depends highly on the production rate and loss processes for these molecules – both of which are highly uncertain at this stage.

We fully agree: re-analyzing data from earlier field campaigns should be very interesting. As we show in the supplementary data, figure S9, the ROOOH steady state concentration scales linearly with the removal rate used in the model.

* The interferences measured in the lab based ozonolysis experiments conducted by Novelli et al. (2014) and Rickly and Stevens (2018), have been shown to be removed upon addition of a reaction partner for Criegee intermediates (sulphur dioxide (Novelli et al., 2017) and acetic acid (Rickly and Stevens, 2018)). This suggests that stabilized Criegee intermediates decomposing in the FAGE inlet may be responsible in these cases.

Maybe the addition of reaction partners for Criegee intermediates suppresses also the decomposition of Criegee within the reactor, and thus formation of OH and RO$_2$, and thus formation of ROOOH. But again, re-analysis of these data under this new aspect should be very interesting.

* The experiments conducted by Fuchs et al. (2012) did show a 30 – 40 % higher measurement of OH in a few cases, involving methyl vinyl ketone and toluene, which is indeed interesting. However, these runs were carried out under comparable NO conditions to other runs, for example containing isoprene, earlier in the campaign.

A close inspection of Table 2 in the Fuchs paper shows that on days with a slight disagreement between FAGE and DOAS the NO concentration has a tendency to be lower than on the other days. And as our model has shown, there is a very strong increase in ROOOH concentration at NO concentration below around 100 ppt, i.e. a difference of less than a factor of 2 in NO concentration might make a big difference in the interference. But again, this is only a hint and an idea; it should be very interesting to re-analyze these data sets under the aspect of including the reaction of RO$_2$ + OH into the models.
References:


