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Atmospheric Measurement Techniques Discussions

Evaluation of three new laser spectrometer techniques for in-situ carbon monoxide measurements

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Abstract

Long-term time series of the atmospheric composition are essential for environmental research and thus require compatible, multi-decadal monitoring activities. However, the current data quality objectives of the World Meteorological Organization (WMO) for carbon monoxide (CO) in the atmosphere are very challenging to meet with the measurement techniques that have been used until recently. During the past few years, new spectroscopic techniques came on the market with promising properties for trace gas analytics. The current study compares three instruments that are recently commercially available (since 2011) with the up to now best available technique (vacuum UV fluorescence) and provides a link to previous comparison studies. The instruments were investigated for their performance regarding repeatability, reproducibility, drift, temperature dependence, water vapour interference and linearity. Finally, all instruments were examined during a short measurement campaign to assess their applicability for long-term field measurements. It could be shown that the new techniques provide a considerably better performance compared to previous techniques, although some issues such as temperature influence and cross sensitivities need further attention.

1 Introduction

Measurements of carbon monoxide (CO) have been made using a large number of different measurement techniques. The most commonly applied analytical methods are gas chromatographic techniques combined with either a mercuric oxide (HgO) reduction detection or a flame ionization detector (FID), and photometric methods such as non-dispersive infrared absorption (NDIR), vacuum ultra-violet resonance fluorescence (VURF) and tuneable diode lasers spectroscopy (TDLS). Despite the importance of CO in the troposphere as the dominant sink for the hydroxyl radical (Logan et al., 1981) and the reasonably large numbers of different analytical techniques, there is still a considerable remaining uncertainty in the determination of the atmospheric mixing ratio of

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CO. To address this issue, a number of comparison studies have been performed (Ou Yang et al., 2009; Zellweger et al., 2009).

More recently, new analytical techniques became commercially available for the measurement of CO. These techniques include closed path Fourier Transform Infrared (FTIR) absorption, cavity enhanced off-axis Integrated Cavity Output Spectroscopy (ICOS) or multi-path Quantum Cascade Laser (QCL) absorption in the mid-infrared range, and Cavity Ring Down Spectroscopy (CRDS) in the near infrared range.

To date, no comparison studies including the above techniques have been published. This work presents the first evaluation of the performance of three new and commercially available CO analysers in comparison with the VURF technique and complements a previous publication that reported a comparison of HgO, FID, NDIR and VURF techniques (Zellweger et al., 2009). Next to a four day comparison of ambient air measurements, the instruments have been characterized for precision, drift, linearity, temperature dependence and the influence of water vapour on corresponding mixing ratios of carbon monoxide.

2 Instruments

The following analytical techniques were used for this comparison study:

VURF: Vacuum UV resonance fluorescence measurements were made with an Aerolaser AL5001 analyser (Aerolaser GmbH, Germany). The instrument was calibrated every 3 h using a natural air working standard. The operating gases were CO_2 (99.995 %) in Ar (99.9999 %) and N_2 (99.9999 %) with a purifier (Aeronex Gate Keeper SS-400KGC-I-4S). The instrument sensitivity was between 47.7–49.4 counts per second (cps) per ppb. The analytical principle has been described elsewhere (Gerbig et al., 1999).

CRDS: for the Cavity Ring Down Spectroscopy a Picarro G2401 $CO/CH_4/CO_2/H_2O$ analyser (Picarro Inc., CA, USA) was used. The instrument was calibrated every 12 h using a natural air working standard during ambient air measurements. The sample air was not dried, and no further correction was applied to the CO mole fraction reported by the instrument since the analyser applies an internal correction (for interferences of H_2O, CO_2, etc.). The basic principle of this measurement techniques has been described elsewhere for a $CH_4/CO_2/H_2O$ analyser (Crosson, 2008).

