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# *Interactive comment on* "Characterisation of an inlet pre-injector laser induced fluorescence instrument for the measurement of ambient hydroxyl radicals" *by* A. Novelli et al.

**Anonymous Referee #1**

Received and published: 25 February 2014

The authors report the application of an chemical titration system (IPI) for OH radicals, in order to determine the chemical zero of an OH LIF instrument. The system is similar to what has been reported by a different group (Mao et al., 2012) for a similar instrument. This system allows to identify interferences in the OH measurement by OH that is artificially produced inside the measurement cell. This OH would be attributed as ambient OH, if only the traditional modulation of the excitation wavelength is used, in order to determine the background signal of the instrument. It turns out that a substantial amount of the total fluorescence signal is caused by artificial OH. Therefore, this paper provides important information about measurements done with this particular

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instrument. Although the magnitude of this interference most likely strongly depends on the specific instrument and environment, in which OH measurements by LIF are performed, as pointed out by the authors, this report is also of great interest for other groups applying LIF for the detection of ambient OH.

This LIF instrument with the IPI system measured in three campaigns. The authors discuss in detail the technical part of the IPI system and how they determined ambient OH concentrations from the different signals they got from the LIF system, when they use the chemical titration scheme. They also report instrumental tests that were done during the measurement campaigns. A short discussion about the potential impact of the large background OH signal they observed in these campaigns, when they applied the IPI-system, on measurement during previous campaigns is given. All this is carefully done and clearly written in the manuscript.

The major criticism I have concerns what is not discussed in the manuscript. The manuscript is limited to what has been achieved during the three measurement campaigns. Most parts of the paper are like a technical description of the instrument which describes, how measurements were performed during the specific campaigns. This alone is important and makes certainly a paper that well fits within the scope of this journal. A major improvement of the instrument is described that is of great interest for the readership. However, I expected to read more about laboratory tests, comparison with a similar systems and literature, analysis of the dependence of the OH background signal on instrumental parameters and an analysis of potential reasons for this signal. This could include the following points:

- Application of the IPI-system with an OH source in laboratory tests, in order to determine the OH-loss in the IPI-system.

- Analysis of the dependence of the interfering signal on instrumental parameters such as laser power or pressure in the low pressure region of the instrument.

- Tests of potential candidates which could be responsible for the observed background signal in laboratory experiments. Such tests would be also interesting even if no interference is found, in order to exclude potential interferences.

- Mao et al. report a significant removal of the interfering OH inside the measurement cell. They report a destruction of 80-94% of ambient OH in their inlet system when they add 1-3.3sccm C3F6 (residence time 100ms). Here, the authors also remove 95% of the ambient OH within 2.5-4ms residence time in the IPI, so that the OH reactivity of the sampled air is most likely even larger than for the system described by Mao et al., when they add the OH scavenger. One may suspect that also a significant part of the artificial OH inside the measurement cell would be removed in the HORUS system. This concerns also the question, where the artificial OH is produced as extensively discussed by Mao et al..

- The authors presented at the AGU meeting 2012 (cited by a different paper from the same group of authors, Hens et al., 2013) the hypothesis that Criegee radicals may cause artificial signals in the LIF instrument. This was also hypothesized by Mao et al. 2012, when they report similar effects. Mauldin et al. 2013 presented the same hypothesis for a background signal observed in the CIMS instrument applying a similar titration scheme as done here. However, no discussion or test of this hypothesis is found here. Do the authors reject this hypothesis? If so, why did they do so?

- The authors only discuss the interference signal for their OH detection cell. Is something similar also observed in the HO2 cell (e.g. if the cell is operated without the addition of NO)? Could it be that a similar interference is also present in the HO2 measurements (see also my comment regarding results from the HOx-Comp campaign below)? Is it possible that the magnitude increases with reaction time (distance between inlet nozzle and fluorescence detection) and/or addition of NO? What would be the consequences for the HO2 measurements?

The authors may have their reasons, why they limit themselves to the description of the application of the IPI-system in the three campaigns, but the paper would clearly benefit from a broader investigation of the nature of the background signal and the application of the IPI in laboratory tests. In my opinion, a discussion of the last three points are essential for this paper, because these questions arise from what has been reported in literature (see also my specific comments).

