Side by side comparisons of FTIR and CRDS analysers for CO_2 and CH_4 in air: Persistent biases and dealing with water vapour

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Introduction

- In 2019 – 2020 we operated FTIR (Spectronus, ACOEM/Ecotech) and CRDS (Picarro 2300 or 2400 CO_2/CH_4) analysers side by side on the Research Vessel Investigator (RVI, mobile GAW station, Northern Australian coast) and at the Kennaook/Cape Grim GAW station in Tasmania, Australia
- We found consistent but different biases between instruments up to 0.4 ppm for CO_2 and 1 ppb for CH_4 when sampling from a common inlet. Example data from Cape Grim are shown in Fig. 1 and a summary in Table 1.
- In 2021 we operated the same FTIR and one CRDS (CFADS2400 Picarro 2301 CO_2/CH_4) analyser in the lab to investigate causes for these biases.
- Two similar FTIR analysers did not show any significant bias when measuring the same air from the same inlet

	CRDS on RVI	CRDS-1 at Cape Grim	CRDS-2 at Cape Grim
CO_2 / ppm	-0.2 - -0.4	+0.2	+0.3
CH_4 / ppb	-1.0	0.0	+0.5

Table 1. Indicative biases observed on RVI and at Cape Grim (CRDS – FTIR)

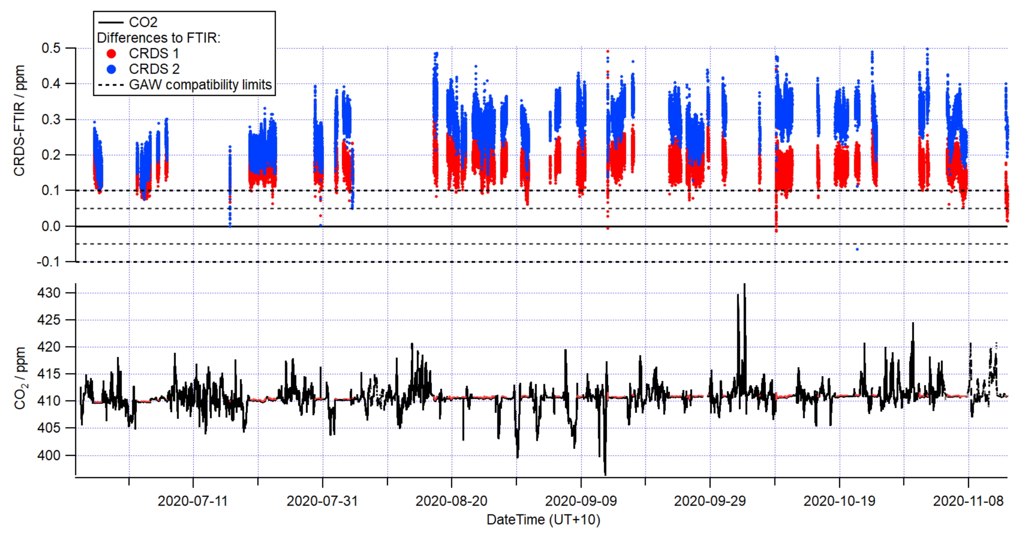


Fig. 1. Comparison of CO_2 measurements at Cape Grim between one FTIR and two CRDS instruments July – Nov 2020. black = mole fraction measurements, red = CRDS-1 blue = CRDS-2 relative to FTIR. Dotted horizontal lines indicate GAW compatibility limits. The two CRDS instruments have different biases relative to eachother.

As possible causes of the biases the lab tests ***we eliminated*** :

- Calibration offsets – There is no bias when measuring the same dry air reference or calibration tanks
- Inlet sampling lines – both instruments used common inlet lines
- Potential effect of a 4°C chiller in the CRDS sampling line on the RVI

We concluded:

- That the origin of the biases lies in the two different treatments of water vapour interference
  - The FTIR dries sample air to < 10 ppm using Nafion followed by magnesium perchlorate
  - The CRDS analyses undried air and corrects for the water vapour dependence of its response.
    - The coefficients for water vapour correction were determined by CSIRO for each analyser periodically using the "droplet method"