ICOS-QCL: a cavity enhanced off-axis Integrated Cavity Output Spectroscopy (ICOS) (Baer et al., 2002) Quantum Cascade Laser (QCL) instrument (Los Gatos Research (LGR) Inc., CA, USA, model LGR-23d) $CO/N_2O/H_2O$ analyser was used for the instrument tests and comparison. The instrument was not featuring the enhanced performance package with improved thermal control of the cavity. The same calibration scheme as for the CRDS instrument was applied during ambient air measurements. The water vapour interference was corrected with an experimentally determined correction function (see following section).

Mini-QCL: an Aerodyne Quantum Cascade Laser Mini Monitor (Aerodyne Research Inc., MA, USA) with an astigmatic multiple pass absorption cell was used (McManus et al., 2010, 2011). In contrast to the other instruments, no active pressure control of the measurement cell has been implemented in this analyser. Water vapour correction as well as calibration was made analogue to the ICOS-QCL instrument.

All experiments were carried out in an air-conditioned laboratory ($23.5 \pm 1.0\,^{\circ}C$) except the for the temperature gradient experiments where the lab was actively cooled and heated.

Ambient air measurements were carried out using an air inlet with a common glass manifold which was flushed with a high flow rate for keeping the residence time of the air in the inlet system short. Each instrument was connected to the manifold by 1/4 inch Synflex-1300 tubing, and these lines were additionally flushed by external pumps to minimise potential time lags. The ambient air comparison was performed at the Empa campus in Dübendorf, a suburban area of Zürich, Switzerland.

Calibration: all instruments were calibrated using working standards containing CO in natural air. The working standards were calibrated against certified NOAA/ESRL

(National Oceanic and Atmospheric Administration/Earth System Research Laboratory) standards, WMO-2004 CO calibration scale).

3 Results

Several tests (instrument noise and drift, temperature dependence, linearity, water vapour correction) assessing the performance of the different instrument were made; the results of these experiments are summarised in the following sections. To complete the inter-comparison, parallel measurements of ambient air were made with all four instruments to assess the compatibility of the different analytical techniques in the field. Finally, an overall assessment highlighting pros and cons of the different techniques with respect to long-term field applications is presented.

3.1 Instrument tests

3.1.1 Noise and drift

To determine the short term analytical noise of the instruments, a working standard containing natural air was measured simultaneously with all four instruments over a period of one hour. During this time, no calibrations were applied to the analysers; however, all data were normalised to the same CO mole fraction. Figure 1 shows the instrumental noise over a 1 h-period for all instruments for a 1 Hz time resolution (Mini-QCL and ICOS-QCL) and at the highest possible time resolution, respectively (CRDS, 0.33 Hz, VURF, 0.18 Hz). It can be seen that the precision of the VURF technique is approx. one order of magnitude better compared to CRDS, and the QCL instruments are again one order of magnitude better compared to VURF. However, for long-term monitoring programs, such high temporal resolution is not required, and appropriate averaging intervals will lead to compatible data with all techniques. The precision of the tested ICOS-QCL analyser was slightly better (standard deviation of 0.09 ppb over

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one hour at 271.1 ppb CO) compared to data acquired with a prototype instrument (0.2 ppb over 10 min at 32.7 ppb) (Provencal et al., 2005).

A further aspect that potentially compromises the instrument performance is instrument drift, i.e. changing sensitivity of instrument response with time. To assess the drift of the instruments in environmentally well controlled conditions, the same working standard as during the above experiment was measured simultaneously with all instruments over a 10 h-period. The results are presented in Fig. 2 based on 1 min-averages for all analysers. It can be seen that all instruments show a significant drift within this 10 h-period except for the CRDS technique; however, the much larger instrument noise makes it more difficult to detect small drifts in the sub-ppb range with this technique. In contrast, due to the very high precision, even a small drift of less than 0.1 ppb CO over a period of minutes to hours can be detected with the QCL instruments. It should be noted that all individual 1 min-values were within ±0.5 ppb (Mini-QCL) and ±0.1 ppb (ICOS-QCL) over the 10 h-period. This is well below the Data Quality Objectives (DQOs) of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) of ±2 ppb (WMO, 2010).

