Please find below our answers to the reviewers: in black is repeated the comments of the reviewers, in blue are our answers and in *blue italic* are the changes applied to the manuscript. Following especially the many good comments of the anonymous reviewer, we have changed many details in the manuscript, not all listed in the answers. For this reason, we have attached at the end the new manuscript with all changes tracked and visible.

Answer to Hartwig Harder

ROOOH: the Missing Piece of the Puzzle for OH measurements in low NO Environments The authors study an interference of the OH signal measured by an instrument based on the FAGE technique in a lab experiment where they photolysis a mixture of Ozone, water and isoprene or other VOCs with a varying number of laser pulses. After decay of the OH produced a non-zero signal remains, which increases with the number of photolysis laser pulses. The authors attribute this signal to trioxide (ROOOH) formed from recombination of RO_2 and OH and claim this to be the interference observed by other LIF-FAGE instruments. They further analyze the potential abundance of ROOOH in the atmosphere by using the UM-UKCA global model.

The paper is concisely written. The idea of the potential role of ROOOH in contributing to the observed FAGE-LIF background OH as well as in the atmosphere is interesting and worth publication. However, previous work is not adequately taken into consideration and contradicts some of the conclusions. Also, the authors base their conclusions on a less than 10% signal increase observed in their experiment and do not explain the remaining 90% of their signal. What is the cause of 90% of the signal?

The remaining 90% of the signal is due to stray light from the excitation laser as well as ambient light entering through the photolysis window and the nozzle. This has now been explained Page 4. The conclusion of this work is based on the fact that we observe an increase in this background signal only under conditions where RO_2 will partially react with OH, under any other condition the background is stable.

I recommend publication only after major revisions resolving this and the following issues.

P2 L19, 23, 28…..: "real" OH

The OH at the time of fluorescence is real. Suggestion: Consider 'atmospheric' vs 'internally formed' or 'background' instead.

We have changed "real' into "atmospheric"

P2 L20 ff *Even though in practice this method is highly uncertain, given the generally low OH concentrations (and the resulting low S/N ratio) and the high temporal variability of OH radical concentration, the high OH concentrations observed in the different field campaigns seems to arise from "real" OH and not from the photolysis of other species.*

I would rather say the concentration of the background signal matters, not the signal of the OH concentration. The background signal found during HUMPPA 2010, Novelli et. al 2014, has a sufficiently high S/N, see. Fig. 14 in their paper demonstrates that the background signal observed does not show a square dependence on laser power.

Page 2 we have added:

This was also confirmed by Novelli et al (Novelli et al., 2014a) who observed a strong background during HUMPPA2010 with good S/N ratio, allowing to unequivocally exclude photolysis being at the origin of the background signal.

P2 L27: …the generation of OH radicals during the expansion into the FAGE cell… Please give citation and specify how do you define 'during the expansion' ? i.e. Do you refer to the cluster formation, shock front, evaporation phase ?

Indeed, we do not know how exactly the ROOOH leads to formation of OH radicals in our FAGE system. We have shown that is it NOT due to photolysis, but for the rest, we don't know. It could be thermal decomposition within the shock front, however one would expect mostly (or even exclusively) a decomposition to HO_2 and RO, given that this decomposition path is around 10 kJ mol^{-1} cheaper. According to Müller et al (sup data), the thermal decomposition of ROOOH is very slow and not a major fate of this species under atmospheric conditions. Also, they estimate the exclusive reaction products being CH_3O + HO_2 and CH_3OH + O_2. It is therefore rather unlikely that the ROOOH decomposes thermally within the shockwave, or even in the photolysis reactor, leading to a low steady-state concentration. Maybe the decomposition is heterogeneous, either on the nozzle or on the wall of the FAGE cell. This would mean of course even more that different FAGE instruments will show different sensitivity to ROOOH. We have added at the end of the experimental part:

No clear explanation can be given on the mechanism of this OH formation: a homogeneous decomposition within the shock wave of the expansion is unlikely, because the pathway leading to CH_3O and HO_2 is thermodynamically more favoured (Assaf et al., 2018a). Therefor a heterogeneous decomposition on the walls of the FAGE cell or the entrance nozzle are more likely. The residence time of the gas mixture between entrance nozzle and detection beam can be calculated from the volume of the cell (0.25 l) and the gas flow (3 l min^{-1} STP) to around 1 sec, leaving ample time for collisions with the reactor walls.

P2 L 33 : *This technique was used for the first time in 2012 in a forest in California (Mao et al., 2012)* While all the credit of the using an OH scavenger mechanism should go to the group of Brune, Hens et. al 2014, reported measurements from a campaign in 2010. Novelli et al 2014 reported from campaigns conducted in 2010 (Finland & Spain), 2011(Germany), 2012 (Germany).

In order to keep to credit of having "invented' this technique and still being precise, and given that your paper appeared 2 years after Mao et al., we have changed the sentence to the following:

The use of this technique was **reported** for the first time in 2012 showing results for a field campaign in a forest in California (Mao et al., 2012). It led to the identification of a large fluorescence signal following scavenging of all ambient OH radicals, corresponding to up to 50% of the total OH concentration.

P3 L1: *fluorescence signal following scavenging of all ambient OH radicals, corresponding to up to 50% of the total OH concentration.*

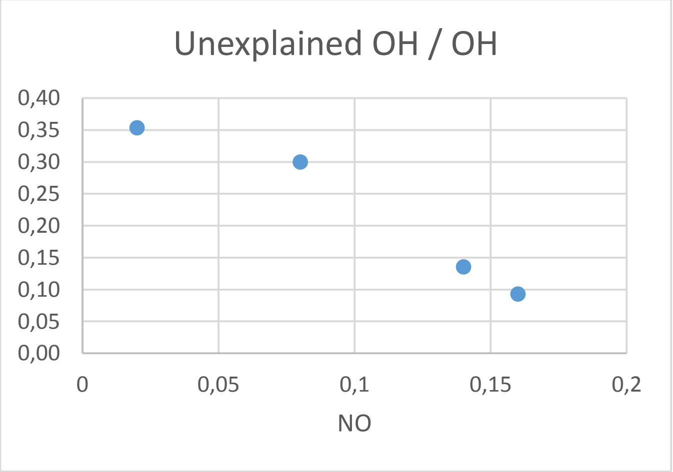
Stating a relative contribution of the interference to a molecule that drops during nighttime close to zero is not meaningful. During nighttime, the relative contribution of the background signal is well above 90%. While during daytime it has been reported to be anything between 10-90%. I recommend to give equivalent OH mixing ratios/concentrations.

We have now linked this information to the paper of Mao and not as a general statement on observed interferences.

P3 L13ff: *Fuchs et al. (Fuchs et al., 2016) could not confirm this source: well below the detection limit of the FAGE.*

Not all LIF FAGE groups reported a significant interference, like the FAGE of the Jülich group, which does not observe a strong background signal in ambient air measurements in the first place. Extrapolation from instruments which do not see an interference in ambient air to those which do might not be valid.

We do not claim that all FAGE instruments behave the same. This has now been emphasized on several occasions, and also in the abstract. However, there are hints that the Jülich FAGE also suffers from some interference in the OH measurements. First there is the still unexplained high OH measurements from the PRIDE campaign with the disagreement correlating with decreased NO concentration, in line with the present hypothesis. Second, they have recently (Tan et al. 2017) used for the first time a pre-injector prototype and have observed some unexplained OH, even though some technical issues made the measurements uncertain. However, taking from the 6 values in Table 2 only the 4 values at low NO, then the unexplained OH (divided by the total OH concentration to "normalize" to overall photochemical activity) increases with decreasing NO, also in line with the current hypothesis of ROOOH being source of OH in FAGE instruments.



Finally, as we already replied to Winiberg: "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."

But: the reaction of O_3 + alkene does not lead to an interference in their FAGE that is high enough to explain these observations. But again, we do not say that the reaction between O_3 and alkene cannot be a source of interference in your FAGE.

P3 L21ff: *Following several years of interference studies in various environments, recent work from W. Brune's group (Feiner et al., 2016) concluded that the interference observed in their FAGE system; a) ;b);c); & d)*

P3 L28 In this work we present convincing experimental and modelling evidence that this sought-after species is the product of the reaction between RO_2.

This might be true for the PennState instrument, though not for the Background of the Mainz instrument. a)-d) refer to the point given in the paper.

Yes, point a-d refer only to the observations from the Brune group (line 22: in **their** FAGE system), we do not state anything about the background observed with your instrument. It is of course possible that there are different sources of interference for different instruments and for different conditions. As mentioned already, this has now been emphasized at different occasions.

a) *was due to a rather long-lived species because the interference persists into the evening,* Persistence into the night could be due to the persistence not just of the interfering species but of its precursors. Like O_3 and terpenes, which are also temperature controlled and their emissions extend into the night.

b)
c) it strongly increased with increasing $O(^1D)$*, hence it must somehow be linked to photochemistry* The strong correlation with O^1D is not the case, see Novelli et al. 2014, 2017; Mallik et al. 2018 the correlation is stronger with other parameters, like temperature, inverse of the square of the water vapor concentration, O_3, concentration of some of the terpenes. Novelli et al. 2014, 2017 demonstrates the increase of the OH background signal during nighttime, when OH and $J(O^1D)$ are very low.

d) the species responsible for this interference was linked to a low NO_x *oxidation pathway, because the extent of the interference steeply decreased with increasing NO concentration*. There is no indication of an NO dependence on the abundance or production rate of the background OH in Novelli et al. 2017 or Mallik et al. 2018.

Indeed, Novelli et al. 2017 or Malik et al 2018 did not show any dependence of the background signal on NO. However, comparison of the OH background signal measured during the HUMPPA-campaign (Figure 8 in Novelli et al. 2014) with the NO concentration data (Figure 9 of Hens et al. 2014) show, that during the last days of the campaign (August 7 and 8), when NO is extremely low, the ratio of atmospheric OH to background OH is much higher than in the beginning of the campaign, when NO increases above 100 ppt (unfortunately, OH data are not complete, especially during the "high" NO periods). For example, on August 2 and 5, NO reaches 200 ppt and the background makes only roughly 50% of the total signal, while on August 7 and 8 nearly 100% of the OH signal is due to background and

NO is well below 100ppt on these days. But again, only a detailed re-analysis of the data taking into account the reaction of RO_2 + OH can show if part of the background signal might be correlated with the turnover of the reaction of RO_2 radicals with OH.

P5 L17 *This can be interpreted as interference…*

What about other possible second order isoprene oxidation products?

In order to distinguish between the products of the reaction of RO_2 + OH and other oxidation products, we have carried out experiments for isoprene and butane with increased VOC concentration, but the same OH and O_3 concentrations: under these conditions the mixture contains nearly equal concentrations of all other oxidation products, except for RO_2 + OH. Under these conditions, the background is stable (Figure S5 and S7, now in the main text). From this observation we conclude that the rise in background is due to the product of RO_2 + OH and not from any other second order isoprene oxidation product.

P6 Fig2

While the increase of the signal with the number of pulses is consistent with this hypothesis, I find it disturbing that the signal remaining with just one pulse is already above 90% of the interference signal observed (0.051 according to Fig. 2) and is actually larger by an order of magnitude than the increase measured when the number of pulses is increased to 40 (which produces a signal of 0.056 according to Fig. 2). This makes it seem likely that there is an underlying interference not due to anything produced by the photolysing laser pulse, but present in the gas mixture even without photolysis. No explanation is provided by the authors for the large signal after just one photolysis pulse. Also, no information is given about the signal observed when no photolysis pulse is applied, or when no VOC is added. Since ozone mixing ratios used of 600 ppb are high compared to ambient air, it should be stated whether there is a signal in humid air containing just VOC and ozone, or even just ozone, with and without a single photolysis pulse.

As explained above, the signal present already even at the first photolysis shot is due to laser stray light and ambient light entering through photolysis window and pinhole. As given already in our answer to Winiberg, a signal with only O_3 is not useful because the OH signal does decay much too slow to reliably measure the background. Again, the most convincing test is the experiment with high VOC, showing that the background does not increase under these conditions. We have now added in Figure 1 (now figure 2) the pre-photolysis signal as well as a zoom on the background signal for the different pulses.

P10 L 9ff *…the observed disagreement between model and measurements…*

The model result does not reflect the abundance of the observations of the OH background signal reported by Novelli et al 2014 & 2017 as well as Mallik et al. 2018. The relative contributions observed is largest during summer in the boreal forest of Finland 2010, larger than on Cyprus 2014 or southern Germany 2012.

