Atmospheric Measurement Techniques Discussions

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Reply on RC2

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-AC4, 2021

We thank the reviewer for the helpful comments.

Comment: Line 64-66: The LIF technique does not require a fiber laser (see Hottle et al., 2009), though a fiber laser is often used. Please include Cazorla et al., 2015 as a reference.

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

Comment: Table 1. This reads as an assessment of the measurement methodologies (Hantsch/CRDS/DOAS), though the figures given refer only to the specific instruments used here. I suggest titling each column with the instrument model.

Response: We added the instrument model as an additional row.

Comment: Line 186. Please provide the name of the reagent used for HCHO scrubbing.

Response: Unfortunately, the manufacturer did not provide which exact material is used, though we asked for this information. Therefore, we cannot give more information than currently done. To make this point clear, we added: "However, the exact scavenging material is not specified by the manufacturer."

Comment: Line 206. It is unclear to me how the reproducibility of 2% on the titration and a 3% uncertainty in flow measurements adds together to get an 8.5% measurement accuracy. Please clarify.

Response: In order to explain, how the accuracy is calculated we changed the text L206: „Error propagation results in a total uncertainty of the HCHO concentration of 3.6,% that adds to the reproducibility of the calibration procedure of 5% (Section 3.1)." We changed also the text in L285: "The 1 sigma reproducibility of the calibration measurements was 5% and has been included in the HCHO measurement accuracy of 8.6% (Table 1)."

Comment: Line 214. Please quantify "close".

Response: We changed the text to "approximately 0.5m away from".

Comment: Line 223. It is unclear where the stated accuracy of 10% comes from. It is not derived or demonstrated in this study. The referenced paper (Russell et al., 2020) discusses the Picarro instrument uncertainty in the supplement. It states "The CRDS from Picarro is factory calibrated and has a precision of 1.2ppb + 0.1% of the reading for HCHO readings, with no dependence on humidity levels [...]. For the determination of absolute concentrations of HCHO, for instance during chamber testing, the accuracy is $pm10$%". Glowania et al. show a humidity dependence and gives a higher precision. It seems the two papers are not in agreement, so it does not seem that the accuracy in the reference given can be applied here.

Response: The number is taken from the datasheet provided by Picarro (https://www.picarro.com/sites/default/files/Picarro_G2307%20Datasheet_180328.pdf). We added this as a reference. The precision that the reviewer mention is also from the datasheet and can be regarded as an upper limit that is guaranteed by the manufacturer, so that a higher precision achieved in reality as shown in this work is possible.

Comment: Line 253. The DOAS method relies on cross-calibration with a Hantzsch. While two different Hantzsch instruments are used, is it possible that any systematic offsets related to the Hantzsch methodology could influence DOAS observations? I suggest showing the data used in the regression analysis discussed in lines 248-252.

Response: From our years-long experience in operating Hantzsch instruments we do not see any reason for a persistent systematic offset between two instruments. Both have been calibrated using the same procedure and the same commercially available calibration solutions, hence potential differences in their detection sensitivities would be corrected for by the calibration. Showing the plot of the regression analysis between the DOAS and Hantzsch data, as suggested by the reviewer, would not be of help to detect a possible systematic difference between the two Hantzsch instruments.

Comment: Line 263-265. Again, it is unclear how the 6% accuracy is calculated. More details are needed. Does it take into account the uncertainty in the absorption cross section from the regression described in lines 248-252?

Response: The rotational-vibrational absorption lines of HCHO around 308 nm are very narrow (in the low picometer range) and consequently the experimentally observes cross section is strongly dependent on the spectral resolution of the instrument. Meller and Moortgat used a resolution of 0.025 nm while our DOAS instrument has a resolution of 0.0025 nm and therefore the cross sections are different. We changed the text L252: "The accuracy of the DOAS formaldehyde data is estimated to be 7%. It is mainly determined by the accuracy of the calibration procedure of the former Hantzsch instrument which was used for the comparison with the DOAS. It 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 L253: "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 8.97x10^-21 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: Figure 1. I suggest showing HCHO concentrations using each method in panel 2, rather than a second day showing the same thing as panel 1.

Response: In our opinion, plotting calculated mixing ratios of a zero signal does not illustrate exactly what we intend to show. The point we would like to make is that there is a changing zero signal that needs to be adequately monitored. Plotting mixing ratio would require subtracting the changing zero signal from the measurements and the information,

how much the zero signal changes over time is lost. Therefore, we prefer keeping the plot as it is. The information how the signal converts to an equivalent HCHO concentration is given in the caption.

Comment: Line 291. If the Picarro specifies an anticipated zero drift of 1.5 ppb, I think the offset should not be classified as a "bias", but rather a zero-point that needs to be taken into account. The offset of the Hantzsch instrument is not called a "bias".

Response: We changed the wording as suggested by the reviewer.

Comment: Line 366: Is the intercept -0.13 ppb?

Response: Thanks for noticing the typo that we corrected in the revised version.

Comment: Lines 406-416. It is unclear how the main points of this paper can be applied to future deployments of the CRDS method. How often does a HCHO zero need to be taken with the CRDS instrument if ambient H2O varies? Could the HCHO zeroing system used for the Hantzsch be applied to the Picarro? Can the authors reassess their observations using the new software?

Response: Our observation demonstrate drifts are within the specification of the manufacturer, but that there is need for regular zero measurements, if the user wants to achieve a higher accuracy. From what we see, zeroing once a day would be sufficient and characterization of the humidity dependence on a regular basis. Our dataset does not allow to specify how often this needs to be done. Unfortunately, we could not install the new software version to test, if the water vapour dependence of the zero disappears. We added L425: "Observations in this work suggest that zero measurements should be done once a day and that the water dependence of the zero point of the CRDS instruments does likely not significantly change at least for a month-long deployment."

Comment: Throughout. The authors switch between 1 sigma and 3 sigma LODs. A consistent reporting methodology would improve the readability.

Response: All statements concerning the limit-of-detection are now given as 3- sigma LODs.