The optimal averaging times as well as the optimal frequency of calibrations can be estimated using Allan standard deviation plots (Werle et al., 1993). Figure 3 shows Allan plots using the above data (highest possible time resolution) for all instruments. As indicated by the drift plots, longer integration times lead to better results for the CRDS instrument. No obvious drift was observed within a 1h-period; however, the Allan standard deviation does not become significantly smaller if longer time aggregates are calculated. Therefore, the optimal averaging time for the CRDS instrument is considered to be one hour. This makes the instrument suitable for long-term monitoring programmes where no higher temporal time resolution than one hour is required.

Figure 4 shows the reproducibility of a working standard with 97.9 ppb of CO measured in intervals of one to three days over a two month period with the CRDS analyser. Over this period, no significant drift was observed, although the uncertainties of individual measurements of the working standard are relatively high due to short-term instrument noise. Consequently, standard measurements should be pooled for post-analysis data processing to avoid a bias due to short-term noise. The same issue has already been described for the NDIR technique, which also has been shown to produce accurate CO data if appropriate zero and span calibrations are applied (Zellweger et al., 2009).

The VURF technique showed an optimal averaging time of approx. 20 min; afterwards, drift lead to increased uncertainties. However, calibration intervals of 3 h are usually sufficient for meeting the WMO GAW DQOs. In contrast to the CRDS technique, VURF requires regular calibration due to degradation of the sensitivity over time. This is mainly caused by staining of the optics due to decomposition of e.g. organic compound in the UV (150–160 nm) light, which makes the techniques also maintenance intense.

For the QCL instruments, the optimal integration time was approx. 2 to 5 min, but drift was only significantly contributing for the Mini-QCL analyser. The ICOS-QCL proved to be stable within ±0.1 ppb CO over a 10 h-period. This indicates that the QCL based techniques do not only have a large potential for long-term monitoring, but are also suitable for highly temporal resolved data as well as for flux measurements when appropriate measurement cell flushing times are provided.

3.1.2 Temperature dependence

The above experiments were made under environmentally well controlled conditions with temperature variations of less than ±0.5 °C, but not all measurement sites provide these conditions. Therefore, the influence of temperature variations was tested by measuring a working standard simultaneously with all for instruments over a 12 h-period. For the first seven hours, the air temperature was kept constant at 23.7 ± 0.2 °C; afterwards, the lab was cooled to 19.0 °C within 84 min, and then heated to 25.3 °C within additional 110 min. Figure 5 shows the change in CO mole fraction (1 min data) as a function of temperature and time. Such temperature changes correspond to worst case scenarios as they may happen in not well air-conditioned environments. It can be seen that all instruments respond on the temperature changes except for the CRDS instrument. However, small changes in the mole fractions are more difficult to detect with this instrument due to the relatively large analytical noise. Nevertheless, the temperature of the cavity of the CRDS analyser is very well thermally stabilized, and the temperature change showed also no significant influence on the CH_4 and CO_2 signals with no measureable change of the CH_4 mole fraction and a deviation of ±0.05 ppm for CO_2. A significant bias was observed for the VURF instrument, with an amplitude of approx. 5 ppb. This clearly indicates that this technique needs to be operated in environmentally controlled conditions. Very significant but low deviations in terms of absolute values were observed for the two QCL based techniques. The range of the bias was within (−0.4/+1.1) ppb for the ICOS-QCL instrument, and within (−1.1/+1.8) ppb for the Mini-QCL, which is below the WMO GAW DQOs. However, in order to reach the maximum achievable performance, these instruments need to be operated in well air-conditioned environments. Improvements of the internal temperature control of the analysers are still possible, and e.g. the ICOS-QCL instrument is now available with an active temperature control that was not yet implemented in the instrument used for this study.

