Atmospheric Measurement Techniques Discussions

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Reply on CC1

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-AC3, 2021

We thank Andrew Whitehill for the helpful comments.

Comment: Line 59: "Absorption spectroscopy has the advantage of being calibration-free" - this is highly misleading, as the Picarro instrument's formaldehyde retrieval is based partially on a factory-applied calibration and factory-programmed empirical correction factors. This is also contradicted by the later observation of a water vapor dependence on the accuracy of the instrument.

Response: Calibration-free does not mean that there is no careful characterization of the instrument's properties and/or zero measurements required, but that the concentration can be calculated without applying a sensitivity parameter that is derived from measurements using a calibration standard. We added in L59: "Absorption spectroscopy has the advantage that it does not need regular calibrations with a gas standard. But it requires knowledge of absorption cross sections and careful characterization of instrumental properties to avoid or correct possible spectral interferences and signal offsets."

Comment: Line 62: There are at least 4 commercially available spectroscopic formaldehyde instruments with sub-ppb sensitivity of which we are aware: Aerodyne Research (absorption spectroscopy at ca. 1765 cm-1) Aeris Technologies (absorption spectroscopy at ca. 2832 cm-1) Gasera (Gasera One Formaldehyde, photoaccoustic spectroscopy) Picarro (G2307, cavity ringdown spectroscopy at 5625.85 cm-1)

Response: Thanks for the hints. We added all instruments that are not mentioned yet in Line 62: "While in the past most of the instruments were custom-built and required substantial pre-knowledge of operators, commercial instruments based on absorption spectroscopic methods have recently become available (CRDS by Picarro Inc., TDLS by Aeros Technology and by Aerodyne Research, photoacustic spectroscopy by Gasera).

Comment: Section 2.3: Authors should expand their discussion of how they calibrated the Picarro instrument.

Response: In fact, there was no calibration done in the sense of providing standard additions of HCHO. To better explain, how the zero-point measurements were done, we added L 230: "For determining the instrumental zero in this work, measurements in the chamber are used, when no formaldehyde was present. The humidification process of the

air in the chamber allowed to characterize the dependence of the instrumental zero on water vapour (Section 3.2)."

Comment: Line 223: Authors state that the accuracy of the Picarro G2307 is 10%. However, their own data (including the water vapor interference and the zero drift) contradict this 10% value, especially for low formaldehyde concentrations.

Response: The 10% accuracy is taken from the datasheet provided by Picarro (https://www.picarro.com/sites/default/files/Picarro_G2307%20Datasheet_180328.pdf). Indeed, the accuracy could be worse, if the water vapor correction is not applied as shown in this work.

Comment: Section 3.2 - Authors should make it more clear when they are discussing synthetic (methane-free) air and when they are discussing air with ambient methane concentrations. In particular, authors ignore the potential methane (and methane+water) cross-sensitivities of the instrument and should address his in their discussion and analysis of data.

Response: Thanks for the hint. We are aware of that there is an interference from methane in the CRDS measurements and observed that also in chamber experiments with exceptionally high methane concentrations. However, for ambient concentrations, this interference is rather small and does not significantly contribute to the signal. To clarify this point, we added L 324: "In experiments with exceptionally high non-atmospheric mixing ratios of methane, also an offset appears that depends on methane. However, for atmospheric mixing ratios as experienced in this work, this additional offset was not significant and therefore it is neglected."