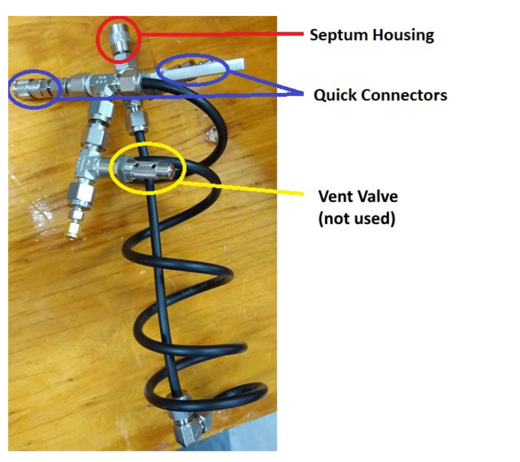
The CRDS water correction: droplet method

- Inject ~0.5 mL H_2O into dry airstream to the CRDS analyser (see injector photo below)
- Allow to dry down (~ 2 hrs) measuring CO_2, CH_4 and H_2O with CRDS continuously
- Fit to quadratic (Fig 2)

$$\frac{C_{wet}}{C_{dry}} = 1 + a.H2O + b.H2O^2 \qquad \text{Eq. (1)}$$

- Use a, b, C_{wet} to correct wet air measurements to C_{dry}

- We suspected that in this method water and CO_2 in the gas phase may not be in equilibrium with the walls of the inlet tubing and analyser if H_2O varies too quickly.
- this may lead to systematic errors in the coefficients a and b applied to the steady state conditions of air sampling



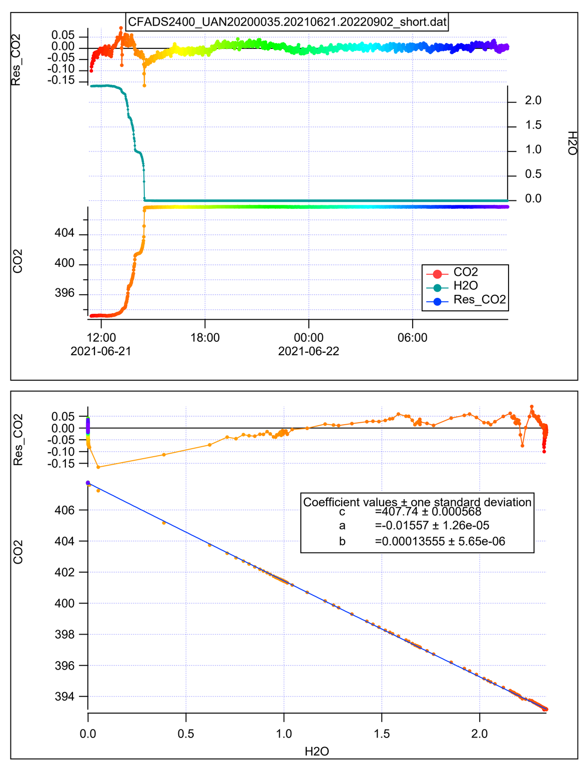


Fig. 2. Upper: time series for CO_2, H_2O and the residual to the fit of Eq. (1) to the data. Colour denotes time.

Fig. 2. Lower: CO_2 vs H_2O, fit to Eq. (1) and residual of the fit.

Mass flow mixer method

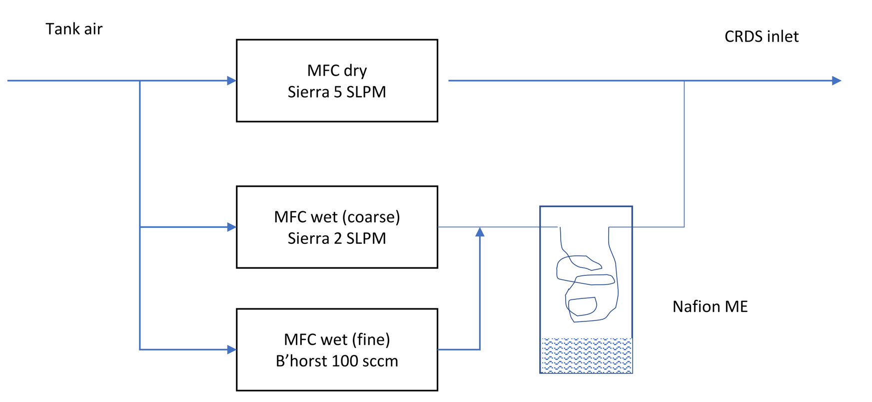


Fig. 3. Schematic set up of the mass flow controlled mixer

See Fig. 3.

