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Atmospheric Measurement Techniques Discussions

Interactive comment on "Investigation of potential interferences in the detection of atmospheric RO_x radicals by laser-induced fluorescence under dark conditions" *by* H. Fuchs et al.

H. Fuchs et al.

h.fuchs@fz-juelich.de

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We thank the reviewer for the helpful comments

Comment: The experiments were performed with two instrument configurations, one with a short inlet and an aircraft instrument with a longer inlet. The major concern I have is the experimental parameters that were employed with the two different configurations. If the critical orifice and therefore the sampling flow rate is the same for the short and long inlet (0.4 mm, 1 slm, Pg 12480 Line 19), why is a different laser repetition rate used for the two configurations? Is this the normal operational configuration that the long inlet and the short inlet have the same critical orifice diameter? If not,

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I think this is a major point that needs to be addressed because the tests were not carried out under normal operational conditions for one (or both?) configurations.

Response: The main intention of the present study was to investigate whether ozonolysis products or NO_3 related reactions may cause unknown, but relevant interferences in our ground-based LIF instruments. The reason why we also tested the OH cell of the aircraft instrument was to study the possible influence of a longer gas inlet on these potential interferences. For that purpose, the OH cell was operated under comparable conditions as in the ground-based instrument. We used an 0.4 mm inlet nozzle (for aircraft application, we normally use a larger orifice of 1.0 mm) and the same cell pressure as in the ground-based instrument to have the same volume flow in the detection system. The laser repetition rates that were used in these experiments are exactly the rates normally used for the two systems. In the system with the long inlet, the velocity of air going through the fluorescence cell is smaller than in the fluorescence cell with the short inlet. The reason is that the gas beam has more time to broaden across the diameter of the long inlet, whereas in the cell with short inlet the distance between the critical orifice and the fluorescence cell is short enough that the diameter of the gas beam does not become as broad.

We will change the text p12480 l13-l20: "The body of the OH detection cell of the aircraft instrument has the same cubical design and size as the ground-based version. However, it differs in the distance between the tip of the inlet and the fluorescence detection (Fig. 1), which needs to be longer in order to sample ambient air through the aircraft fuselage. In the current work, the OH cell of the aircraft instrument was used to study the possible influence of the extended gas inlet on potential interferences for otherwise comparable experimental conditions used for ground-based measurements. Both ground-based and aircraft measurement cells have a critical inlet nozzle with an orifice diameter of 0.4 mm (1 slm sampling flow rate) and were operated at the same cell pressure (4 hPa). In both cells, a sheath flow of 1 slm of dry nitrogen was added downstream of the inlet nozzle."

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Comment: The short inlet and long inlet configurations differ not only in inlet length but also in nozzle design. How much influence does the nozzle itself have? Have tests been done with placing the skimmer nozzle on the long inlet and the drilled nozzle onto the short inlet?

Response: The design of the inlets does not allow for an exchange of nozzles, because the instrument with the long inlet is deployed on the aircraft HALO with a specific mounting of the cell inside the pylon. We agree that specifics of the nozzles may influence artifacts and are currently working on designing different nozzles.

Comment: Can you quantify the interference from acetone photolysis for the long inlet/lower repetition rate configuration?

Response: We did not do the experiment with the long inlet. The investigation of photolytical interferences for the aircraft instrument was not subject of this study.

Comment: What is the ozone interference for the instrument with the short inlet and higher repetition rate? Is this ozone interference always subtracted from the measurements obtained with the FZJ LIF instruments?

Response: The ozone interference in both instruments are similar. The value was measured in each experiment and subtracted (p12488 l11-14). We will add on p12488 l16: "The reproducibility of the ozone background measurement limited the accuracy of OH in these experiments. Therefore, the limit of detection of approximately 1.5×10^6 cm^{-3} was higher compared to field measurements, when ozone concentrations are much lower. ... These values were similar in experiments with both instruments."

Comment: Ozonolysis experiments were done with the long inlet. I think it would be valuable to see the results for the short inlet as well, and would be also beneficial to have several other inlet lengths (and therefore residence times) in between those. From Novelli et al. (PCCP 2014), at least for the MPIC LIF instrument, it seems as though there is a peak residence time for "optimal interference" and it would be interesting to

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see if the FZJ instrument shows something similar.