3.1.3 Linearity

The instruments were tested for linearity using either dilution of a high (ppm) CO standard with CO-free zero air (VURF instrument) or a manometric preparation of small 3 l flasks by adding a known amount of CO (using a standard with high CO mole fraction) to CO free air. For the flask preparation, the CH_4 content of the high (ppm) standard was also known, and the dilution air was CH_4 free (methane free synthetic air for the flask preparation). The flasks were then analysed for methane using a Picarro G1301 $CH_4/CO_2/H_2O$ analyser, which allowed an independent check of the dilution ratios of the manometrically prepared flasks. Figure 6 shows the results of the linearity assessments for all instruments. It can be seen that all instruments except the ICOS-QCL analyser were linear in the range of 0 to 700 ppb CO. For the ICOS-QCL analyser a quadratic calibration function was applied to appropriately characterise the instrument response function. The regression residuals were within ±2 ppb for all techniques, and even within ±0.2 ppb for the Mini-QCL instrument. The upper limit of the linear range was also tested, and linear response was found for the VURF and Mini-QCL instruments up to approx. 1.5 ppm CO, and up to 20 ppm CO for the CRDS analyser.

3.1.4 Water vapour correction

Atmospheric water vapour mole fractions vary from a few ppm up to several per cent in the troposphere. CO as well as other trace gas measurements are usually referred to dry air mole fractions, and calibration gases are also dry. Therefore, in most cases, appropriate drying of the sample is necessary to account for the dilution by water vapour. However, instruments based on spectroscopic techniques often allow to simultaneously measure the water vapour content in addition to the target gas, and consequently, a water vapour correction is theoretically possible. Such corrections can also include spectroscopic effects, e.g. pressure broadening of the spectroscopic lines. They have been successfully implemented for the measurements of CO_2 and CH_4 with CRDS instruments (Chen et al., 2010).

All of the tested CO analysers were measuring water vapour in addition to CO except for the VURF instrument. The sample air of the VURF instrument is dried with a Nafion® drier, and dry air mole fractions are reported. Consequently, no further corrections are required for the VURF instrument, which was confirmed by humidifying a CO working standard (not shown). A potential loss of CO over the dryer is also not expected to bias the measurements, since both sample air and calibration gases pass through the dryer. The CRDS analyser collects both humid and dry mixing ratios for CH_4 and CO_2, but the software version of our instrument only reported a CO mole fraction which includes a correction of water vapour dilution and spectroscopic influences (Rella, 2010). The ICOS-QCL analyser reports both corrected and uncorrected mole fractions, whereas only humid results are reported for the Mini-QCL. However, the ICOS-QCL corrections are only based on the dilution by water vapour and do not consider other effects such as line pressure broadening. The H_2O signals of the analysers were not calibrated since

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the analysers' H_2O readings were only used for correction and were not considered to be used for determination of absolute H_2O mole fractions.

To determine the water vapour corrections or to assess the already implemented corrections of the analysers, the following experiments were made. A small amount of water (approx. 0.8 ml) was directly injected into a Synflex-1300 coil, and a constant flow (approx. 500 ml min^{-1}) of a working standard gas was delivered to the instrument. A schematic view of the measurement set-up is shown in Fig. 7. With this set-up, the working standard was humidified to up to 3 % (corresponding to 30 000 ppm H_2O), and then slowly dried to a few ppm within 1–2 h. This gives a continuous coverage of the 0–3 % humidity range whilst the dry CO mole fraction is kept constant. Compared to previously published experimental setups (Chen et al., 2010; Winderlich et al., 2010), this setup has the advantage that a complete coverage of the relevant water vapour mixing ratios can be achieved. It further does not require a sophisticated setup and is consequently rather straightforward to be performed both in field and laboratory experiments. The time series of such an experiment is plotted in Fig. 8 for the ICOS-QCL instrument. The water vapour influence can now be expressed with sufficient agreement by a quadratic fit, $CO_{wet}/CO_{dry} = 1 + a \cdot H_2O + b \cdot (H_2O)^2$. Such experiments were performed with varying CO levels (all instruments) and at different operating pressures (Mini-QCL only). The operating pressure was varied for the Mini-QCL instrument in order to assess this effect for this instrument, since the pressure in the measurement cell was not actively controlled in our analyser. The results of the CO_{wet}/CO_{dry} ratios vs. the H_2O mixing ratio are presented in Figs. 9 to 11. Since the CRDS instrument reports already a CO mole fraction that is corrected for cross sensitivities, $CO_{reported}/CO_{dry}$ ratios were calculated for this instrument. This was done to verify if the implemented correction function correctly compensates for dilution and spectroscopic effects; in this case, the $CO_{reported}/CO_{dry}$ ratio should be 1 and not depend on the H_2O mixing ratio. It can be seen from Figs. 10 and 11 that the CO mole fraction is underestimated due to pressure broadening effects for the instruments without implemented corrections (Mini-QCL and ICOS-QCL). However, correction functions can be applied for both analysers.