We think that in saying: ”**If** occurring also with a comparable intensity in other FAGE instruments, it **can** be high enough ….” we are careful. To more emphasize this fact, we have added :

The intensity or even the occurrence at all can depend on the design and working conditions of the FAGE set-up, which is different for different groups. However, if occurring also with a comparable intensity in other FAGE instruments, this interference might be high enough to explain numerous observations obtained with FAGE instruments from other research groups including: ……

In any case, we do not state that the observations with your FAGE can be explained by ROOOH (even if they might).

P10 L 13 ff : *Variability of interferences observed in field campaigns*

This might be valid for the PennState group, but the data reported by Novelli, etc do not support the dependence on $J(O^1D)$ and low NO_x conditions.

This is what we say: "…. such as observed by the group of W. Brune"

Answer to anonymous referee

The paper is an interesting one, and suggests that ROOOH, present in the atmosphere from the reaction of RO_2 with OH, can somehow generate OH within the inlets and fluorescence chambers of instruments that use laser-induced fluorescence to determine OH levels in the atmosphere. Results are shown for the Lille system, where a signal is seen from a mixture of isoprene and an OH precursor ($O_3/H_2O/hv$) when the RO_2 + OH reaction is initiated within a flow-tube that is sampled by the FAGE instrument. The paper then discusses that ROOOH present in the atmosphere may act as a source of interference for OH measurements in order to explain some previous model/measurement discrepancies.

The results are interesting, and I agree that ROOOH decomposition within the inlet or cell of the instrument should certainly be considered as a possibility for generating some artificial OH signal. Nowadays FAGE instruments by some groups are operated with a scavenger inlet, which would enable any OH from ROOOH to be allowed for, so this finding is more relevant to previous field measurements without a scavenger inlet where the signal may partly be from an interfering species.

The range of experiments performed certainly seems to show that there is OH signal at long times (which grows after exposure of the OH reactivity flow tube to multiple photolysis laser shots) which is only present for the longer chain RO_2 (butane and also isoprene as the VOCs) where the ROOOH yield is expected to be larger. The RO_2 + OH reaction until recently was largely overlooked as important in the atmosphere, but work by the Lille group, and more recently from a US group, have measured the rate coefficient. For $R=CH_3$ there is still a significant disagreement in the rate coefficient (the disagreement was initially worse, but a revised rate coefficient from Lille brought the values closer to each other). Lille have studied RO_2+OH now for a number of R, and have measured the HO_2 yield, which decreases for larger R (Assaf et al., IJCK 2018), providing evidence that the yield of ROOOH increases as R gets bigger. Recently the yield of CH_3OH from CH_3O_2+OH was quantified experimentally to be small (there had been some theory on this reaction regarding the CH_3OH yield).

Although there is clearly a signal in the Lille FAGE system at long times which grows further with the number of photolysis shots and which may derive from the ROOOH product of RO_2+OH, it is surely a considerable stretch to say that this constitutes convincing evidence that the disagreement between model and measurements seen in previous field campaigns (under relevant conditions like low NOx forests where ROOOH is expected to have higher concentrations) is due to interference by the decomposition of ROOOH, and that ROOOH reflects the missing piece of the puzzle. There are several parameters which are unknown or poorly known, the most important of which is the concentration of ROOOH in the atmosphere, another is the fraction of ROOOH which may decompose within the fluorescence inlet/cell (which will be instrument dependent). In order for the atmospheric model in this paper to generate something that would generate a relevant level of OH, a decomposition fraction is assumed (based on an estimate from the Lille lab. data) and the loss rate of ROOOH was varied over 3 orders of magnitude and a value chosen to give a level of OH similar to atmospheric levels.

Another major point is even if ROOOH in the atmosphere were to constitute an interference that needed consideration, different FAGE instruments behave differently when it comes to interference formed in the inlet / fluorescence cell. This depends on a variety of factors including the residence time inside the instrument, inlet length from sampling pinhole to fluorescence cell, cell geometry (size, distance from walls), fluorescence imaging volume (e.g. single pass or multi-pass as the case here) and others like the pumping rate. For the case of HO_2 interference from RO_2 for example, the residence time and the geometry of the sampling/cell system has been shown to control the level of interference shown. This needs to be stated in the paper.

We completely agree that the effect might be very different in different FAGE systems. It was already mentioned in the beginning of the discussion that the results are only valid for the UL-FAGE (Page 10: If occurring also with a comparable intensity in other FAGE instruments, it…..), but we have now emphasized this fact on several occasions (Page 4, line 9ff and Page 7, line 26ff) as well as in the abstract.

Concerning the mechanism of the decomposition of ROOOH within the low-pressure FAGE cell, it is not clear what the mechanism is? It is colder (initially in the expansion) and the number density is low so what is the source of the energy? Is it a homogeneous or a heterogeneous process? For a gas phase process the energetics (Assaf et al., IJCK 2018) seem to suggest if decomposition occurs this would be via RO + HO_2 rather than RO_2 +OH? As the energetics are known can the ratio of RO_2+OH to RO +HO_2 be calculated? Is the ROOOH decomposing at all in the OH reactivity flow-tube (which is at atmospheric pressure – presumably any OH is then very quickly removed but could decomposition sustain a small steady-state level).

Indeed, we do not know how exactly the ROOOH leads to formation of OH radicals in our FAGE system. We have shown that is it NOT due to photolysis, but for the rest, we don't know. It could be thermal decomposition within the shock front, however one would expect mostly (or even exclusively) a decomposition to HO_2 and RO, given that this decomposition path is around 10 kJ mol^{-1} more energetically favourable. According to Müller et al (in their supplementary data), the thermal decomposition of ROOOH is very slow and not a major fate of this species under atmospheric conditions. Also, they estimate the exclusive reaction products being CH_3O + HO_2 and CH_3OH + O_2. It is therefore rather unlikely that the ROOOH decomposes thermally within the shockwave, or even in the photolysis reactor, leading to a low steady-state concentration. Maybe the decomposition is heterogeneous, either on the nozzle or on the wall of the FAGE cell. This would mean of course even more that different FAGE instruments would show different sensitivity to ROOOH. We have added at the end of the experimental part:

No clear explanation can be given on the mechanism of this OH formation: a homogeneous decomposition within the shock wave of the expansion is unlikely, because the pathway leading to CH_3O *and* HO_2 *is thermodynamically more favoured (Assaf et al., 2018a). Therefor a heterogeneous decomposition on the walls of the FAGE cell or the entrance nozzle are more likely. The residence time of the gas mixture between entrance nozzle and detection beam can be calculated from the volume of the cell (0.25 l) and the gas flow (3 l* min^{-1} *STP) to around 1 sec, leaving ample time for collisions with the reactor walls.*

There will be mixing in of non-photolysed gas where 266 nm is not present – and so not all of the gas will have been illuminated by the same number of pulses? Also, would the 266 nm radiation generate any OH from hitting the metal pinhole at the end of the flow-tube?

The diameter of the photolysis beam is 2.5 cm while the reactor has a diameter of 5 cm. We have not considered in our model that a part of the mixture will not be illuminated and that diffusion will dilute the mixture. This will add to the uncertainty of the estimated ROOOH concentration and lead to an overestimation, given that the key reaction is a radical-radical reaction and relies on the concentration of RO_2 generated in the previous laser pulse, which will have time between two pulses to diffuse into the non-illuminated volume.

Generation of OH from 266nm light hitting the pinhole would probably have no impact on the signal at long reaction times and only influence the signal shortly after the laser pulse.

The OH signal does not decay to zero at long times for the isoprene (and to a lesser extent butane) and the long time signal (plateau signal) increases for the number of 266 nm laser shots – and this is the main evidence that OH (signal in the FAGE cell) builds up with time as more ROOOH is made in the OH reactivity flowtube for longer exposure as the isoprene gets used up. Monitoring the OH reactivity with the number of photolysis shots is a clever idea, and it clearly decreases as the isoprene gets used up. It would be nice to see the t<0 baseline level to compare with the long time plateau signal. The t<0 signal is not shown for any of the plots. For Figure S8 for methane, there is no build up of the long time signal with the number of pulses (evidence for no ROOOH being formed for $R=CH_3$), but the signal is not zero? Presumably the t<0 signal should be zero? Why is there a "constant" underlying signal at long times, even for just 1 photolysis pulse there seems to be a long time signal, i.e. for Figure 2, for 1 photolysis pulse the plateau value is around 0.05 or so (right axis) and it only increases to 0.055 or so after 40 pulses?

The t<0 signal is not zero due to stray light from the excitation laser as well as some ambient laboratory light entering through the photolysis window and the nozzle. This has now been explained on Page 4. The conclusion of this work is based on the fact that we observe an increase in this background signal only under conditions where RO_2 will partially react with OH; under any other condition the background is stable. We have now zoomed in Figure 2 onto the background, and have also shown the t<0 signal (we measure 15 ms before the laser pulse), even though this signal is at 2 Hz repetition rate nearly equivalent to the data points at long reaction time: there are only 100 ms without data points between the end of one trace and the beginning of the next one.

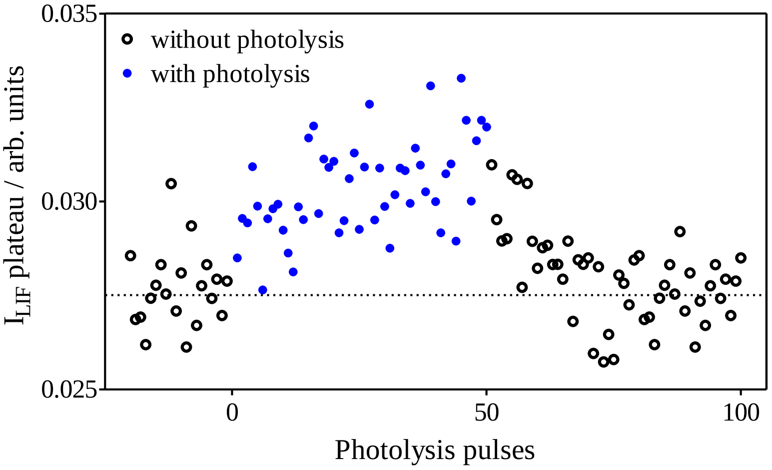
There are some processes not considered in the model, namely RO_2, isoprene (products) and ROOOH photolysis at 266 nm, which will generate products that may undergo secondary chemistry (e.g. second order isoprene oxidation products?) and build up something which makes OH in the FAGE cell?

Except for the photolysis of ROOOH all other processes will also take place in the same way when we do the experiments with higher VOC concentrations. And one of the main evidences of our hypothesis is the fact that we do NOT observe an increase in the background when we work under conditions (high VOC concentration) where all RO_2 chemistry is the same except for the competition between RO_2 and OH. Also, any OH generated through photolysis would react within the photolysis reactor and would not be detected as a signal at long reaction times.

If the photolysis is stopped after say 20 shots, could the loss of ROOOH from the flowtube be monitored in some way?

Yes, we did such experiments. The signal was recorded for 20 shots before uncovering the photolysis laser, then the mixture was photolysed for 50 shots and then the laser was covered again for 50 shots: open black symbols are traces with photolysis laser covered and represent the average of all data points of that trace; full blue symbols represent traces with photolysis and have been obtained as the plateau from a mono exponential fit between 20 ms and the end of the trace. The dotted line is a guidance for the eye and shows the average of all data points for the first and last 20 shots.

The result for an isoprene experiment under conditions comparable to Figure 1 is shown in the following figure:



For the determination of the OH reactivity, was the same fitting window used for all of the decays, i.e. was it the same for the Pulse 1 decay as for the Pulse 40 decay? Or was a different start and end time used?

The same time window has been used for all traces: the full trace has been fitted, only the first 20 ms, showing some stray light from the photolysis laser as well as the rise of the OH signal, have been discarded.

There is no doubt that the work is interesting, and the idea that ROOOH decomposing to OH and hence constituting a potential interference for OH instruments is worthwhile, and needs further exploration. However, it is unknown what the mechanism of decomposition might be, and it is a complex chemical system and the model used to explain the laboratory results has many assumptions/simplifications – and there may be other species generated in the system which could release OH once inside the FAGE cell. There is likely to be a cascade of chemistry over the 40 photolysis shots generating many species (some of the products and intermediates formed will be different to the real atmosphere owing to the conditions and wavelength of light present).

We agree that we have not attempted to precisely understand what is going on in the photolysis volume. Again, one of the major pieces of evidence for our hypothesis is the fact that we see a clear difference in experiments with low and high VOC concentrations, i.e. under conditions where RO_2 react or not with OH radicals. Indeed, if the reaction of ROOOH with OH or its photolysis leads to rather stable species that in turns leads to OH signal in our FAGE, we would not be able to distinguish it. On the other hand, if something like this happens, it might also happen in remote environments.

