

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 RO₂ 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 RO₂ 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 it is 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 HO₂ 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 CH₃O + HO₂ and CH₃OH + O₂. 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 CH₃O and HO₂ is thermodynamically more favoured (Assaf et al., 2018a). Therefore 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.

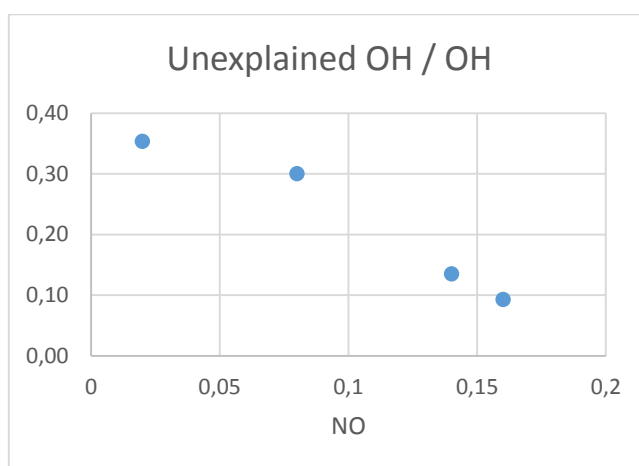
We have now linked this information to the paper of Mao and not as a general statement on observed interferences.

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 $O_3 + \text{alkene}$ 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 O₃ 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 O¹D 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, O₃, 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(O¹D) 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 RO₂ + OH can show if part of the background signal might be correlated with the turnover of the reaction of RO₂ 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 RO₂ + OH and other oxidation products, we have carried out experiments for isoprene and butane with increased VOC concentration, but the same OH and O₃ concentrations: under these conditions the mixture contains nearly equal concentrations of all other oxidation products, except for RO₂ + 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 $\text{RO}_2 + \text{OH}$ 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 $\text{J}(\text{O}^1\text{D})$ and low NO_x conditions.

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