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These functions proved to be quite stable and independent of the CO mole fraction for the ICOS-QCL instrument and for the Mini-QCL instrument; however, for the latter, the differences between different mole fractions were slightly larger. No significant change of the Mini-QCL instrument behaviour could be observed due to variations of the cell pressure within a range of 53 ± 10 Torr (see Fig. 10). The picture looked significantly different for the CRDS instrument (Fig. 9). For this instrument, the correction functions are more difficult to derive experimentally due to larger signal to noise ratios compared to the QCL instruments. Nevertheless, it can be seen that the CO mole fractions were overestimated in the order of roughly 10–20 % for low mole fractions, whereas higher mole fractions tended to be slightly underestimated. Based on this experiment, it is clear that implemented correction function of the tested CRDS analyser was not optimal for low CO mole fractions. The analysis also disclosed that the difference of $CO_{reported} - CO_{dry}$ is not a suitable measure as it did not reveal a consistent pattern when plotting vs. H_2O (not shown here).

In order to estimate the contribution of the water vapour correction to the overall uncertainty of the CO measurements, the maximum difference between the different correction function was calculated for a humidity of 2.5 %. For the Mini-QCL instrument, a maximum difference of 0.81 % was observed; this value covered a mole fraction range of 68 to 1245 ppb CO as well as different operating pressures of the instrument. For the ICOS-QCL analyser, the maximum difference was 0.26 %; however, only a smaller mole fraction range of 57 to 262 ppb CO was covered. In both cases, the WMO GAW DQOs of ±2 ppb would be achieved for typical ambient CO mole fractions up to 250 ppb. In contrast, the maximum difference between the correction functions in the range of 89 to 982 ppb CO was 21.5 % for the CRDS instrument; especially low mole fractions were overestimated in the presence of water. The CRDS instrument tested during this study was the first instrument that was rolled out (serial number #2001); in the meantime, further optimisations were implemented. Since the measurements of CO are performed in the near infrared-region, where also H_2O and CO_2 are interfering, these effects have to be quantified and appropriate corrections are needed.

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Figure 12 shows the corrected CO mole fraction for a recently produced Picarro G2401 instrument (serial number #2028) with optimised compensation of the CO_2 and H_2O interferences. The CO mole fraction was varied between 66 and 246 ppb, and the experiments were made for two different CO_2 levels. It can be seen that the corrected CO mole fraction of the optimised instrument is not significantly influenced by the CO_2 and H_2O level, which implicates that the corrections adequately account for the CO_2 and H_2O interferences.