- Air from a single tank is split into two streams, one dry and one humidified, and recombined in varied proportions
- A combination of three mass flow controllers (MFCs) ensures all changes are slow and allow the gas and walls to come to equilibrium after each step change.
  - In the wet branch a combination of coarse and fine MFCs allows very small steps at the dry end of the range
- In the humidified stream, the dry air is passed through a 36" single strand type ME Nafion tube acting as humidifier.
  - The Nafion is contained in a 500 mL jar containing ~ 50mL liquid water not in contact with the tubing and flushed with air of the same composition as the tank air.
  - This does not affect CO_2 or CH_4 in the airstream within GAW compatibility limits (<0.05 ppm, < 1 ppb)
- Water mole fraction is stepped slowly from dry => wet (~2% mol fraction H_2O) => dry to ensure reproducibility and lack of hysteresis between the humidifying and drying phases, and no systematic residuals.
  - A complete cycle takes typically >12 hours or overnight.
- As with the droplet method, the data are fitted to the quadratic Eq. 1 to determine a and b

$$\frac{C_{wet}}{C_{dry}} = 1 + a.H2O + b.H2O^2$$

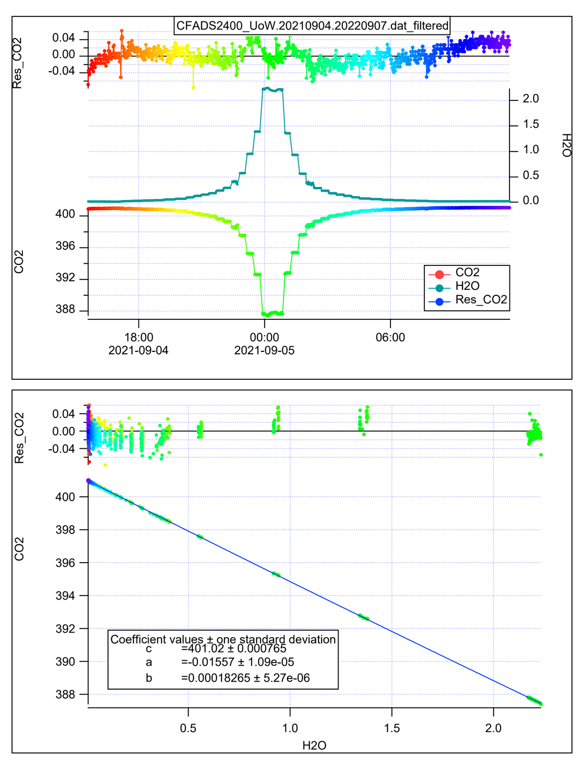


Fig. 4. Time series of a dry => wet => dry cycle for CO_2 and fit to Eq. 1, compare to Fig. 2 for the droplet test . Coloured by time red -> violet. The residuals of the fit are plotted in both panels and can be compared to residuals from the droplet method. Note the good reproducibility and lack of hysteresis during the wetting and drying phases.

Application (1):
Apply the MFC correction to urban air measurement - Wollongong

- Fig. 5 below shows 2 weeks of parallel measurements of urban air with CRDS and FTIR analysers following application of the water correction derived above from the MFC method to the CRDS data.
  - In the difference plot, red = urban air , blue = dry reference tank air measured daily.
- The differences are not significantly different from zero, and there is now no measurable systematic difference between the CRDS – FTIR differences for wet and dry air

