

Supplement of Atmos. Meas. Tech., 12, 1767–1783, 2019
<https://doi.org/10.5194/amt-12-1767-2019-supplement>
© Author(s) 2019. This work is distributed under
the Creative Commons Attribution 4.0 License.



Supplement of

Adaptation and performance assessment of a quantum and interband cascade laser spectrometer for simultaneous airborne in situ observation of CH₄, C₂H₆, CO₂, CO and N₂O

Julian Kostinek et al.

Correspondence to: Julian Kostinek (julian.kostinek@dlr.de)

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.

S1 Compatibility & Comparison with other instruments

- We have computed the differences between flasks and the CRDS in the same way they have been computed for the QCLS in the main manuscript by interpolating high frequent in situ data to the flask end fill times. This has been done to get an idea on what spread can be expected due to the long flask sampling time compared to the fast measurement cycles of CRDS and
- 5 QCLS. Although the spread in Fig. S1 might be slightly bigger for the QCLS compared to the CRDS it remains unclear if this is due to higher sampling rate and/or response time of the QCLS.

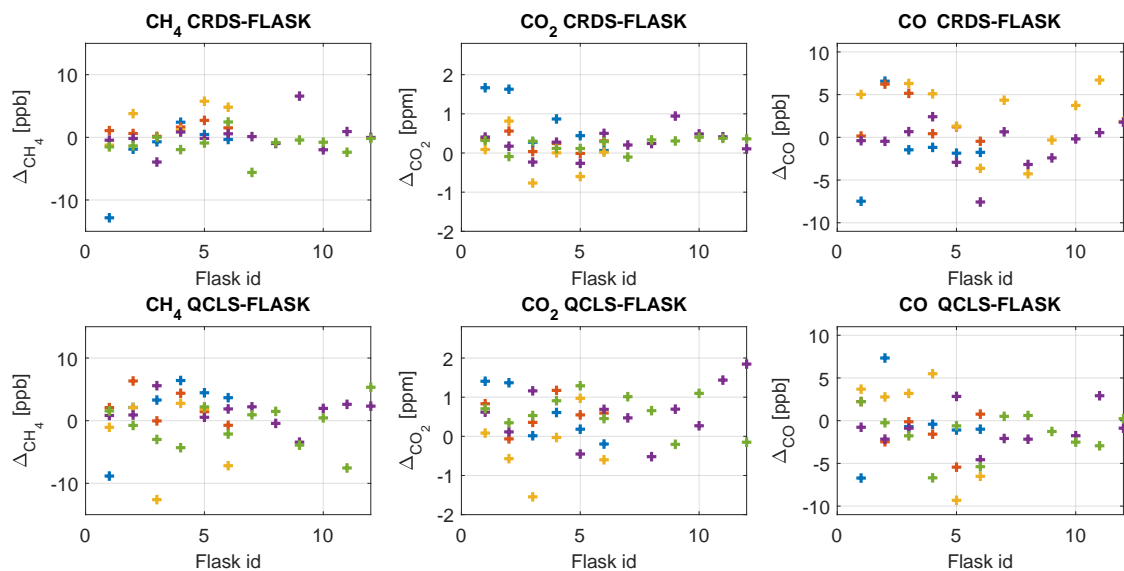


Figure S1. Comparison of CRDS (upper row) and QCLS (lower row) derived mole fractions to flask samples. Interpretation of the errors against flask samples is difficult for high-variability flight segments, due to the large flask sampling time. The residual plots show color-coded data from 5 typical flights on 10/03/2017, 10/11/2017, 10/14/2017, 10/18/2017 and 10/20/2017.