3.1.5 Summary of the analyser performance tests

Our study complements a previously published CO comparison (Zellweger et al., 2009) and gives an update of current measurement techniques with exception of the FTIR method (Griffith et al., 2012). This technique became recently commercially available and has the potential for providing compatible CO data. First instrument performance tests of an FTIR analyser have recently been published (Hammer et al., 2012). The results of our instrument tests are summarised in Table 1. It can be seen that compatible data within the WMO GAW DQOs of ±2 ppb can be achieved with all techniques if the averaging time is sufficiently long. However, the Mini-QCL and ICOS-QCL instruments allow very fast and precise measurements even at 1 Hz temporal resolution. Drift potentially compromises measurements made with the VURF and also the Mini-QCL instruments. Thus, appropriate calibration schemes are required for these instruments. All CO data of the tested instruments with the exception of the CRDS technique were further influenced by temperature changes of the laboratory; this needs clearly to be improved for continuous operation of these instruments in the field, since many measurement stations are not sufficiently air conditioned. Currently, improvements were made on the latest ICOS-QCL instruments (enhanced performance package), but this has not yet been tested. It was shown that a water vapour correction is possible for all instruments; however, correction functions have to be determined for each individual instrument and need also to be verified in regular time intervals.

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3.2 Ambient air comparison

The instruments described above were measuring ambient air over a 4 day-period using a common air inlet. The measurements were made at Dübendorf, a suburban area of Zürich, Switzerland. This measurement site is representative for suburban background mixing ratios of CO, but it can be influenced mainly by traffic emissions of nearby roads (Steinbacher et al., 2007). The residence time in the air inlet system was minimised to avoid a time lag between the measurements of the different instruments. A time series plot of 1 h-values for all four instruments as well as the difference to the ICOS-QCL analyser is shown in Fig. 13. It can be seen that the CO mole fraction was highly variable and ranged from 100 to 500 ppb. This covers most of the CO mole fraction range which normally occur in ambient air, although very low mole fractions are not covered by the current study. The CRDS instrument was initially calibrated using a suite of NOAA/ESRL standards, and the calibration was verified by additional measurement of working standards. The QCL and ICOS-QCL instruments were initially calibrated with a suite of six Empa working standards and four NOAA/ESRL standard gases covering the CO mole fraction range from 0 to 1170 ppb. During the ambient air comparison, two working standards were measured every 11.5 h on all instruments except the VURF analyser, which was automatically calibrated every 3 h using another working standard. The VURF working standard was traced back to the same NOAA/ESRL standards that were used for the initial calibration of the other analysers. With this calibration scheme, traceability of all measurements to the same set of NOAA/ESRL standards on the WMO-2004 carbon monoxide scale (Novelli et al., 2003) is ensured. The Mini-QCL and the ICOS-QCL were post calibrated based on the working standard measurements, and no further corrections were applied to the CRDS data due to the relatively high instrumental noise of individual working standard measurements with this instrument.

It can be seen from Fig. 13 that most of the 1 h-data were within ±2 pbb (DQOs) for all instruments, although the VURF measurements were slightly higher compared to the other techniques. Relative difference histograms are shown in Fig. 14; no significant bias on the 95 % confidence level ($k = 2$) compared to the ICOS-QCL was observed for all instruments based on 1 h-values; however, a significant bias of +0.94 ± 0.16 % ($k = 2$) was observed for the VURF analyser over the entire period, whereas the biases of the CRDS (−0.07 ± 0.13 %, $k = 2$) and the Mini-QCL (−0.02 ± 0.08 %, $k = 2$) instruments were not significant. Table 2 summarises the regression parameters of an orthogonal regression analysis (York, 1966) for all possible instrument combinations. All four measurement techniques were highly correlated ($R^2 > 0.999$). Such high correlations are only possible if (a) the instruments are properly calibrated over the measured mole fraction range, (b) the repeatability and reproducibility is sufficiently good for the used averaging time, (c) the instruments are reacting comparably fast on mole fraction changes in the measured air, (d) the temporal coverage of the measurement is able to capture short term variation within the used averaging time, and (e) no interference with other species occur.