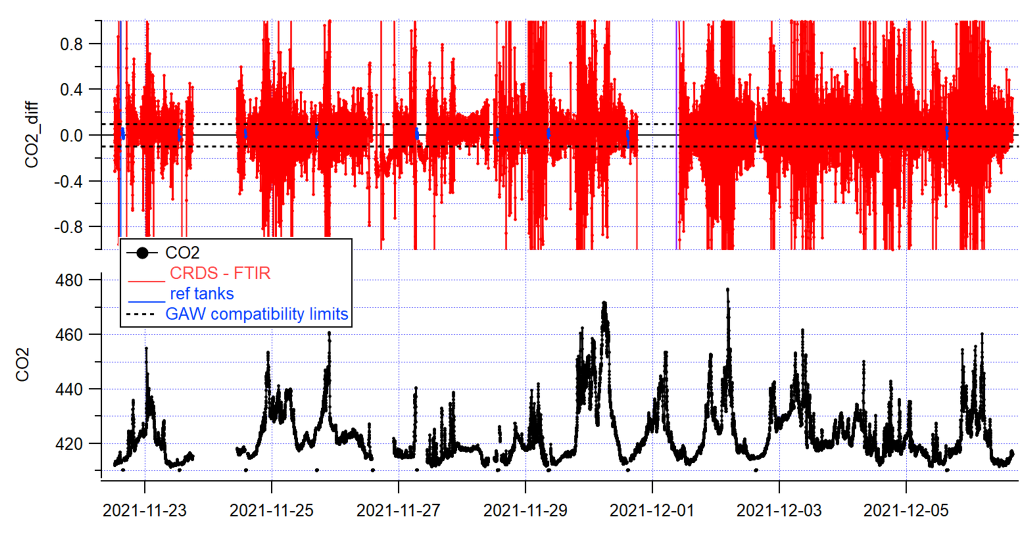


Fig. 5. Measurements of urban air with CRDS – FTIR differences. CRDS corrected with MFC correction (Fig. 4.)

Comparison of droplet and MFC mixer method stability

- At CSIRO Aspendale the MFC mixer method was further developed now working at a lower total flow rate (500mL/min vs 1L/min) and using a 18" Nafion ME humidifier held in a temperature regulated glass jar (27°C).
  - The system was integrated with and controlled by GCWerks software.
- This method was implemented on two CRDS (CFADS2400 and CFKADS2298) and compared with a series of traditional droplet tests with two different cylinders of dry air.
- ***Conclusion: MFC tests are more consistent than droplet tests (Fig. 6).***