S2 Cross-sensitivities

- There was doubt if the water vapor correction is deteriorating compatibility between instruments. Figure S2 shows cross sensitivities of the QCLS-CRDS residuals for the flight highlighted in the original manuscript (10/03/2017) with respect to cell pressure, cell temperature and water vapor after correcting for a constant bias. The residuals have been computed by linearly interpolating the higher frequency QCLS to the CRDS time scale, due to different sampling times and patterns. From this figure, we would argue, that the water vapor correction (center row in Figure S2) is not systematically deteriorating compatibility between the instruments.
- 10

S3 Large bias in CO₂

- 15 Explaining the large bias in retrieved CO₂ requires an estimation of the influence of the isotopic composition of the working standards and the sampled air within this study. We have used working standards of synthetic nature from *Air Liquide* due to the large amount of needed calibration gas. Usually these are produced with CO₂ from natural gas & oil combustion processes. We determined the CH₄ and CO₂ values of each working standard gas cylinder using a Picarro G-1301m. This has the drawback

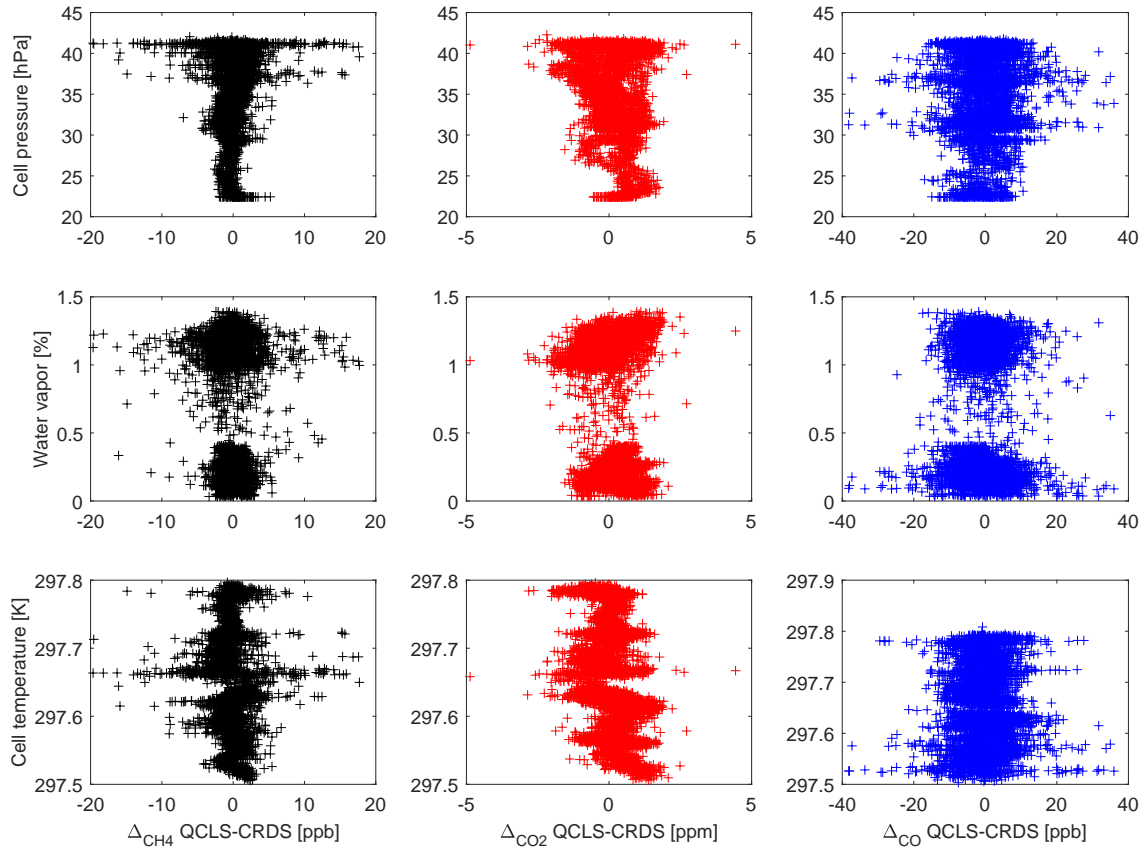


Figure S2. Cross sensitivities of the QCLS-CRDS residuals for the flight highlighted in the original manuscript (10/03/2017) with respect to cell pressure, cell temperature and water vapor after correcting for a constant bias. Due to different sampling times and patterns the higher frequency QCLS data have been linearly interpolated to the CRDS time scale.