Based on the above discussed instrument performance tests, good results could have been expected for most of the above points (a–e), which are briefly discussed in the following:

(a) Calibration: with the exception of the ICOS-QCL instrument, all analysers were entirely linear over the mole fraction range measured during the comparison. The ICOS-QCL raw data was in a first step corrected for non-linearity based on the calibration function determined during the linearity experiment (Fig. 6), and in a second step adjusted to the working standards measured during the comparison. This procedure seems to adequately determine the calibration function. During our study, all instruments were calibrated with working standards that were traceable to a common set of NOAA reference standards. Traceability to a common reference is important (Buchmann et al., 2009), since a lack of appropriate standards may result in a significant bias between different time series (Ou Yang et al., 2009).

(b) Repeatability and reproducibility: the instrument precision (repeatability of raw data over a time period that is short enough to be unaffected by drift) is sufficiently good for all instruments, but large differences exist between different techniques (Fig. 1). However, the averaging time of one hour results in compatible data for all techniques. Instrument drift, which potentially influences the reproducibility of measurements, was an issue mainly for the VURF and the Mini-QCL instruments. Frequent automatic calibrations sufficiently compensated these effects for the VURF instrument; the drift of the Mini-QCL instrument potentially explains part of the observed deviations compared to the ICOS-QCL instrument, since a bias of up to 1 ppb can be expected based on results of the drift experiment (Fig. 2). It should be noted that such stable results can only be achieved in well air-conditioned environments; drift would become a much more serious issue if the lab temperature varies.

(c) Reaction time: the instruments were able to capture changes in mole fractions sufficiently fast to avoid a significant bias due to different reaction times. The sample's residence time in the inlet to the various instruments was made as short as possible by using bypass pumps to flush the inlet lines. The reaction times of the analysers themselves depend mainly on the flow rate and the volume of the measurement cells. The flushing time is variable for the Mini-QCL and the ICOS-QCL instruments, but these instruments were also operated with relatively low flow rates of about 200 ml min^{-1}, which is sufficient for capturing changes in mole fractions as they occurred during the comparison.

(d) Temporal coverage: all instruments used in this work are continuous techniques, and data loss occurs only during calibrations including some time with transient data between changes from ambient air to calibration gas and back. Since ambient CO data can be highly variable on short terms even during periods with relatively stable hourly values, a complete temporal coverage is important for accurate measurements of hourly data. For example, Zellweger et al. (2009) found highest correlations between continuous techniques for CO measurements made at Jungfraujoch (R^2 = 0.992), despite the fact that a non-dispersive infrared (NDIR) instrument which shows significant short term noise was compared against a VURF instrument. Significantly lower but still very significant correlations (R^2 between 0.935 and 0.981) were observed at

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Jungfraujoch when quasi-continuous gas chromatographic techniques were compared. In the current study, R^2 was higher than 0.999 for all possible instrument combinations. This clearly points out that the temporal coverage factor cannot be neglected if the accuracy of an analytical technique is assessed, and significantly adds to the uncertainty of values generated by quasi-continuous methods such as gas chromatographic techniques.

(e) Interferences: the main potentially interfering molecule is water; the air was dried in the VURF analyser with a Nafion dryer, and corrections were applied to the QCL instruments. The CRDS instrument was only reporting H_2O corrected CO mole fractions; however, the correction algorithm of this instrument was shown to be insufficient for mole fractions below 100 ppb CO. During the comparison, the water vapour mixing ration ranged from 0.8 to 2.0 % (CRDS raw data), whereas all CO mole fractions were above 100 ppb. Within this CO and H_2O range (indicated by the box in Fig. 9), the correction used by the CRDS instrument was sufficiently good to account for interferences and dilution effects. However, a significant bias in the order of 10–20 % would be expected for CO mole fractions below 100 ppb. The correction implemented in the CRDS instrument also accounts for cross talk between CO and CO_2; a test with constant CO of approx. 260 ppb and varying H_2O (0–3 %) and CO_2 (178–1321 ppm) did not show any dependency in the corrected data (not shown). The good agreement between the other techniques is indicating that the correction functions applied for the QCL instruments were appropriate and constant over time.