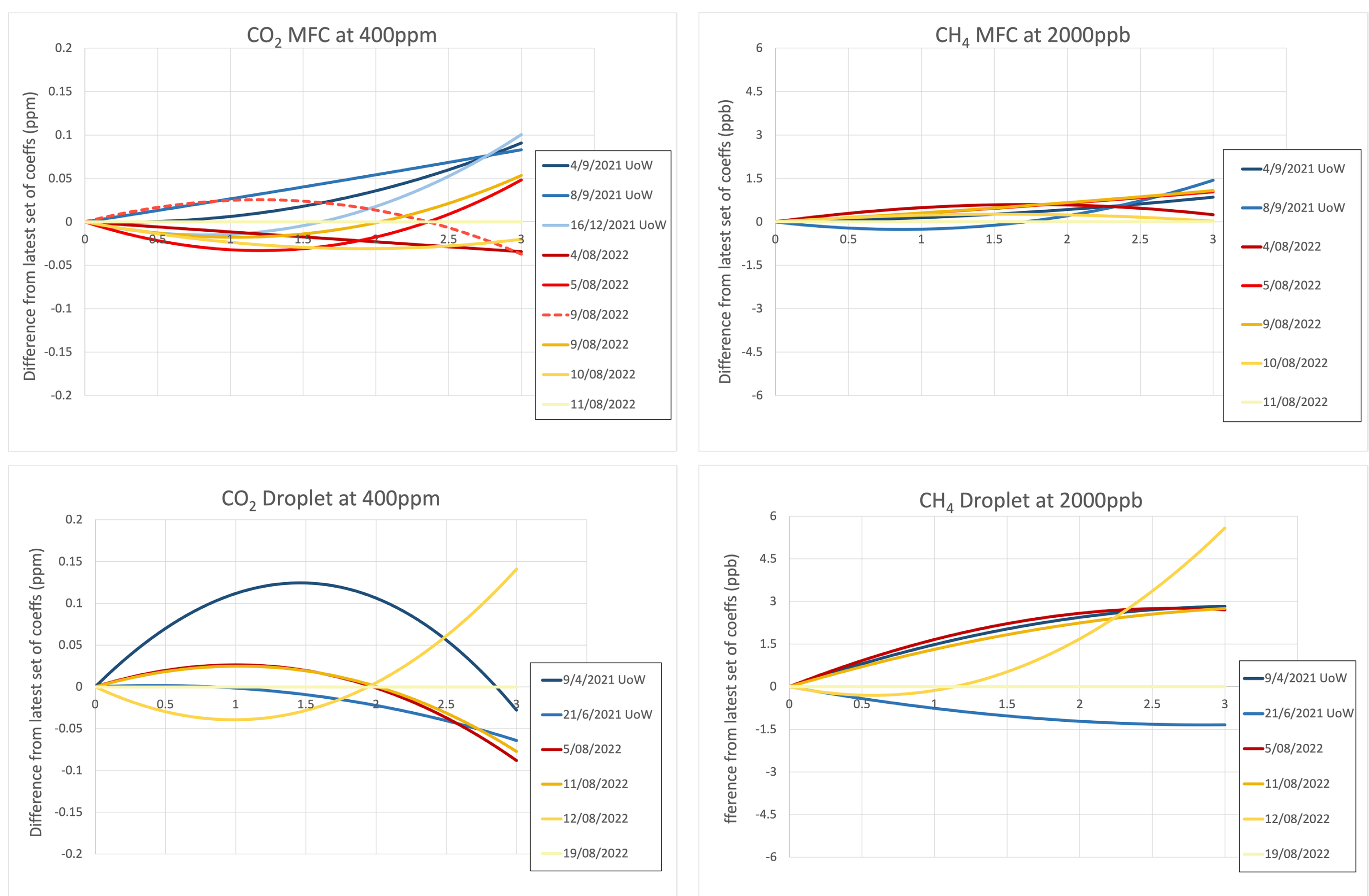


Fig. 6. Variability of the water correction between successive runs in the MFC mixer method (top) and droplet method (bottom) for CFADS2400 collected at UoW (blue) and CSIRO Aspendale (red - cylinder 1, yellow - cylinder 2). The plots show the water corrections at 400 ppm CO_2 and 2000 ppb CH_4 relative to then first correction in the series.

Left: CO_2 Right: CH_4 upper MFC, lower Droplet

Application (2) – CSIRO Aspendale data

- Two Aspendale CRDS (CFADS2400 and CFKADS2298) measured air from a common intake port for a about 2 weeks.
- Both instruments were calibrated on the WMO X2019 CO_2 and X2004 CH_4 scales using the same reference tanks.
- We applied three different water corrections to an overlapping period of ambient air measurements
  1. *Factory* – Used the in built factory correction for both instruments
  2. *Droplet* – Droplet run conducted in the Aspendale laboratory on 12/8/2022 for CFADS2400 and 19/8/2022 for CFKADS2298.
  3. MFC – The MFC mixer tests conducted in the Aspendale laboratory on 11/8/2022 for CFADS2400 and 25/8/2022 for CFKADS2298.

  We then examined the effect of the different water corrections on the offset between the instruments.