Specific comments:

p.820 l.5-7 and l.23: The authors should clearly state from the beginning (as they do later) that the background signal has only been observed in one other instrument and that it is not clear, if this applies to other LIF instruments.

p.822/823: Although the instrument has been described in detail before, the authors may want to give some more details of the instrument such as laser power, distance between inlet and fluorescence detection (residence time of the air), so that the reader can clearly see the differences and similarities between this and other LIF instruments.

p.823/824 Eq. 1-3, p.825 l.17, p.831 l.8-10: The authors assume in Eq. 1-3 that there is no removal of OH that is artificially produced in the measurement cell. As mentioned above Mao et al. experimentally found that this is not the case in their system for presumable less OH reactivity, when they add an OH scavenger. Why do the authors think that this does not apply for their instrument, although the general design of both instruments is the same as stated on p.822 l.19-22? How do they derive the removal efficiency of OH in the low pressure region given on p.831? Where do they think that the artificial OH is produced inside the system? How does this compare to what is reported by Mao et al.?

p.824 l.23: The numbers for the flow rate are not consistent with numbers in Table 1.

p.824 l.25: Could the authors add more details about the grid such as grid size, material, consequences for the sensitivity of the instrument? How do they know that the flow

becomes more homogeneously for the complicated flow situation right downstream of the inlet orifice? Why is this important?

p.825 l.24-29 and Fig. 3: It is not clear, what the purpose of the second synthetic air line with the frit is. I assume that this line is for the purge flow when switching to the measurement mode without the addition of the OH scavenger, but some explanation would help to avoid confusion. The position, where the excess flow leaves the IPI would be helpful to be shown in Fig. 3.

p. 827 Section 2.3: The measurement campaigns and instrumentation have been partly described in previous papers. However, concerning the specific topic of the comparison between the HORUS instrument and the CIMS instruments, more details of the experimental set up of both instruments could be given here, so that the reader is convinced that measurements of both instruments are comparable. This would include e.g. distance between instruments, heights of inlets, surrounding of instruments with respect to the question, if both instruments indeed sample the same OH concentration.

p.827 l.26: Capital letters in "German Weather Service".

section 3.1: As mentioned above this would be the place where the reader would expect to read more about laboratory tests and not only about tests done in the field. All basic tests concerning the general operational parameters, proof of concept (such as titration efficiency of ambient OH), and OH loss in the IPI are given, but I would expect that this could be done with higher precision and accuracy in laboratory experiments instead of doing this under field conditions. I could imagine that especially the question of OH loss in the IPI would be much better determined in laboratory tests with an OH source. Tests in the field would certainly add valuable information like loss of species which cause the interference and can show consistency with laboratory tests.

p.828 l.15-18: Although the general procedure to estimate loss of species causing an OH signal is clear from the description given here, more information is required, in order to understand in detail what was done. How often was measured without the IPI? What

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was the reproducibility of the loss measurement? Did the authors observe any trend in the loss (during the day or over the campaign)? How long was measured without the IPI during one test? How was the loss exactly calculated? Did the authors interpolate signals between measurements before and after the IPI was removed? Are the large error bars caused by the variability of measurements during the time periods, over which measurements were averaged? Please define the exact meaning of the error bars. It would be helpful to see a figure showing single measurements and averages from an example, when the instrument sampled with and without the IPI showing, how the loss was determined.

p.829: The authors assume that the 7% loss of equivalent OH signal observed during the night can be taken as general loss of the interfering species in their inlet system, so that they can use this number also to correct daytime observations. Is this really justified? This loss is only 5 times smaller than that for OH. Therefore, I would assume that the interfering species is also a reactive, short-lived species. The authors do not present any hint about the nature of the interfering species, so that I wonder, if the same mechanism necessarily applies during day and night. One hint that this could not be the case is that during the HOxCOMP campaign large differences between the HORUS instrument and the other instruments were only observed for nighttime conditions. In contrast, the background signal during the field campaigns reported here was much larger during daytime than during nighttime.

p.831 l.14 and p.832 l.20: Figure 7 is mentioned before Figure 6.