Response: We will add results from the cell with the short inlet in Fig. 4. We did not perform all experiments with high reactant concentrations shown in Fig. 5 on the cell with the short inlet, but results from experiments with this system are shown in Fig. 6. We did not attempt to study the dependence on the residence time in more detail, because ozonolysis has turned out to be a non-significant interference problem for our instrument. However, we agree, that further tests beyond this paper would be of interest in order to understand to what extent different instrumental designs may influence possible artifacts.

Comment: Since the residence times are just estimates and itś unclear where/what process is generating the internal OH signal, how can you be sure that propane is not scavenging internal OH? Pg. 12489 Lines 5-7 suggest that since the ozone interference signal is constant that no internal scavenging is taking place. But if the internal OH resulting from ozonolysis is being generated directly after the nozzle in the gas expansion, then depending on the cell configuration, the OH interference generated by ozone photolysis is taking place at a later time.

Response: The residence time in the short inlet detection cell is relatively well known. From previous studies with short-inlet measurement cells we know that the gas expansion through the inlet nozzle produces a fast collimated gas jet which has a diameter of about 1 cm and crosses the detection volume after a travelling time of 1 to 2 ms (Holland et al., 1995; Fuchs et al., 2011). This is also supported by the observation of the pulsed OH signal in our OH reactivity measurement instrument. In that instrument, OH is produced in front of a short-inlet OH cell by laser flash photolysis (duration of 10ns). The OH which enters the cell is monitored by LIF using a multi-channel scaler with a time resolution of 1 ms. After about 2 ms, the OH signal reaches its maximum demonstrating that it takes about this time for OH to reach the detection volume. This residence time is very much shorter than the OH lifetime with respect to reaction with propane at the reduced cell pressure.

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The internally produced OH from ozone photolysis is produced on the laser axis and has an even shorter residence time than OH potentially formed near the inlet nozzle. We agree that our tests only show that OH that is internally produced is not scavenged by OH on a short time scale. However, internally produced OH from ozone photolysis was also not scavenged by ten times higher propane concentrations (p12489 l7) than used in the alkene ozonolysis experiments. In addition, the dilution of reactants in the low pressure cells gives a lifetime of internally produced OH of 1 s in the presence of the 10 ppmv propane, so that an error in the estimates of the residence times is negligible.

We will add on p12489 l1-7: "In contrast, the lifetime of OH inside the measurement cell is increased by a factor of approximately 250 due to the reduced pressure **(e.g. 1s in the presence of 10ppmv propane)**. ... **An example for internal OH production is given** by the ozone interference signal...".

We will modify the text on p12481 l1-8 to better explain our estimate of residence times inside the fluorescence cells: "From previous studies with short-inlet measurement cells, we know that the gas expansion through the inlet nozzle produces a fast, collimated gas jet, which has a diameter of about 1 cm when it crosses the detection volume after a travelling time of 1 to 2 ms (Holland et al., 1995; Fuchs et al., 2011). In case of the long inlet, the gas beam eventually slows down, mixes with the sheath gas and fills the whole cross-section of the inlet tube. The estimated residence time for air between sampling and detection is on the order of 30 ms in this case."

Comment: The magnitude of the interference signal for the ozonolysis experiments is larger for the long inlet configuration (Pg. 12490 Line 19-20). Any speculation on why this might be?

Response: We see this as a hint that the internal OH production depends on the residence time. This would be consistent with OH production in the gas phase from e.g. decomposition of ozonolysis products as we discuss later (e.g. p12492 l18-29).

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Comment: Table 1 lists laser power as around 13 mW. Was this the case for both inlet lengths/repetition rates? Is that the normal operational power?

Response: The power of the laser differs depending on the state of the dye laser. It was similar for both instruments in these experiments. It is on the lower edge of what is applied in field campaigns but not exceptionally small. Good alignment of the dye laser can give laser power between 20 and 30mW.

Comment: Figure 7 mentions "Subtraction of an offset in OH by LIF." What is this offset? Is it the unexplained/interference OH?

Response: This is correct. We will change the caption: "Subtraction of an offset in OH by LIF for each α-pinene oxidation period that would be an interference leads to corrected LIF data (LIF-corr) in reasonable agreement with DOAS and modelled concentrations."

Technical comments will be corrected accordingly to the comments of the reviewer.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 12475, 2015.