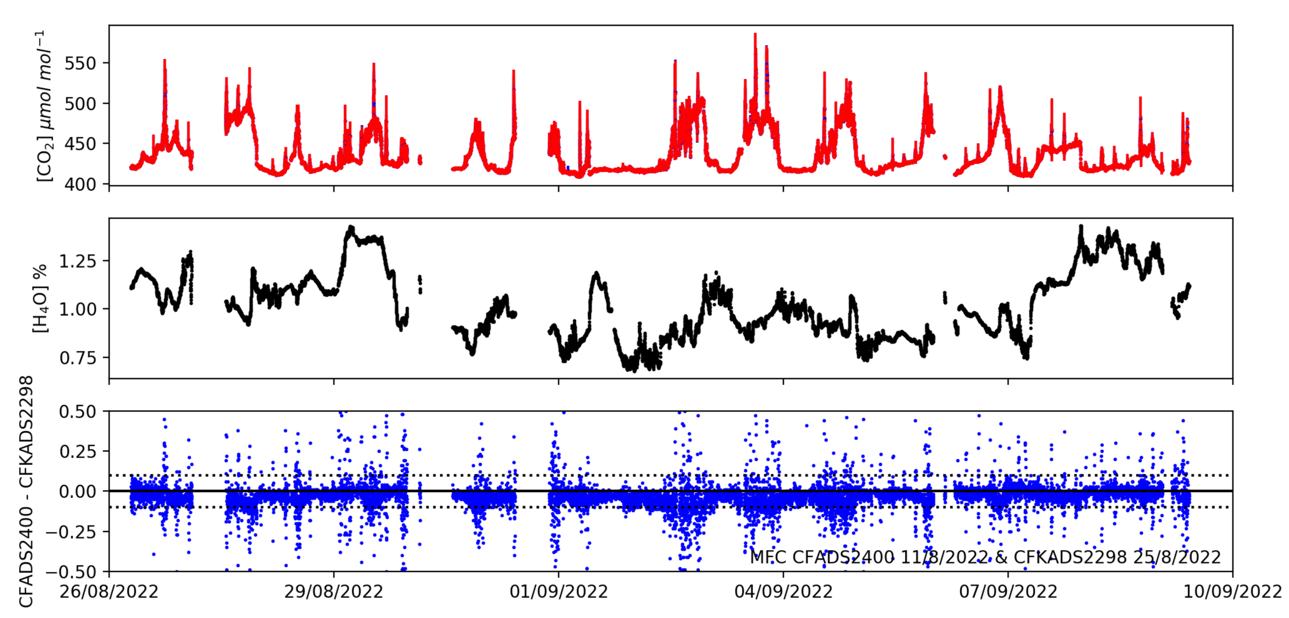


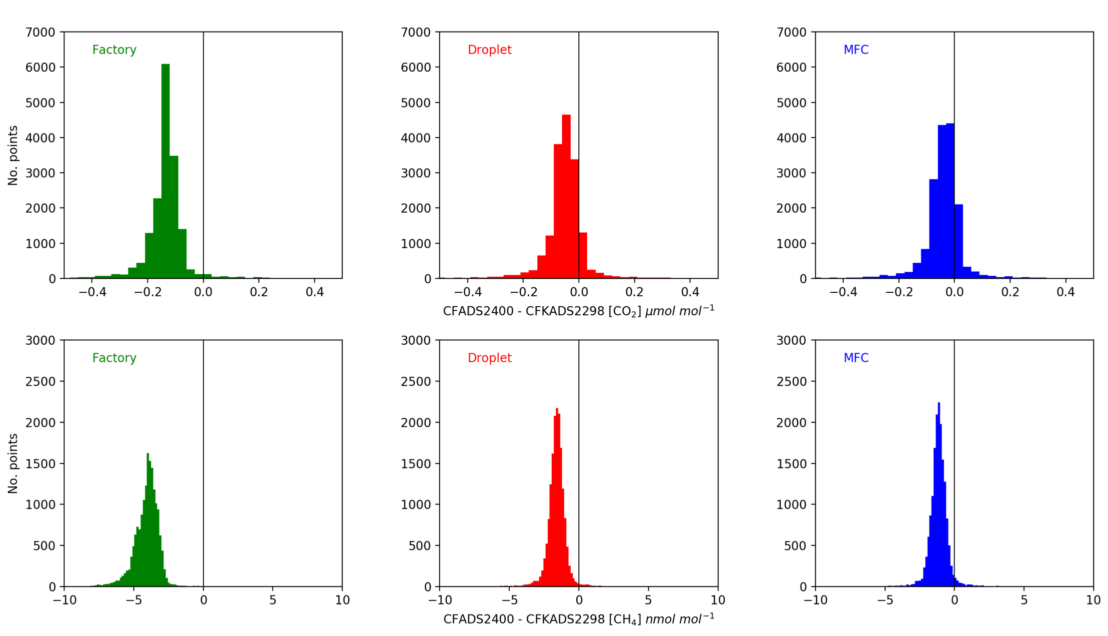
Fig 7. Ambient air data collected at CSIRO Aspendale, Australia between 26/8/2022 and 9/9/2022 using CFADS2400 and CFKADS2298. Both instruments were corrected using an MFC mixer correction, determined on 11/8/2022 and 25/8/2022 for CFADS2400 and CFKADS2298, respectively.

Top: CO_2 in ppm CFADS2400 (blue) and CFKADS2298 (red, overlapping)

Middle: H_2O in % (black)

Bottom: CO_2 difference CFADS2400 – CFKADS2400 (blue)

Fig. 8 Histograms of the differences between the two CRDS (CFADS2400 - CFKADS2298) for the three water correction types – Factory (green), Droplet test (red) and MFC mixer tests (blue).



Next steps

- Develop a field ready system, deploy it at Cape Grim and repeat the FTIR vs. CRDS experiment.
- If feasible back-correct (recent) historical data with revised water corrections.