p.832 l.23: Looking at the error bars, the authors may want to add the statement that they did not observe any significant difference. Once again, it is not clear, why the authors do not present a systematic investigation of the effect of OH production from propene ozonolysis in a laboratory study. I assume that they could determine the OH signal from propene ozonolysis for typical situations they experienced in the field by overflowing their inlet with synthetic air and ozone and doing the propene titration.

p.833 section 3.2: The good correlation between both instruments is quit convincing. However, the authors should give some more information about the CIMS-measurements including a short statement about the major contributions to precision and accuracy of measurements. What are there differences between the two CIMS instruments used here? In Berresheim et al. 2000 and Mauldin et al. 2013 a similar titration system with propane is described as used for the LIF. Was this also applied here? If so, are the background measurements for the CIMS instrument similar to what is observed for the LIF? What does this mean for the nature of the background signal in the LIF measurements?

p.833 l.21-23 and Fig. 8: A similar figure is presented in a paper by the same group of authors (Fig. 6 in Hens et al. 2013). However, the error bars (LIF and CIMS) are different in both figures and therefor also the fit results are different. Please define the error bars in the correlation plots (e.g. 1sigma precision of data). Please add why the presentations are different or make them consistent, in order to avoid confusion.

p.834 l.10-18 and Fig. 11: The authors state that the offset is caused by observations of nighttime OH by LIF that is not observed by CIMS. This is surprising regarding the fact that in general the background signal was smaller during the HOPE campaign compared to the other campaigns. Is there any suspicion what the cause of this OH signal is in the LIF instrument? Is it possible that the CIMS instrument did not observe ambient nighttime OH or the instruments did not observe the same air mass? Does the regression indeed significantly changes, if only daytime measurements are included in the fit? I have the impression that the OH values measured by LIF are smaller than those measured by CIMS for higher OH values, so that the data set is deviating from a linear relationship. This may also cause the positive intercept in the regression analysis.

p.835 l.1-10: It is not clear, if monoterpene concentrations were similar or different in the two campaigns. I would suggest to rephrase the sentences to avoid confusion. Is there any hint for differences in OVOC concentrations during both campaigns? Are

there more differences in the conditions during the campaigns which may be related to the different contributions of the background signals to the total OH signal? Are there laboratory tests of potential interferences (as mentioned above)? Does any other measured quantity correlate with the magnitude of the background signal (like ozone, NOx, VOC species, laser power of the LIF instrument...)?

p.837: The authors discuss the results from the HOxCOMP campaign regarding the now identified OH background signal. However, they do not try to use the observations during HOxCOMP, in order to discuss potential reasons for the unrealistic large background signal that was also observed during HOxCOMP for nighttime conditions. Especially the relatively simple experiments performed in the SAPHIR chamber (Schlosser et al. 2009) may give hints of the nature of the background signal. Also the fact that OH values measured for dark conditions were much larger for the HORUS instrument compared to other LIF instruments may contain valuable information as mentioned above. Larger signals of the HORUS instrument compared to other LIF instruments were also observed for HO2 measurements during dark conditions of certain SAPHIR experiments (Fuchs et al., 2010). Is it possible that also HO2 measurements are affected by the interference reported here exclusively for the detection of OH (see above)?

p.838: The authors also discuss results from the GABRIEL campaign. They clearly state that they cannot exclude that part of the large OH concentration that could not be explained by traditional chemical models is caused by a background signal similar to that found for the campaigns reported here. One argument that an interference may have not been present during the GABRIEL campaign is that newly proposed isoprene degradation models predict more OH than traditional models. However, the authors do not mention that the theoretical study by da Silva et al. 2010 does not predict large additional OH. The experimental study by Crounse et al. 2011 and one recent study in a simulation chamber (Fuchs et al. 2013) do not show a production of additional OH precursors (HPALD) and additional OH from isoprene oxidation, respectively, which would be large enough to explain their observations during GABRIEL. One further

argument is that a short-lived species may cause the interference which is only present very close to the emission source, so that airborne measurements are not affected. Is there any idea or speculation what this could be?

Fig. 3, 7, 9, and 10: Please enlarge the size of symbols in the legends.

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