The language in the paper needs moderating considerably regarding extrapolating the laboratory observations to the conclusion that the work presents convincing evidence that previous model-measurement uncertainties in low NOx environments containing isoprene is due to ROOOH (R from isoprene or similar) decomposition. Our knowledge of ROOOH abundance and removal processes is virtually non-existent, and the model has been optimised using adjustable parameters so as to give a level of OH in the instrument which becomes important compared with atmospheric levels. The wording over the implications of the work, and also the title of the paper, needs changing.

We have removed the word "convincing" from the manuscript and have also more often used the subjunctive form. We are fully aware that our work does not present a final proof that the disagreement between modeling and measurement can be resolved by taking into account ROOOH. Unfortunately, we do not have any datasets with our FAGE system from remote environments that would allow us to test our hypothesis; this now could only be done by the corresponding groups that have these data sets.

We have also changed the title by adding an "a" and changing it to a question:

ROOOH: **a** missing piece of puzzle for OH measurements in low NO environments**?**

Other points:

Title, abstract and conclusions – these need to be toned down to report the observations made, that ROOOH needs to be considered as a potential source of OH inside instruments. Any implication that the puzzle is solved is going too far and is rather premature. The title cannot remain as is. The abstract and conclusion also need to make it clear that any OH from ROOOH would be highly dependent upon the instrument design, and make implicit any assumptions made in the model.

Words such as "convincing" are of course subjective – and should be toned down or removed completely.

The title has been changed (see above), we have removed "convincing", we have used several times the subjunctive form. We have also changed the abstract to the following:

Abstract. *Field campaigns have been carried out with the FAGE technique in remote biogenic environments in the last decade to quantify the in situ concentrations of OH, the main oxidant in the atmosphere. These data have revealed concentrations of OH radicals up to a factor of 10 higher than predicted by models, whereby the disagreement increases with decreasing NO concentration. This was interpreted as a major lack in our understanding of the chemistry of biogenic VOCs, particularly isoprene, which are dominant in remote pristine conditions. But interferences in these measurements of unknown origin have also been discovered for some FAGE instruments: using a pre-injector all ambient OH is removed by fast reaction before entering the FAGE cell, and any remaining OH signal can be attributed to an interference. This technique is now systematically used for FAGE measurements, allowing the reliable quantification of ambient OH concentrations along with the background OH. However, the disagreement between modelled and measured high OH concentrations of earlier field campaigns as well as the origin of the now-quantifiable background-OH is still not understood. We present in this paper the compelling idea that this interference, and thus the disagreement between model and measurement in earlier field campaigns, might be at least partially due to the unexpected decomposition of a new class of molecule, ROOOH, within the FAGE instruments. This idea is based on experiments, obtained with the FAGE set-up of University Lille, and supported by a modelling study. Even though the occurrence of this interference will be highly dependent on the design and measurement conditions of different FAGE instruments, including ROOOH in atmospheric chemistry models might reflect a missing piece of the puzzle in our understanding of OH in clean atmospheres.*

The balance of the main paper and the supplementary information seems skewed. There is information in the SI which really ought to be in the main paper (there is no compelling reason this has to be done for space reasons). e.g. Figures S1 and S4, S6 (this seems central to show) and probably one panel for butane and methane.

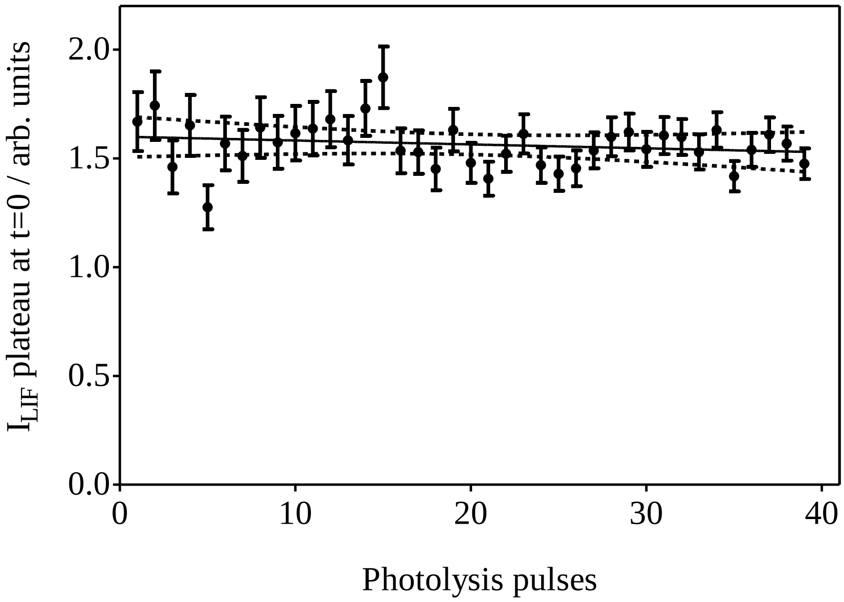
We have shifted a large part of the supplementary data into the main manuscript, notably the modelling of the chemistry in the photolysis reactor, all experiments and figures concerning the different tests with laser energy, different isoprene concentration and the tests with butane and CH_4.

Page 4, line 18, it should be 200 microseconds (not ms).

Has been corrected.

Figure 1. It is not clear how the t=0 maximum in OH signal varies with the number of shots? Does this change with pulse 1 to 40 in any systematic way?

The LIF intensity at time 0 decreases slightly, probably due to the slow depletion of O_3 within the photolysis volume. The following figure shows the LIF intensity at time 0 for the experiments from Figure 1 (note that the fit to Figure 1 has been changed compared to the initial manuscript after close inspection of the data with respect to this question, now taking only data from 20 msec on, while before it was 10 msec. This has a slight influence as well on the decay rate and the plateau, therefore Figure 2 has also slightly changed). From pure photolysis one would expect at each photolysis shot a decrease of the signal of : $OH / O_3 \approx 1.4\times10^{10} / 1.5\times10^{13} \approx 1\times10^{-3}$, in good agreement with the decrease of the OH signal at time 0 : $(1.8 \pm 1.5)\times10^{-3}$.



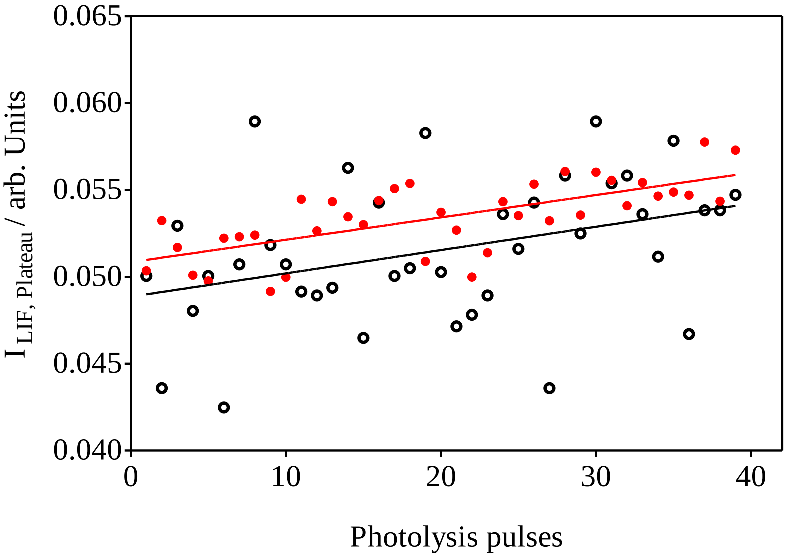
Also what does “data analysis is carried out with raw data” mean?

We wanted to express that the averaging is just done for better visualisation: “raw data” has been replaced by “non-averaged” data.

Figure 2. The red line shows the plateau OH signal from the fit, gradually increasing with the number of photolysis pulses. Given the very small magnitude of the plateau OH compared with the initial OH signal the accuracy of the fit at long time is very important. Could Figure 1 at long times be plotted on a very expanded vertical scale (perhaps from y=0 to y=0.15) and the fits be shown with it? The results are very dependent on how well things fit at long times. Related to this point I would like to see Figure 2 plotted when the plateau is averaged using the data at later times. As the OH reactivity becomes smaller with the number of photolysis pulses, it takes longer for the signal to reach the plateau, so does this slower decay promote the increasing baseline signal in any way? There are certainly some decays in the SI that do not seem to have reached the baseline before the averaging window to obtain the plateau signal begins.

We agree that the increase of the signal is very small compared to the initial signal, and also compared to the scatter and the uncertainty. However, we are confident that the results really show an increase in OH signal, because consistently we always observe this increase only when we are in conditions where RO_2 reacts with OH, at any other experiments the background is stable within the uncertainty.

We have now plotted the data from Figure 2 in the manuscript (former Figure 1) with an inset showing the pre-photolysis signal as well as the first and the last trace blown up vertically, together with their fits. It can be seen that even for the slowest decay (shot 40) the fit has reached the plateau value at around 0.3 sec. In the figure below we show the data from Figure 4 (former Figure 2, without error bars) together with the raw data averaged from 0.35 to 0.41 sec. While the scatter is much larger using the averaged values, the overall trend of an increasing background with increasing photolysis pulses is the same.



Page 6, lines 5-15. Excitation laser energy and photolysis energy are both used here – be clearer about which pulse energy was changed. Clearly Fig S2 and S3 are for probe (excitation) laser energies, but unclear if photolysis (266 nm) energy was changed also?

Everything else was kept constant, only the probe laser was varied. This has been clarified in the manuscript. This part has also been moved from the supplementary data to the main manuscript.

The error in [ROOOH] from the model after 40 shots (figure S6 model) needs to be stated.

The error in [ROOOH] is very large, the model just serves to get a rough estimate. As we state, there are many processes that are not taken into account in the model (diffusion into unphotolysed volume, wall loss, photolysis of ROOOH, reaction of OH with several products, inhomogeneous photolysis beam (this can make a large error for radical-radial reactions, but is very difficult to quantify) etc.). So we think that the uncertainty is at least a factor of 10, but rather over- than underestimated (most of the neglected processes would either consume or produce less ROOOH).

Why was 10^{-4} s^{-1} chosen as the loss rate for ROOOH in the atmosphere? Presumably as this gave an OH concentration of around $1x10^6$? There is a very large uncertainty in [ROOOH], and so the statement on page 9, line 8 that [ROOOH] is predicted to be of the order of 50-200 pptv seems very optimistic in terms of the range of concentrations? For Figure 4, were there RO_2 measurements made in the field to constrain the model, or was modelled RO_2 used?

We agree with the reviewer that there is very large uncertainty in the atmospheric abundance of ROOOH. As we state on page 4 line 15 of the manuscript, the removal rate (and dominant process) is unknown at present. The use of a loss rate of 10^{-4} s^{-1} was chosen as an educated guess of a lifetime. This is on the order of the lifetime of ROOH (which is typically > 1 hour) and much longer than RO_2 (which is typically < 10 seconds). As we state on page 115 line 9 of the manuscript, we evaluated a range of 3 orders of magnitude in the loss rate of ROOOH in our modelling but for space reasons and to focus the discussion we opted to discuss the intermediate loss rate of 10^{-4} s^{-1}. We proposed the manuscript to make this clearer:

As neither the removal rate nor the dominant process of these ROOOH species are currently known, different removal rates were tested, ranging from 10^{-5} to 10^{-2} s^{-1}.

Figure 3 *shows the average diurnal peak concentration of ROOOH in the Boreal (left) and Austral (right) summer obtained using a removal rate of 10^{-4} s^{-1}, leading to ROOOH lifetimes of around 3 hours, on the same order as the lifetime of ROOH species. Peak concentrations of several 100 ppt are reached in this scenario, especially at tropical latitudes, which would lead to an interference in the UL-FAGE system of the order of 1×10^6 cm^{-3}. However, we would like to insist on the fact that both, the modelled concentration of ROOOH in the atmosphere as well as the sensitivity of the UL-FAGE against ROOOH species, bear currently an uncertainty of at least a factor of 10,*

For Figure 4 (Figure 10 in the revised manuscript) we did not constrain RO_2 but have made clearer in the text which species were constrained to the data reported in Feiner et al (2016)}

Discussion

Page 10, line 6.

It is stated that the product of the RO_2+OH reaction leads to an OH interference. The signal may originate from that, but there may be other origins of the signal also, and so the wording needs to be more flexible. This is also where a statement about the different FAGE designs is needed.