that we do not know the isotopic composition of our working standards. The reason why we did not send our working standards to a central lab is because the influence of the isotopic composition had been considered negligible at this stage (Chen et al., 2010). It was only in late summer 2018, when we found that the instrument was using a $^{13}\text{C}^{16}\text{O}_2$ line to derive ambient CO_2 . We assume the large bias originating from differences in isotopic composition in our working standards relative to the natural terrestrial abundances. This requires an estimate on the possible influence which will be given here.

It is commonly assumed that differences in isotopic composition only make up for errors on the order of 0.1 ppm in CO_2 . This is true if measuring the primary isotopologue, as done with the Picarro CRDS. If the CO_2 concentration is derived from the secondary isotopologue ($^{13}\text{C}^{16}\text{O}_2$) the influence of isotopic composition is much larger. Let us take the $\delta^{13}\text{C} = -8.6\%$ reported for the NOAA standard Cert.-Nr. CB11361 as an example to estimate the influence of isotopic composition on retrieved mole fractions. Per definition $\delta^{13}\text{C}$ is given by

$$\delta^{13}\text{C} = \left(\frac{R_x}{R_{vpdb}} - 1 \right) \times 1000$$

Inserting the values from above and re-arranging this equation yields

$$R_{noaa} = (1 - 8.6 \times 10^{-3}) \times R_{vpdb}$$

Inserting the standard ratio for the reference materials of the Vienna Pee Dee Belemnite $R_{vpdb} = 0.011180 \pm 0.000028$ (Tohjima et al., 2009; Chen et al., 2010) yields the corresponding isotopic ratio of

5 $R_{noaa} = (1 - 8.6 \times 10^{-3}) \times 0.011180 = 0.011083$

According to HITRAN the primary isotopologue and secondary isotopologue together make up 99.5261 % of atmospheric CO₂. To satisfy both equations we obtain an abundance of 0.984350 primary isotopologue and 0.010910 ¹³C¹⁶O₂ for the NOAA standard dealt with here. However, spectral line intensities S_{ij} as defined on <https://hitran.org/docs/definitions-and-units/> are weighted according to the natural terrestrial abundances reported in HITRAN. Retrieved mole fractions are thus scaled by their terrestrial natural abundance from HITRAN. We'll first compute the unscaled ¹³C¹⁶O₂ using the natural abundance from HITRAN (98.4204 % primary and 1.1057 % secondary CO₂ isotopologue) from a hypothetical 400 ppm background (with a natural isotopic composition as defined in HITRAN) resulting in

$$^{13}CO_{2,unscaled} = 400 * 0.011057 = 4.4228$$

15 We can now estimate the influence of the different isotopic composition (NOAA example) from above by scaling the unscaled ¹³CO_{2,unscaled} with the secondary isotopologue abundance computed above. For the given absorption line, a retrieval algorithm based on HITRAN will retrieve an abundance of $CO_{2,retrieved}$ according to

$$CO_{2,retrieved} = \frac{4.4228}{0.010910} = 405.4 \text{ ppm}$$

From this example we see that the **small perturbation in isotopic composition already has an impact of 5.4 ppm** in retrieved CO₂.

