

Atmos. Meas. Tech. Discuss., author comment AC5
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Reply on RC3

Marvin Glowania et al.

Author comment on "Comparison of formaldehyde measurements by Hantzsch, CRDS and DOAS in the SAPHIR chamber" by Marvin Glowania et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-10-AC5>, 2021

We thank the reviewer for the helpful comments.

Comment: Line 65: LIF for HCHO does not require a custom fiber laser, e.g., St. Clair et al., 2019. <https://doi.org/10.5194/amt-12-4581-2019>

Response: We changed the text: "LIF instruments also custom-built and instruments often make use of a fibre laser for the excitation."

Comment: Line 83: "Comparisons" should not be capitalized.

Response: Done.

Comment: Line 211: The Russell et al., 2020 citation uses the Picarro instrument, but provides no understanding of the instrument itself and adds no value to this manuscript. Perhaps it can be considered an instrument intercomparison, but that seems a real stretch. Your work here is considerably better on that topic.

Response: We agree that the reference does not serve as a reference for understanding the instrument and cancelled it in L211.

Comment: Line 111: "Reports of instrument comparisons concluded that the measurement of formaldehyde remains challenging specifically for atmospheric concentrations in the low ppbv range." This may be true for commercially available instruments, but is not true for research-grade instruments. You should qualify this statement.

Response: We added at the end of the sentence "in particular for commercial instruments" to qualify the statement.

Comment: Line 253: "Therefore, DOAS measurements can be regarded as independent from Hantzsch measurements in the comparison here." I strongly disagree with this statement. The DOAS data is produced using an empirical calibration where a Hantzsch instrument was the standard. They each may provide some unique information for data evaluation, but they should not be considered independent measurements. On that point, I do not understand how the DOAS measurement can have a higher accuracy (6%) than the technique used to calibrate it (Hantzsch, 8.5%).

Response: We agree with the reviewer and deleted the statement in line 254. We corrected the stated accuracy of 6 % which misleadingly refers to the calibration uncertainty of the OH radical cross section and added the following text (L253): "The combined accuracy of the DOAS instrument is 7%. It is basically given by accuracy of the calibration procedure of the former Hantzsch instrument which was used for the comparison with the DOAS. The given accuracy also takes into account the uncertainty in the absorption cross section from the regression between the DOAS and Hantzsch data which was 0.16%." We give additional explanation in the same paragraph: "The high-resolution cross section determined in this work compares very well with the value inferred from concurrent chamber measurements by a low-resolution DOAS and the high-resolution instrument by Brauers et al. 2007, which resulted in a differential cross section of $8.97 \times 10^{-21} \text{ cm}^2$, a value which is well within the stated accuracy of 7%. Therefore, DOAS measurements in the comparison here can be regarded as independent from Hantzsch measurements."

Comment: Section 3.2: How do you know that the size of the water-dependent offset determined at $\text{HCHO}=0$ is the same size as the water-dependent offset in the presence of HCHO? Since this is a spectroscopic interference, it seems possible that the fitting error caused by water will be dependent on the magnitude of the HCHO signal as well. A zeroing approach that removes HCHO but preserves humidity would be one solution. Is the 1.5 ppbv zero drift specified by Picarro due to this water interference or due to other factors?

Response: Indeed, there would be the chance that the water-dependent offset changes for higher HCHO. In this work, the water vapour dependence was determined, if no HCHO was present. This was then applied to all data. The correlation between measurements by the CRDS and the other instruments results in a good agreement over a wide range of typical atmospheric concentrations. The level of agreement does not exhibit a water vapour dependence. This suggests that the water vapour dependence is applicable in the same way also for non-zero formaldehyde concentrations. The reviewer argues that the fitting error caused by water might also be dependent on the magnitude of the HCHO signal itself. Since details of the spectral evaluation, the modelling of the spectral overlap between the HCHO, H_2O , and CH_4 absorption lines, and the additionally applied empirical corrections are not publicly available this question is difficult to answer quantitatively. However, the poster presentation of Hoffnagle et al. at AGU 2017 can help. It shows the intensity of the overlapping absorption lines of CH_4 @ 100 ppm, HO @ 2.2 %, and HCHO @ 7.4 ppm. From this one can estimate the HCHO line at a typical atmospheric mixing ratio of 5 ppb being about a factor of 6000 smaller than the water vapour line at 1 % water vapour. Taking this into account it seems unlikely that the presence of HCHO at atmospheric conditions would have an influence on the fitting error.

We added in the discussion of the correlation between measurements (L372): "This also demonstrates that the zero-point corrections determined can be applied over a wide range of atmospheric HCHO concentrations."

Comment: Figure 7 is rather small for the amount of data it contains. Please consider making it bigger.

Response: We scaled the figure to fit the width of one column in a final publication in AMT. We will pay again attention, if the figure is large enough, if the paper is type-set for final publication.