We think that the results of the different experiments carried out in this work show clearly that the increase in OH signal in the UL-FAGE does indeed originate from the products of the reaction of RO_2 + OH, so the wording seems suitable to us. There was already a (small) statement that other FAGE systems might behave differently (If occurring also with a comparable intensity in other FAGE instruments….), but we emphasized this fact by adding:

The intensity or even the occurrence at all can depend on the design and working conditions of the FAGE set-up, which is different for different groups. However, if occurring also with a comparable intensity in other FAGE instruments, this interference might be high enough to explain numerous observations obtained with FAGE instruments from other research groups including: ……

Supplementary material.

I think much of section 1 on the FAGE and probe system needs to go in the main paper.

We have added the Figure of the set-up into the main manuscript as well as a few details, but have preferred to leave most details of the set-up in the sup data.

What is the residence time of the FAGE detection cell (inlet from the pinhole and fluorescence cell)? There is no discussion of this and it is an important point. Was the pumping rate of the cell changed to change the residence time?

The volume of the FAGE cell between the inlet nozzle and the excitation laser beam is 0.25 l, the pumping into the FAGE is 3 l, this leads at 2 Torr to a residence time of the gas of around 1 sec. No, pumping rate was not changed in these experiments. Such experiment would indeed have been a good idea, but we did not do and now the experiment is in a different configuration.

Figure S2 – in the caption add a line saying what the black line is.

Has been done.

Line 187 of SI – "is consistent with" is better than "is indeed due to"

Has been done.

For all of the OH signal versus time plots the y axis ends at zero. Are there any negative points, or is the "baseline" some value a bit above zero?

There are never negative values, because the signal is obtained by counting photons. Therefore, it is either zero (if no photon occurred at that time window during any of the 20 individual decays) or above.

Figure S6. The concentrations versus no of photolysis pulses. This seems central and should be in the main paper.

Has been done

Line 220, reword "very basically"

Has been done.

ROOOH: ~~the~~ A missing piece of the puzzle for OH measurements in low NO environments?

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Abstract. Field campaigns have been carried out with the FAGE technique in remote biogenic environments in the last decade to quantify the *in situ* concentrations of OH, the main oxidant in the atmosphere. These data have revealed concentrations of OH radicals up to a factor of 10 higher than predicted by models, whereby the disagreement increases with decreasing NO concentration. This was interpreted as a major lack in our understanding of the chemistry of biogenic VOCs, particularly isoprene, which are dominant in remote pristine conditions. But interferences in these measurements of unknown origin have also been discovered for some FAGE instruments: using a pre-injector, all ambient OH is removed by fast reaction before entering the FAGE cell, and any remaining OH signal can be attributed to an interference. This technique is now systematically used for FAGE measurements, allowing the reliable quantification of ambient OH concentrations along with the background OH. However, the disagreement between modelled and measured high OH concentrations of earlier field campaigns as well as the origin of the now-quantifiable background-OH is still not understood. We present in this paper ~~convincing~~ ~~experimental and modeling~~ ~~evidence~~the compelling idea that this interference, and thus the disagreement between model and measurement in earlier field campaigns, ~~is~~ might be at least partially due to ~~interference by~~ the unexpected decomposition of a new class of molecule, ROOOH, within the FAGE instruments. This idea is based on experiments, obtained with the FAGE set-up of University Lille, and supported by a modelling study. Even though the occurrence of this interference will be highly dependent on the design and measurement conditions of different FAGE instruments, i~~I~~ncluding ROOOH in atmospheric chemistry models might reflect~~s~~ a~~the~~ missing piece of the puzzle in our understanding of OH in clean~~the~~ atmospheres.

1 Introduction

OH radicals are the most important oxidant in the atmosphere, and the detailed understanding of their formation and reactivity is key for the understanding of the overall chemistry. Upon reaction with Volatile Organic Compounds (VOCs, such as methane and isoprene), OH oxidation leads to the production of organic peroxy radicals (RO_2) who play a crucial role in the chemistry of tropospheric ozone and secondary organic aerosol (Monks et al., 2015). The concentration of OH radicals has been measured for several decades now (Holland et al., 2003;Creasey et al., 1997;Brune et al., 1995), and comparison of OH concentration profiles with model outputs is taken as a good indicator on the degree of understanding of the chemistry going on. Good agreement is often obtained between measurements and models for polluted environments (where levels of nitrogen oxides (NO_x=NO+NO_2) are in excess of 500 pmol/mol, or ppt), however remote and clean environments show much less good agreement (Stone et al., 2012). Several field campaigns in remote environments, dominated by natural biogenic emissions, have been carried out during the last decade (Whalley et al., 2011;Lelieveld et al., 2008;Hofzumahaus et al., 2009), and a very poor agreement has been found, with measured OH concentrations exceeding model predictions by up to a factor of 10. These findings have been interpreted to reflect a lack in our understanding of the oxidation mechanism of biogenic VOCs under low NO_x conditions and have triggered a large number of studies aiming at improving the atmospheric oxidation mechanism of biogenic VOCs (Peeters et al., 2009;Crounse et al., 2011;Paulot et al., 2009;Archibald et al., 2010). Improvements have been made especially in the oxidation mechanism of isoprene (Wennberg et al., 2018), and new reaction pathways leading to OH recycling have been found. However, none of these new chemical pathways has led to a sufficiently significant increase in modelled OH concentration to bring models into reasonable agreement with measurements (Rohrer et al., 2014).

An alternative explanation for the unexpectedly high OH concentrations measured in biogenic, low NO environments is that the measurements suffer from an unidentified interference. Indeed, all of these measurements have been carried out using a technique named FAGE (Fluorescence Assay by Gas Expansion). Briefly, ambient air is rapidly expanded into a low pressure volume, where OH radicals are excited by 308 nm light and the resulting fluorescence is detected (Heard and Pilling, 2003). Calibration of the fluorescence signal allows the determination of absolute concentrations (Dusanter et al., 2008). Interferences can arise from different sources such as photolysis of suitable precursors by the fluorescence excitation laser (*e.g.*, O_3), the presence of fluorescing species other than OH or the decomposition of labile species during the gas expansion into the FAGE cell (Ren et al., 2004). The first source of interference can, in principle, be identified by varying the excitation laser energy: ~~“real”~~ambient OH radicals only need one photon to fluoresce, whilst other species need two (one for generating OH radicals by photolysis, another for their excitation). Therefore the fluorescence intensity would not vary linearly with the excitation energy. Even though in practice this method is highly uncertain, given the generally low OH concentrations (and the resulting low S/N ratio) and the high temporal variability of OH radical concentration, the high OH concentrations observed in the different field campaigns seems to arise from ambient~~“real”~~ OH and not from the photolysis of other species. This was also confirmed by Novelli et al (Novelli et al., 2014a) who observed a strong background during HUMPPA2010 with good S/N ratio, allowing to unequivocally exclude photolysis being at the origin of the background signal. The second source of interference can be identified by regularly measuring the fluorescence signal with the excitation laser wavelengths slightly tuned off the OH line. This procedure is always adopted during measurements as it enables to account for stray light reaching the detector from the excitation laser or from the sun.

The third source of interference, the generation of OH radicals during the expansion into the FAGE cell, is more difficult to identify because only one photon is needed and hence the interfering species would appear as ambient~~“real”~~ OH. Following the large disagreements between measurements and models, the group of W. Brune has conceived a method to quantify such possible interferences (Mao et al., 2012): a pre-injector device is installed just above the inlet into the FAGE cell, which injects regularly into the airflow a high concentration of a species rapidly reacting with OH radicals. This way all ambient OH radicals are scavenged before entering the FAGE cell, and any remaining signal can be identified as interference. The difference between the signal with and without the scavenger allows the quantification of the real ambient OH. The use of this technique was ~~used~~ reported for the first time in 2012 showing results for a field campaign in a forest in California (Mao et al., 2012). It~~and~~ led to the identification of a large fluorescence signal following scavenging of all ambient OH radicals, corresponding to up to 50% of the total OH concentration. The OH concentrations obtained with the scavenger agreed well with models, while the OH concentrations obtained without the scavenger exceeded modeled concentrations by up to a factor of 3. Other groups have also developed a pre-injector system in the following years (Griffith et al., 2016;Novelli et al., 2014a;Tan et al., 2017). Using this system, Novelli *et al*. (Novelli et al., 2014a) have observed strong interferences in their FAGE system during three field campaigns in remote biogenic environments in Germany, Finland and Spain, while Griffith *et al*. (Griffith et al., 2016) was able to account for the observations through known interferences by O_3 photolysis. Tan *et al*. (Tan et al., 2017) have very recently observed a small unexplained OH concentration using a prototype pre-injector device during a field campaign in rural China. However, technical difficulties with the prototype made it uncertain to draw final conclusions about the origin of this unexplained OH signal.

Novelli *et al*. proposed that ozonolysis of alkenes, leading to the formation of Criegee intermediates and the subsequent decomposition of these Criegee intermediates within the FAGE cell, was responsible for the interference (Novelli et al., 2017). However, Rickly and Stevens (Rickly and Stevens, 2018) and Fuchs *et al*. (Fuchs et al., 2016) could not confirm this source: even though they detected internally formed OH when mixing high concentrations of O_3 and alkenes in the laboratory, when they extrapolated their results to ambient conditions they found that the possible interference generated this way would be well below the detection limit of their FAGE. Chamber studies were carried out at the SAPHIR chamber in Jülich (Fuchs et al., 2012), simulating remote forest conditions (*i.e.*, high biogenic VOC and low NO concentrations). OH concentrations were measured simultaneously by FAGE and by absolute DOAS absorption. No sizeable interference was detected in these experiments, even though the same group had previously observed unexpected high OH concentrations in the Pearl River delta in China (Hofzumahaus et al., 2009;Rohrer et al., 2014), exceeding modelled concentrations by up to a factor of 8.

Following several years of interference studies in various environments, recent work from W. Brune's group (Feiner et al., 2016) concluded that the interference observed in their FAGE system (a) was due to a rather long-lived species because the interference persists into the evening, (b) it had been observed in different environments dominated by MBO, terpenes or isoprene, hence it must originate from a class of species rather than from only one species such as isoprene, (c) it strongly increased with increasing $O(^1D)$, hence it must somehow be linked to photochemistry and (d) the species responsible for this interference was linked to a low NO_x oxidation pathway, because the extent of the interference steeply decreased with increasing NO concentration.

In this work we present ~~convincing~~ experimental and modelling evidence that this sought-after species could be~~is~~ the product of the reaction between RO_2 radicals and OH radicals. In recent works it has been shown that this reaction is fast (Assaf et al., 2017b;Assaf et al., 2016; Yan et al., 2016) and could be competitive to other sinks for RO_2 radicals (Fittschen et al., 2014;Archibald et al., 2009), *i.e.* it becomes increasingly important with decreasing NO concentration. *Ab-initio* calculations (Müller et al., 2016;Liu et al., 2017;Assaf et al., 2018b) have shown that the initial reaction product is a trioxide, ROOOH, obtained from the recombination of RO_2 and OH. The formation of this adduct is exothermic by around 120 kJ mol^{-1} compared to the initial reaction partners and by around 110 kJ mol^{-1} compared to the major decomposition products, RO + HO_2, largely independent of the size of the alkyl moiety of the RO_2. While for the smallest RO_2 radical, CH_3O_2, stabilization of CH_3OOOH is not the major fate of the initial adduct (Assaf et al., 2017a;Müller et al., 2016) and the major products are

CH_3O + HO_2, the HO_2 yield has been found to decrease with increasing size of the alkyl group and it is expected that for C_4 peroxy radicals the stabilization of the initially formed ROOOH is the major product (Assaf et al., 2018a). For RO_2 radicals obtained from an initial attack of OH radicals on biogenic VOCs, it can thus be expected that the major reaction product will also be the corresponding trioxides. Depending on the removal rate of ROOOH (which is not known to date),~~ and that~~ sizeable concentrations of this new class of species can possibly accumulate and thus be present in low NO environments.

2. Results and Discussion

In the first part, the experimental evidence for the interference generated in the UL-FAGE by the presence of ROOOH molecules will be presented. It should be noted that the intensity of interferences or even the presence at all can depend on the design of the FAGE instrument (inlet design, pressure drop, residence time etc) and the results presented here are only valid for the FAGE instrument of University Lille. Other FAGE instruments need to be tested individually for the possible presence of an interference in OH measurement due to the presence of ROOOH. In the second part, model calculations are used in order to estimate the steady state concentration of ROOOH molecules that can possibly build up in different environments.