20 Chen et al., 2010 reported on synthetic air with added CO₂ from burned petroleum or natural gas with $\delta^{13}C = -37 \pm 11$ ‰. Using this value, and repeating the math from above, we obtain a **change of 17.2 ppm in retrieved mole fractions** resulting solely from a different isotopic composition. Given this estimate, we find that, precise knowledge of the $\delta^{13}C$ of the working standards and the sampled air is needed to enhance CO₂ compatibility when operating on the 2227.604 cm⁻¹ ¹³C¹⁶O₂ absorption line. In the absence of other error sources, achieving WMO compatibility using this absorption line at ambient CO₂ concentrations of 400 ppm requires the sum of $\delta^{13}C$ from the working standards and the sampled air to be known better than 4.9 ‰. In reality other error sources are not negligible, which will further reduce the stated margin.

S4 Calibration cycles

We included distribution diagrams of the calibration cycles during the flight highlighted in the main manuscript (10/03/2017) in Figure S3.

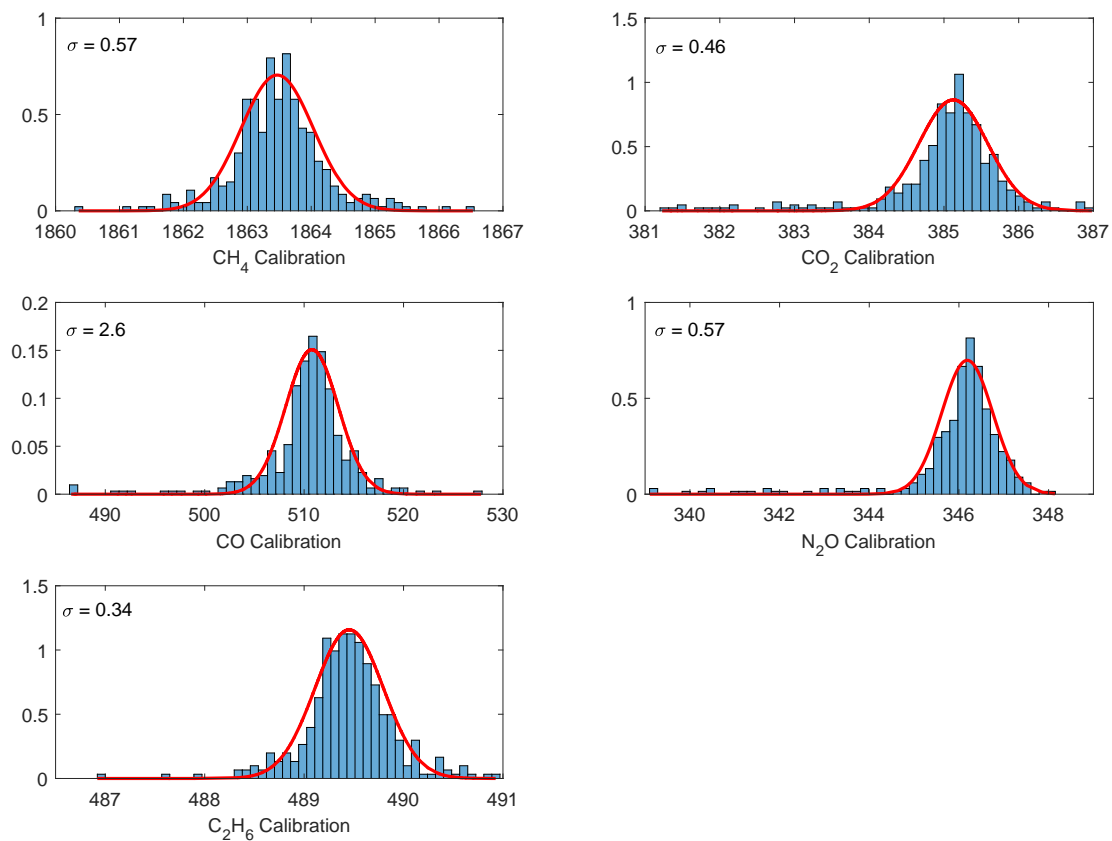


Figure S3. Distribution diagrams of the calibration gas measurements during the flight highlighted in the main manuscript on Oct. 3, 2017.