Review acp-2018-441 Fittschen et al., 2018

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 ?

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 .

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.

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 ?

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).

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.

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.

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 RO2.

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.

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 JO1D are very low.

d) *the species responsible for this interference was linked to a low NOx 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.

P5 L17 *This can be interpreted as interference*…

What about other possible second order isoprene oxidation products ?

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.

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.

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 JO1D and low NOx conditions.