2.1 Experiments

With the goal of forming sizeable amounts of trioxide (ROOOH), experiments have been carried out in a pump-probe FAGE instrument of the University Lille (UL-FAGE), describes already in detail in earlier publications (Fuchs et al., 2017;Hansen et al., 2015;Parker et al., 2011). Briefly, a gas mixture containing the VOC (isoprene,~~ (or~~ C_4H_{10} or CH_4~~, see Supplementary material~~) and O_3/H_2O is photolysed at 266 nm at a repetition rate of 2 Hz. The photolysed mixture is expanded into the FAGE cell, and the OH concentration is monitored by time-resolved Laser Induced Fluorescence (LIF). The excitation laser operates at 5 kHz, hence the OH profiles are obtained with a time resolution of 200 µ~~m~~s. The residence time of the gas mixture in the photolysis cell is around 20 s, therefore the mixture is photolysed around 40 times before it reaches the FAGE inlet. A schematic view of the experimental set-up is shown in **Figure 1**, more details can be found in the Supplementary data.

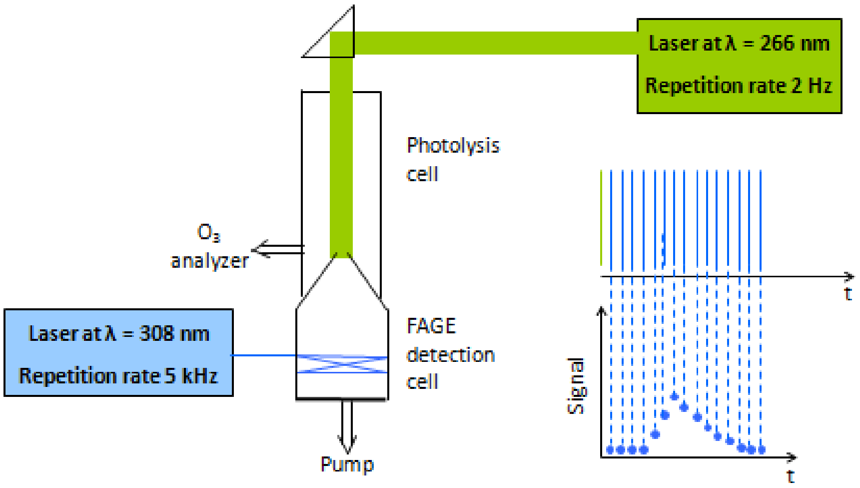

Figure 1: Schematic view of the experimental set-up

Experiments start with a fresh mixture (*i.e.*, with the photolysis laser manually covered) and 40 decays are then recorded~~gistered~~ every 0.5 s for 20 s. After 40 photolysis pulses the laser is covered again for 2 minutes to allow the mixture to completely refresh and, in order to improve the S/N ratio, a new series of measurements is started. After 20 series, the signals are averaged so that one OH decay profile is obtained for each sequential photolysis pulse. An example is shown in **Figure ~~1~~ 2** where, for clarity, only one in every 10th decay profile is plotted. The open black signals in **Figure 2** show the pre-photolysis signal, i.e. the signal registered just before uncovering the photolysis laser. This signal is not zero, because some stray light from the excitation laser is always detected. Also, some ambient laboratory light can reach the detector through the photolysis window and the nozzle opening.

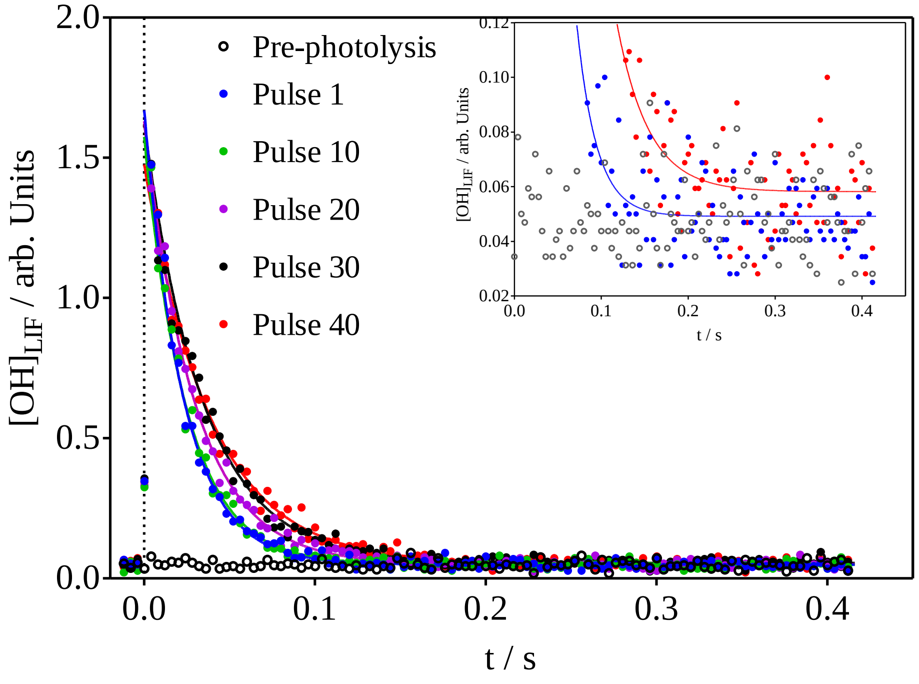

Figure ~~1~~2: OH concentration time profiles following the photolysis of 600 ppb O_3 (leading to initial OH concentrations of around 1.4×10^{10} cm^{-3}) in the presence of 3×10^{11} cm^{-3} isoprene. For clarity, only every 10th photolysis shot is shown. Open black symbols show the FAGE signal before the first photolysis shot. Time resolution was decreased from 200 µs to 4 ms by averaging 20 data points for clarity only: full lines show a fit to a single exponential decay, ~~data analysis is~~ carried out ~~with~~using non-averaged ~~raw~~ data between 0.02 s and the end of the data set. The inset shows a vertical zoom, for clarity only the pre-photolysis signal as well as the signals for the first and last pulse with the corresponding fits are shown.

The initial isoprene concentration (3×10^{11} cm^{-3} in **Figure 2~~1~~**) was chosen to be low enough to make the reaction of RO_2 with OH compete efficiently with that of isoprene with OH after several photolysis pulses: with initial OH concentrations of 1.4×10^{10} cm^{-3} (obtained from calibration in separate experiments, see Supplementary data), the isoprene concentration decreases with each photolysis shot, while the RO_2 radical concentration increases. It can thus be expected that the concentration of ROOOH increases with every photolysis pulse. With the goal of getting a good idea of the ongoing chemistry in the photolysis cell and to get a rough estimate of the concentration of ROOOH being produced during this experiment, a very simple model was run using the conditions shown in **Figure 2**.

Table 1: Model used to estimate the accumulation of ROOOH in the photolysis cell before entering the FAGE cell, all rate constants have been taken from the most recent IUPAC evaluations (Atkinson et al. 2006, Atkinson et al., 2004)

Reaction	k / cm^3 s^{-1}
OH + Isoprene → RO_2	1×10^{-10}
OH + RO_2 → ROOOH	1×10^{-10}

OH + ROOOH → products	1×10^{-11}
$OH + O_3 \rightarrow HO_2 + O_2$	7.3×10^{-14}
$OH + HO_2 \rightarrow H_2O + O_2$	1×10^{-10}
$RO_2 + RO_2 \rightarrow$ products	1×10^{-12}
$RO_2 + HO_2 \rightarrow ROOH$	1.7×10^{-11}

A yield of 1 is estimated for the formation of ROOOH in the reaction of RO_2 with OH. The other major reaction path for the RO_2 radicals under these conditions is the self-reaction. The reaction of ROOOH with OH radicals has been estimated (in comparison with ROOH) to 1×10^{-11} cm^3s^{-1}, but only a small fraction of ROOOH will have reacted with OH after 40 photolysis pulses.

This model was run 40 times for 0.5 s, with the final concentrations of the different species obtained at each run being used as initial concentrations in the following run, always adding 1.4×10^{10} cm^{-3} OH radicals to the mixture. The evolution of the different species with each photolysis shot is shown in **Figure 3**.

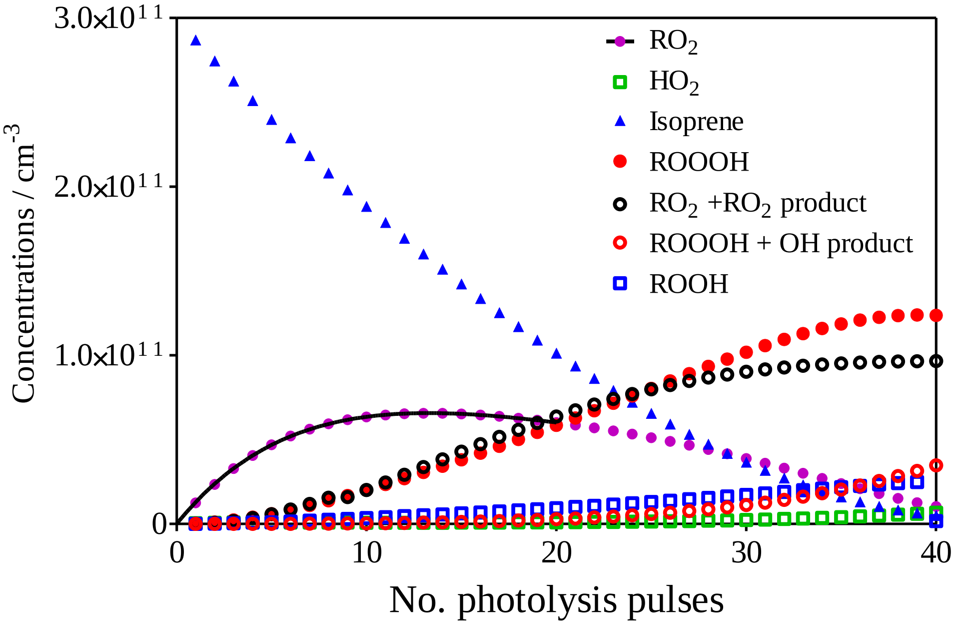

Figure 3: Evolution of different species in the photolysis cell as a function of the number of photolysis pulses. Full black line describes evolution of RO_2 by exponential rise (see section on CH_4 experiments)

The goal of this model is not to precisely describe the ongoing chemistry, but rather to get a good idea of how much ROOOH is possibly accumulated. The model uses different simplifications: (i) OH radicals only react with species present in the model, i.e. no wall loss or reaction with impurities is taken into account; (ii) the possible photolysis of ROOOH at 266 nm or a heterogeneous loss on the reactor walls is not taken into account; (iii) no reaction of OH with the products of RO_2 self-reaction are considered; (iv) the photolysis beam has been considered homogeneous, the inhomogeneity of the beam profile of our photolysis laser has not been considered. All these simplifications lead to an uncertainty in the final ROOOH concentration, possibly up to a factor of 10. Most of the simplifications will lead to an overestimation of the final ROOOH concentration (either ROOOH is consumed or less is formed), except the inhomogeneous photolysis beam where the direction of uncertainty is not easy to determine (higher formation of ROOOH in the hotspots of the laser beam and lower in the rest of the volume). The model predicts the formation of around [ROOOH] ≈ 1×10^{11} cm^{-3}.

The model predicts the consumption of most isoprene over the 40 photolysis pulses, which should lead to a decrease in the decay rate, given the much faster rate constant of OH with isoprene compared to the reaction products. A single-exponential decay was then fitted to the experimental OH profiles from **Figure ~~1~~ 2** and the resulting pseudo-first order decay rates are shown as blue dots in **Figure ~~2~~4**. It can be seen that the decay rate decreases over the 40 shots by around 20 s^{-1} ~~with increasing number of photolysis pulses. This is expected due to the ongoing transformation of reactive isoprene (and RO_2 radicals) into less reactive species. The decrease of ~20 s^{-1}~~, corresponding~~s~~ to a decrease in isoprene concentration of around 2×10^{11} cm^{-3}, in good agreement with predictions of a kinetic model ~~(see Supplementary data)~~. The OH LIF signal at long reaction times, obtained as the plateau of the single-exponential fit (red dots in **Figure 4~~2~~**), increases with increasing number of photolysis pulses (m = (1.2±0.3~~2~~) × 10^{-4} arb. Units / photolysis pulse). This can be interpreted as interference due to decomposition of the increased concentration of ROOOH within the FAGE, however more tests will be presented further down to strengthen this hypothesis.

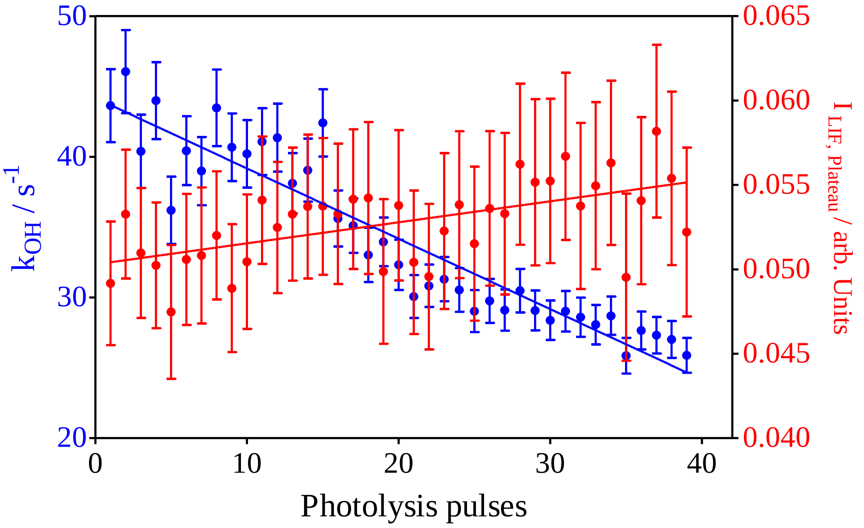

Figure ~~2~~4: Results of fitting a mono-exponential decay to the raw signal of the experiments shown in Figure 1. Blue dots: OH decay rates from the mono-exponential fit between 0.02 s and the end of the data set (left *y*-axis). Red dots: fluorescence signal after reaction of all OH radicals obtained as plateau of the single-exponential fit (right *y*-axis). Error bars show 95% confidence interval such as obtained from the fit ~~of the raw data~~.

In order to better understand the origin of the increase of the LIF signal, a~~A~~dditional experiments have been carried out.

2.1.1. Is the increase due to a 1- or 2-photon process?

~~with the goal to test if the observed increase in LIF signal at long reaction times is due to a 1- or 2-photon process. Experiments have been carried out with either decreased excitation laser energy (factor 2 lower) or with decreased excitation laser repetition rate (1 kHz instead of 5 kHz). Because p~~Photolytically generated interferences need two photons for generating one fluorescence photon, and can thus be identified by either varying the fluorescence excitation laser energy (the signal intensity would increase with the square of the excitation laser energy) or by changing the repetition rate of the excitation laser (photolytically generated interferences appear because the air mass within the excitation volume is not completely renewed between two excitation laser pulses (200µs at 5 kHz), and thus OH radicals generated with one pulse can be excited with the following pulse. Hence, such interference would be expected to decrease with decreasing repetition rate). Separate test experiments with CH_3COCH_3 as a known source of photolytically generated OH radicals are described in the supplementary data. ~~it would be expected that at lower photolysis energy the residual LIF signal would decrease with decreasing excitation laser energy:~~ Three experiments with isoprene (3.2×10^{11} cm^{-3}) have been carried out, keeping all other parameters constant (266nm photolysis energy and repetition rate, O_3 concentration): two experiments at 5 kHz with different excitation laser energies (1.7 and 0.8 mW) and one series with a lower excitation laser repetition rate (1 kHz, 0.4 mW). The results are shown in **Figure 5**.

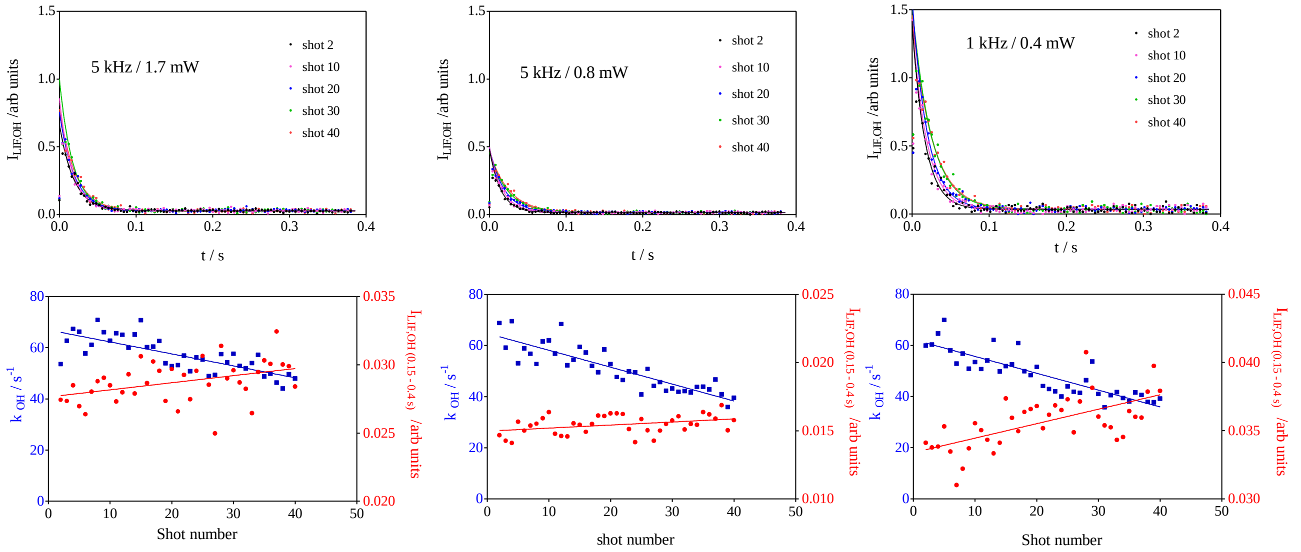

Figure 5: Photolysis of O_3 in the presence of isoprene using different excitation laser energies and repetition rates. Upper graphs: OH decays (for clarity, only every 10th decay is shown), lower graph OH decay rate as a function of photolysis pulses (blue dots, left y-axis) and fluorescence intensity averaged over 0.15 to 0.4 s (red dots, right y-axis).

The blue dots on the lower graphs show the decrease in the decay rate with increasing number of photolysis pulses, on the same order of magnitude for all three experiments, as expected (photolysis energies as well as isoprene and O_3 concentration were identical for all three experiments). The absolute values for the background signals are different for the three experiments, they are highest for the highest pulse energy (0.4 mW at 1 kHz) and lowest at the lowest pulse energy (0.8 mW at 5 kHz), reflecting that the laser stray light is partially at the origin of the “background background”. The background increases with increasing number of photolysis pulses for all three series, but the slope is different. However, the slope is directly proportional to the sensitivity of the LIF detection system, and for comparison needs to be normalized to the initial OH intensity. The results are summarized in **Table 2**:

Table 2: Summary of results from **Figure 5**

Experiment	OH_0 LIF intensity [a]	Slope [b]	Slope / OH_0
5 kHz, 1.7 mW	0.85 ± 0.08	$(5.2\pm2.0) \times 10^{-5}$	$(6.1 \pm 2.5) \times 10^{-5}$
5 kHz, 0.8 mW	0.48 ± 0.04	$(2.2\pm0.9) \times 10^{-5}$	$(4.6 \pm 2.3) \times 10^{-5}$
1 kHz, 0.4 mW	1.50 ± 0.17	$(10.0\pm3.1) \times 10^{-5}$	$(6.7 \pm 2.7) \times 10^{-5}$

[a] **OH_0 LIF intensity obtained as the average of the LIF intensity at t=0 for all 40 photolysis pulses, obtained by fitting to a single exponential decay between 0.015 – 0.4 s, in arbitrary units**

[b]**. Slope obtained by linear regression of red dots in Figure 5, in arbitrary units**

From the observation that the increase in residual LIF signal with increasing number of photolysis pulses is independent of both (a) the fluorescence excitation laser energy and (b) the repetition rate of the excitation laser, we conclude that the observed interference in the UL-FAGE is not due to a photolytic process.

2.1.2. Is the interference really due to the product of RO_2 + OH?

Additional experiments ~~have been carried out with much higher isoprene or butane concentration such that the OH reactivity with the hydrocarbon always remains the major reaction path and that the reaction of OH with the accumulated RO_2 never becomes competitive. Under these conditions, negligible ROOOH will be formed, while still comparable concentrations of RO_2 radicals are generated, and with this, comparable concentrations of the products of their cross reaction or reaction with HO_2. In such conditions no increase in residual OH signal is observed, neither for isoprene nor for butane. This observation further supports the hypothesis that the observed increase in residual LIF signal is due to decomposition of ROOOH and not to any other reaction product (see Supplementary data for details).~~

have been carried out using identical OH concentrations, but much higher isoprene concentrations than in the above experiments. Under these conditions, there is still formation of high concentrations of RO_2, but as the isoprene concentration stays high even after 40 photolysis pulses, the RO_2 concentration never gets high enough to compete with the reaction of isoprene with OH. Therefore, one can expect comparable formation of all products from RO_2 self- or cross reaction or reaction with HO_2, but only very little or no products from the reaction of RO_2 with OH.

The results of these experiments are shown in **Figure 6**. For the conditions in the left graph ($[C_5H_8] = 1.23 \times 10^{12}$ cm^{-3}) the OH decay rate decreases ((-0.5 ± 0.2) s^{-1} $pulse^{-1}$ = 20 s^{-1} after 40 pulses) in the same way than for the experiments above, and this is explained by the replacement of the reactive isoprene by less reactive products. For the conditions in the right graph the C_5H_8 concentration was so high ($[C_5H_8] = 1.23 \times 10^{13}$ cm^{-3}) that it leads to decay rates that are not measurable anymore with our time resolution. For both conditions however, the LIF-intensity at long times does not increase within the experimental uncertainty with the number of laser pulses ((1.2±1.4) × 10^{-5} and (-1.3±1.2) × 10^{-5} for the left and right graph, respectively).

From these observations, it can be concluded that the increase in LIF intensity at long reaction times observed in the experiments presented in Figure 4 is consistent with being generated by the product of the reaction between RO_2 radicals and OH radicals.

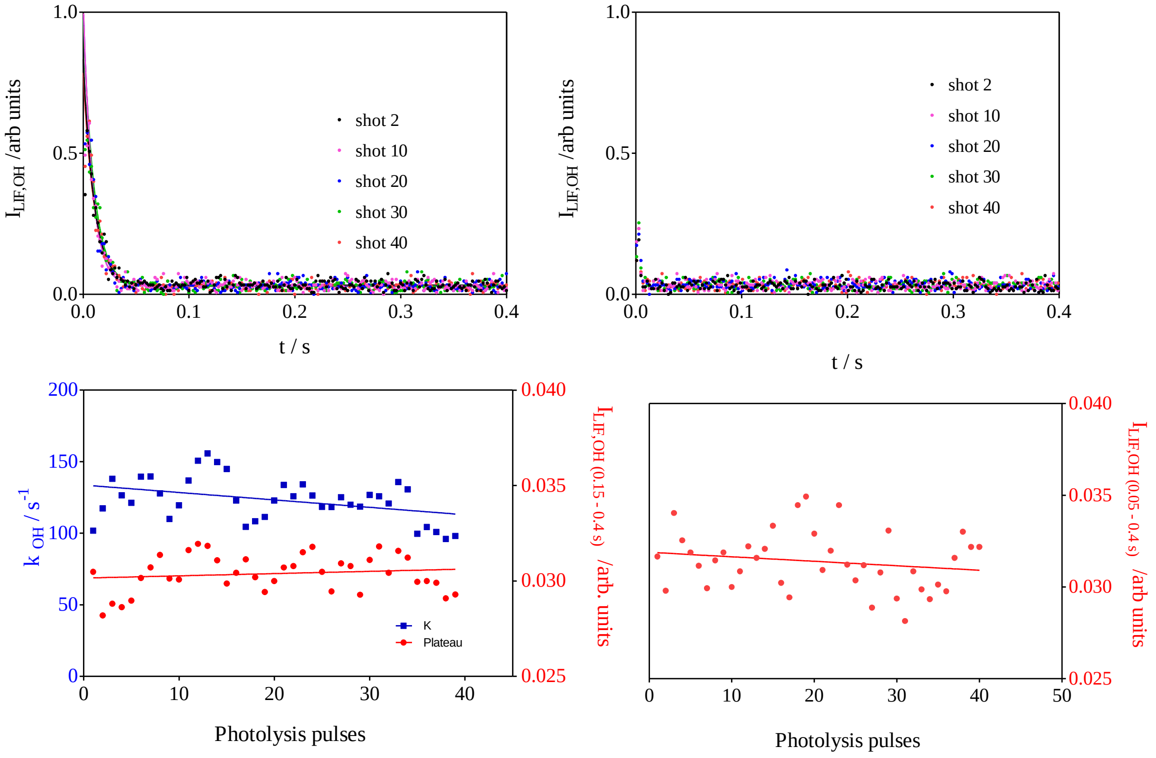

Figure 6: Experiments with high isoprene concentrations: [C_5H_8] = 1.23 × 10^{12} and 1.23 × 10^{13} molecule.cm^{-3} for left and right graph, respectively. Upper graph LIF signals as a function of the number of photolysis pulses (for clarity, only every 10th pulse is shown), lower graph shows the rate constant in blue (left graph only, decay was too fast to be measurable under the conditions of the right graph) and the LIF intensity at long times (plateau from fitting for left graph, average of all data points between 0.01 – 0.4 s for right graph).

2.1.3. Tests with n-C_4H_{10}

~~this was not the case, the same increase of residual LIF signal (relative to the LIF signal at time 0 after the photolysis pulse) was observed for both energies. The same is valid for changing the repetition rate of the excitation laser: photolytically generated interferences appear because the air mass within the excitation volume is not completely renewed between two excitation laser pulses (200µs at 5 kHz), and thus OH radicals generated with one pulse can be excited with the following pulse. Hence, such interference would be expected to decrease with decreasing repetition rate: this also was not the case in our experiments, the increase in the fluorescence signal was of the same order of magnitude for both repetition rates (see Supplementary data for full details).~~

To further support the hypothesis that the observed increase in residual LIF signal is due to an interference generated by the ~~decomposition of ROOOH species~~product of the reaction of RO_2 + OH, additional experiments have been carried out with C_4H_{10} ~~and CH_4~~ instead of isoprene. C_4H_{10} has been chosen because Assaf et al. (Assaf et al., 2018a) have shown experimentally that the HO_2 yield for the reaction of the corresponding RO_2 radical with OH is very low and *ab-initio* and RRKM calculations support the hypothesis that the major reaction product with increasing alkyl size of the RO_2 radical becomes the corresponding trioxide. For the reaction of the corresponding isoprene peroxy radical with OH such direct evidence is currently not available, and it could be imagined that the OH radicals would rather add to the remaining double bond rather than to the peroxy site. Note however, that the major conclusion from the above experiments (the product of the reaction between the isoprene-peroxy radical with OH generates an interference in the UL-FAGE) would still be the same. Three experiments with different butane concentrations have been carried out and the results are shown in **Figure 7**.

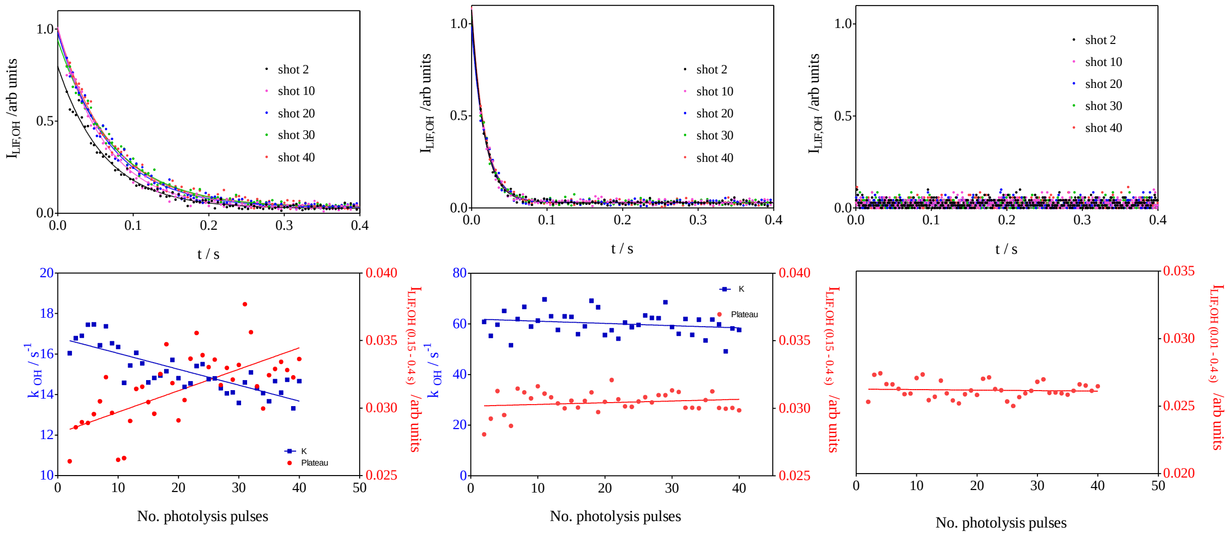

Figure 7: Photolysis of O_3 in the presence different concentrations of n-butane (7×10^{12}, $2 \times 10^{13}$and 7.5×10^{15} cm^{-3} from left to right). Upper graph: OH decays (for clarity only every 10th decay is shown), lower graph: decay rates of OH radicals as a function of photolysis pulses (blue dots, left y-axis), residual LIF intensity taken from mono exponential fit for left graph and as the average LIF intensity between 0.15 – 0.4 s and 0.01 and 0.4 s for the center and right graph, respectively.

For the lowest concentration (left graphs in **Figure 7**) a high formation of ROOOH can be expected: under these conditions OH radicals react slowly with butane and the reaction with the nascent RO_2 radicals becomes rapidly competitive. The concentration has been increased in the middle graph of **Figure 7** such that only a very low concentration of ROOOH is expected. In the right graph, finally, a very high concentration of butane has been used, too high to detect the decay of OH radicals with our time resolution. Under these conditions, it is expected that OH radicals react nearly exclusively with butane and no ROOOH is formed. Note that the initial OH radical concentration is the same in all three experiments. The interference is clearly visible in the left graph (slope $m = (15.8\pm4)\times10^{-5}$ arb. units), barely in the center graph ($m = (1.2\pm1.7)\times10^{-5}$ arb. units) and not present anymore in the right graph ($m = -(0.4\pm1.3)\times10^{-5}$ arb. units). Note that in the experiment of the right graph, the concentrations of all other species are similar to the concentrations in the left graph, i.e. the RO_2 and HO_2 concentrations are similar and with this all products obtained from self-and cross reactions. This is another strong indicator that the observed increase in residual LIF intensity is indeed due to the product of the reaction of RO_2 with OH.

2.1.4 Tests with CH_4~~Using C4H10 as peroxy radical precursor, the same increase in residual LIF signal with increasing number of photolysis pulses is observed (see supplementary data for more details).~~

Experiments with CH_4 have been carried out because it is known that the HO_2 yield in the reaction of CH_3O_2 with OH is very high, and that the yield of stabilized CH_3OOOH is expected to be very low (Assaf et al., 2018a;Assaf et al., 2017a). ~~Therefore, no increase in the residual OH signal would be expected with increasing number of photolysis pulses. And this is what has been observed in our experiments (see Supplementary data for details).~~Therefore, it would not be expected to observe an interference in the FAGE system. Two experiments with different CH_4 concentrations have been performed, the results are shown in **Figure 8**. In both series, one observes for the OH decay rate an increase over the first few photolysis shots. This is expected due to the formation of CH_3O_2 radicals that are more reactive against OH radicals than CH_4. In **Figure 3** it can be seen that the model predicts (for an overall reactivity of 30 s^{-1}) an increase of RO_2 radicals over the first 10 pulses, followed by a steady state period and a slow decay. The decay rates are plotted as a function of the photolysis pulses in **Figure 8** (lower graphs) and have been fitted by forcing to the same rise time as the one obtained from the mono exponential fit of the RO_2 profile in **Figure 3**. A rough estimation of the increase in the decay rate of 8 s^{-1} is obtained, corresponding to a CH_3O_2 concentration (using $k(CH_3O_2+OH) = 1.5\times10^{-10}\ cm^3s^{-1}$) (Assaf et al., 2016) of $5\times10^{10}\ cm^{-3}$, in excellent agreement with the predictions of the model, **Figure 3**. This good agreement gives more confidence in the principle idea of the experiments and the conditions chosen to enhance the formation of ROOOH.

In both experiments the LIF intensity at long times does not change (($-3.0\pm2.5\times10^{-5}$ and $1.0\pm1.7\times10^{-5}$ for left and right graph, respectively). This is expected due to the small yield of CH_3OOOH and further supports the hypothesis that ROOOH, the product of the reaction between RO_2 and OH, leads to an interference in UL-FAGE.

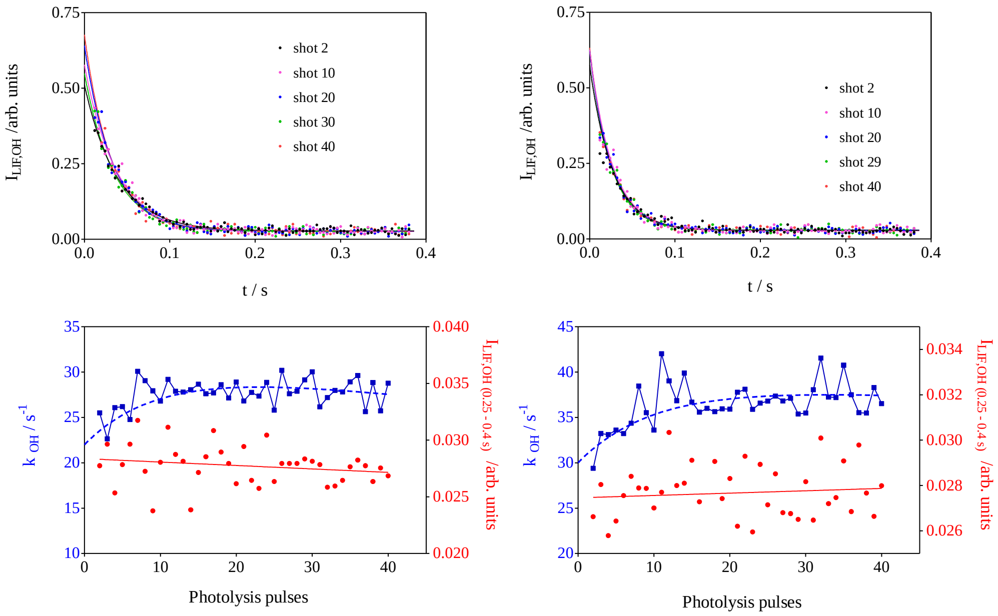

Figure 8: Photolysis of O_3 in the presence different concentrations of CH_4 ($3.3\times10^{15}\ cm^{-3}$ and $4.9\times10^{15}\ cm^{-3}$ for the left and right graph, respectively). Upper graph: OH decays (for clarity only every 10th decay is shown), lower graph: decay rates of OH radicals as a function of photolysis pulses (blue dots, left y-axis), residual LIF intensity taken as the average LIF intensity between 0.25 – 0.4s.

2.1.5 Intensity of interference in UL-FAGE

~~Additional experiments have been carried out with much higher isoprene or butane concentration such that the OH reactivity with the hydrocarbon always remains the major reaction path and that the reaction of OH with the accumulated RO_2 never becomes competitive. Under these conditions, negligible ROOOH will be formed, while still comparable concentrations of RO_2 radicals are generated, and with this, comparable concentrations of the products of their cross reaction or reaction with HO_2. In such conditions no increase in residual OH signal is observed, neither for isoprene nor for butane. This observation further supports the hypothesis that the observed increase in residual LIF signal is due to decomposition of ROOOH and not to any other reaction product (see Supplementary data for details).~~

The increase in residual LIF signal in **Figure ~~2~~ 4** over the 40 photolysis pulses is around 0.005 arb. units. This can be compared with the raw OH decays shown in **Figure ~~1~~2**: the initial LIF signal of ≈ 1.7 arb. units corresponds to an OH concentration of 1.4×10^{10} cm^{-3}. Therefore, the increase in the residual signal corresponds to an equivalent OH concentration of ≈ 4×10^{7} cm^{-3}. The concentration of ROOOH accumulated after 40 photolysis pulses was estimated to be [ROOOH] ≈ 1×10^{11} cm^{-3} using a simple model ~~(see supplementary data)~~, i.e. a fraction of ≈ 4×10^{-4} of ROOOH decomposed to OH radicals during the expansion within the UL-FAGE. No clear explanation can be given on the mechanism of this OH formation: a homogeneous decomposition within the shock wave of the expansion is unlikely, because the pathway leading to CH_3O and HO_2 is thermodynamically more favoured (Assaf et al., 2018a) and thus no OH would be expected. Therefor a heterogeneous decomposition on the walls of the FAGE cell or the entrance nozzle are more likely. The residence time of the gas mixture between entrance nozzle and detection beam can be calculated from the volume of the cell (0.25 l) and the gas flow (3 l min^{-1} STP) to around 1 sec, leaving ample time for collisions with the reactor walls.

It can hence be concluded that in the UL-FAGE an interference signal corresponding to [OH] = 1×10^{6} cm^{-3} (order of magnitude of the disagreement between model and measurements) could be generated by less than 100 ppt of ROOOH. It needs to be emphasized, that this result is only valid for the UL-FAGE and the magnitude or even presence of this interference might be very different for other FAGE instruments and needs to be tested.

In order to estimate if ROOOH concentrations in this range can possibly be accumulated in remote biogenic environments, calculations using global and box models have been performed.

2.2 Modeling Results

The global distribution of ROOOH species produced by the RO_2 + OH reaction was investigated using the Met Office's Unified Model with the United Kingdom Chemistry and Aerosols scheme (UM-UKCA), version 8.4 (Abraham et al., 2012). UM-UKCA is a global chemistry-climate model with a horizontal resolution of 1.875° in longitude × 1.25° in latitude on 85 vertical levels from the surface up to a height of 85 km (in its N96-L85 configuration). The chemistry scheme and emissions used in the present study were described in detail in a recent work (Ferracci et al., 2018) and included isoprene oxidation (Archibald et al., 2010) and isoprene emissions.

Crucially, the model simulated the abundances of a number of peroxy radicals resulting from the oxidation of emitted VOCs: CH_3O_2 (methyl peroxy), $CH_3CH_2O_2$ (ethyl peroxy), $CH_3CH_2CH_2O_2$ (*n*-propyl peroxy), $(CH_3)_2CHO_2$ (*i*-propyl peroxy), $CH_3C(O)O_2$ (acetyl peroxy), $CH_3CH_2C(O)O_2$ (propionyl peroxy), $CH_3C(O)CH_2O_2$ (propyldioxy peroxy). Peroxy radicals from the first oxidation of isoprene were lumped into one species, as those from the oxidation of isoprene oxidation products (methacrolein and methyl vinyl ketone). These were used, along with the modelled number densities of OH and a rate constant k_1 of 1.5×10^{-10} cm^3 s^{-1} for all RO_2 + OH reactions (consistent with laboratory studies (Faragó et al., 2015;Assaf et al., 2017b;Assaf et al., 2016)) to calculate the total rate of production of ROOOH species. The total atmospheric abundance of trioxide species, $[ROOOH]_{ss}$, was then calculated offline assuming steady state between the production and loss (*L*) processes of ROOOH, according to the equation:

$$[\mathrm{ROOOH}]_{\mathrm{SS}} = \frac{k_1[\mathrm{OH}]\sum_{i=1}^{n}[\mathrm{RO}_{2,i}]}{L} \qquad (1)$$

where the sum is across all RO_2 radicals in the model excluding methyl peroxy radicals, for which it has been shown that the production of a trioxide species is only a minor product channel (Assaf et al., 2017a) while the trioxide yield is expected to be close to 1 for larger peroxy radicals (Assaf et al., 2018a).

Steady-state ROOOH abundances were calculated “offline” using the modelled abundances of hourly [OH] and $[RO_2]$ along with a rate constant (Assaf et al., 2016;Assaf et al., 2017b) for ROOOH formation of 1.5×10^{-10} cm^3 s^{-1}. As neither the removal rate nor the dominant loss process ~~the lifetime~~ of these ROOOH species are currently ~~is not~~ known, different removal rates were tested, ranging from 10^{-5} to 10^{-2} s^{-1}. In any case, t~~T~~he modelled [ROOOH] followed a diurnal and seasonal cycle similar to that of its precursors (OH and RO_2). Therefore the highest [ROOOH] values were found around midday-2pm in the summer months (JJA in the Northern Hemisphere, DJF in the Southern Hemisphere). The peak [ROOOH] values shown in **Figure 9~~3~~** and in **Figure S4~~9~~** were determined by producing an average seasonal diurnal cycle for each model grid cell and then plotting only its peak [ROOOH] value. **Figure ~~3~~ 9** shows the average diurnal peak concentration of ROOOH in the Boreal (left) and Austral (right) summer obtained using a removal rate of 10^{-4} s^{-1}, leading to ROOOH lifetimes of around 3 hours, on the same order as the lifetime of ROOH species. Peak concentrations of several 100 ppt are reached in this scenario, especially at tropical latitudes, which would lead to an interference in the UL-FAGE system of the order of 1×10^{6} cm^{-3}. However, we would like to emphasize that both, the modelled concentration of ROOOH in the atmosphere as well as the sensitivity of the UL-FAGE against ROOOH species, bear currently an uncertainty of at least a factor of 10.

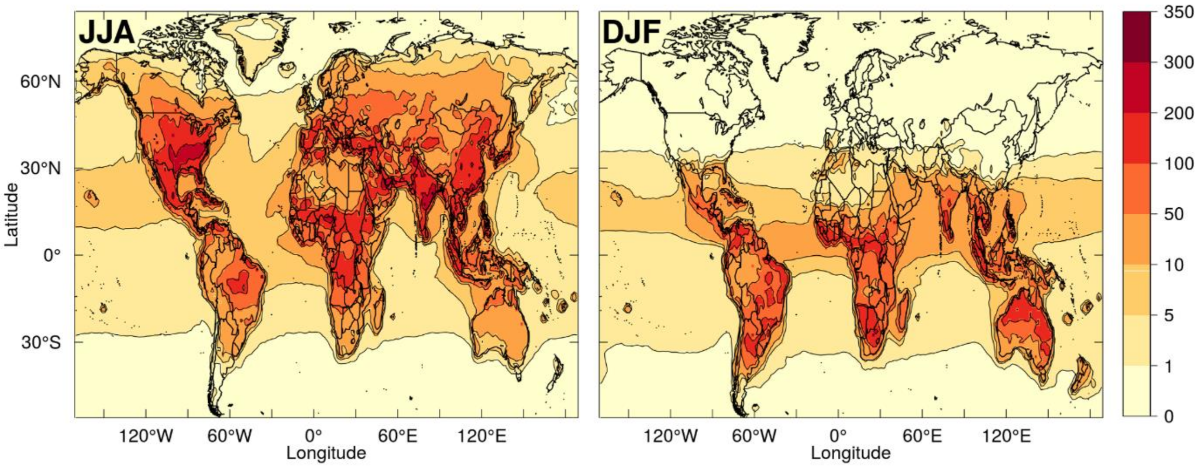

Figure 9~~3~~: Modelled mean diurnal peak ROOOH volume mixing ratio (in ppt) during Northern (left) and Southern (right) summer months, using a combined removal rate for all ROOOH of 10^{-4} s^{-1}.

To confirm these global model results, a steady-state box model, constrained to observations (including OH, NO, Isoprene and HO_2) made in the South East USA (Feiner et al., 2016), was developed. The results of the calculations with the steady-state model are shown in **Figure ~~4~~10**, which highlights that at low levels of [NO] (< 200 ppt), typical in remote BVOC rich environments, levels of [ROOOH] are predicted to be on the order of 50-200 ppt, with a steep increase at [NO] < 100 ppt. The two datasets plotted in **Figure ~~4~~ 10** span a range of different NMVOC (isoprene) mixing ratios and highlight that ROOOH levels increase with increasing [VOC] and decreasing [NO], in agreement with the global 3D modelling results shown in **Figure ~~3~~9**.

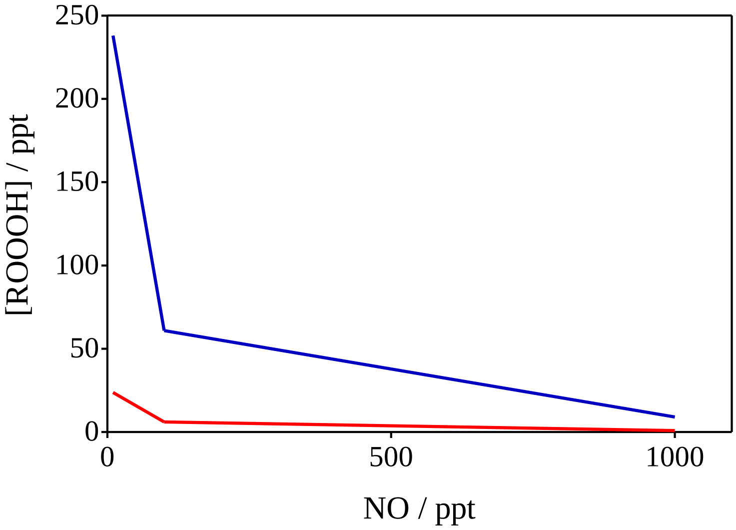

Figure ~~4~~10: Variation in ROOOH as a function of NO (x-axis) and VOC reactivity (different colours) constrained by data from Feiner et al. (Feiner et al., 2016). Those data in red reflect a situation of VOC reactivity of 5 s^{-1} whilst the blue data reflect VOC reactivity of 24 s^{-1} (similar to that seen in regions like the Amazon).

3. Discussion

In this work we have shown that the product of the reaction of RO_2 radicals with OH radicals leads to an OH interference signal in the UL-FAGE instrument. The intensity of such interference or even the occurrence at all can depend on the design and working conditions of the FAGE set-up, which is different for different groups. However, i~~I~~f occurring also with a comparable intensity in other FAGE instruments, this interference might~~it can~~ be high enough to explain numerous observations obtained with FAGE instruments from other research groups including:

(i) Underestimation by models of OH concentrations measured in remote, biogenic environments: the global model predicts ROOOH peak concentrations in remote environments that are possibly~~robably~~ high enough to explain, at least partially, the observed disagreement between model and measurements (Whalley et al., 2011;Lelieveld et al., 2008;Hofzumahaus et al., 2009;Tan et al., 2017).

(ii) Variability of interferences observed in field campaigns: The box model calculations have shown that the concentration of ROOOH species varies with NO, VOC concentration and $J(O^1D)$ in the same way as the amplitude of the interference such as observed by the group of W. Brune (Feiner et al., 2016).

(iii) Interference observed from O_3 + alkenes: the tentative explanation of alkene ozonolysis being the source of internally formed OH radicals through decomposition of the stabilized Criegee intermediate (Novelli et al., 2017) is possibly also, at least partially, due to ROOOH formed in a secondary reaction from RO_2 and OH, both generated during the ozonolysis (Johnson and Marston, 2008) of the very high VOC and O_3 concentrations in laboratory experiments (Novelli et al., 2014b;Rickly and Stevens, 2018;Fuchs et al., 2016). Indeed, it is observed in these experiments that the interference scales with the O_3+alkene turnover rate, i.e. the time that ROOOH can accumulate.

(iv) Interferences observed in SAPHIR chamber: Fuchs *et al.* have carried out experiments under low NO conditions by comparing OH concentrations measured by FAGE and DOAS(Fuchs et al., 2012). Most of the time the agreement between both techniques was excellent, but on a few days towards the end of the campaign higher OH concentrations were measured by FAGE compared to DOAS. The NO concentrations on these days were lower, making the formation of ROOOH more likely, than on days with excellent agreement between FAGE and DOAS (Table 2 in Fuchs *et al*.(Fuchs et al., 2012)).

The results presented in this work thus propose a plausible solution to answer many open questions. Of course, the uncertainties are currently high on both, the observed FAGE interference per ROOOH molecule as well as the maximum ROOOH concentration that can accumulate in real environments. The first point could be improved through well-designed chamber studies under very low NO concentrations: such experiments have already been carried out (Nguyen et al., 2014) and a detailed analysis of the data might support the conclusions from this work. The second point is more difficult to ameliorate because the steady state ROOOH concentration directly scales with its removal rate, and currently nothing is known about the fate of ROOOH. Perhaps the table can be turned by using the evolution of the observed interferences to learn about the fate of ROOOH?

Nonetheless, even with current uncertainties the implications on our understanding of atmospheric oxidation chemistry are significant. We provide ~~strong evidence for~~ a plausible mechanism for how and why high OH levels in some environments are bolstered by a false signal, in a sense validating our current generation of models and reducing the need for speculative chemistry to explain the difference in simulated and observed OH of earlier field campaigns in pristine environments. With further observations and model development, the outcome will be to improve our ability to predict the OH budget in pristine environments and the impacts of changes on the global chemistry-climate system.

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