4 Conclusions

The current study complements a previously published CO instrument comparison (Zellweger et al., 2009) and gives an update of current measurement techniques with exception of the FTIR method which has been recently assessed by Hammer et al. (2012). It could be demonstrated that new spectroscopic measurement techniques (QCL, CRDS) are suitable for high precision carbon monoxide measurements

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in ambient air as well as for the calibration of standards. In addition, they require less maintenance and manpower compared to other techniques, and running costs are also relatively low since these techniques do not use expensive consumables and have a low consumption of calibration gases due to their stability. A further advantage is the simultaneous detection of several species (e.g. QCL: CO, N_2O, H_2O; CRDS: CO, CH_4, CO_2, and H_2O). However, the initial capital investment is higher compared to NDIR or GC techniques. Compared to the VURF technique, a better performance in the range of one order of magnitude is achieved with QCL instruments, and even up to two or more magnitudes compared to the CRDS and NDIR techniques. However, CO measurements fulfilling the current WMO data quality objectives of ±2 ppb are possible even with these techniques if appropriate averaging intervals (in the order of one hour) are selected. All investigated methods of the current study have the advantage that they have a continuous temporal coverage of the analysed air, which results in significantly higher compatibility of these methods compared to techniques with a quasi-continuous temporal coverage (e.g. GC methods).

It could further be shown that the QCL and CRDS measurements can be made without sample air drying, and a correction of the dilution and spectroscopic effects of water vapour can be applied to the measured values. Tests with most recent versions of a CRDS analyzers also revealed that effects of the CO_2–CO cross-talk can be properly accounted for in the software. However, a few issues such as temperature dependence and imperfect compensation of spectroscopic interferences were identified and need further investigation, and technical improvements of the analysers are still possible.

The instruments were successfully deployed during a field measurement campaign; it could be demonstrated that measurements within the current WMO GAW DQOs of ±2 ppb for CO are possible with all investigated techniques if they are appropriately operated and calibrated.

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Table 1. Performance summary of the tested CO analysers.

	VURF	CRDS	Mini-QCL	ICOS-QCL	FTIR[a]
Precision 1-s (ppb)	1.1	11.2	0.06	0.11	
Precision 1-min (ppb)	0.7	2.5	0.04	0.07	0.20
Precision 10-min (ppb)	0.25	1.0	0.05	0.07	0.08
Maximum Drift ($ppb\,h^{-1}$)	< 0.5	ND	0.3	0.1	
Linearity (Range in ppb)	0–2500	0–20 000	0–1500	2nd order	90–620
Temperature changes	−−	++	−	−	−
H_2O correction	NA[c]	−[b]	++	++	NA[c]

ND: not detectable;
NA: not applicable;
−− to ++: poor to good performance (qualitative).
[a] Results from Hammer et al. (2012) and Griffith et al. (2012).
[b] The tested instrument showed poor performance for low mole fractions; in the meantime, correction algorithms have been improved.
[c] H_2O correction is not applicable because the sample air is dried.

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Table 2. Results of the orthogonal regression analysis between the different measurement techniques. X and Y are the corresponding instruments, and *a* and *b* are the intercept and slope of the regression with standard uncertainties ($k = 1$). R^2 is the correlation coefficient, and *N* is the number of data points (1 h-values).

Y	X	*a* (ppb)	*b*	R^2	*N*
Mini-QCL	ICOS-QCL	1.14 ± 0.17	0.9921 ± 0.0001	0.99996	97
Mini-QCL	VURF	2.66 ± 0.29	0.9919 ± 0.0015	0.99989	97
Mini-QCL	CRDS	2.21 ± 0.45	0.9851 ± 0.0024	0.99971	97
ICOS-QCL	VURF	2.54 ± 0.25	0.9927 ± 0.0014	0.99991	97
ICOS-QCL	CRDS	2.10 ± 0.46	0.9859 ± 0.0025	0.99970	97
VURF	CRDS	−0.42 ± 0.53	0.9931 ± 0.0029	0.99960	97

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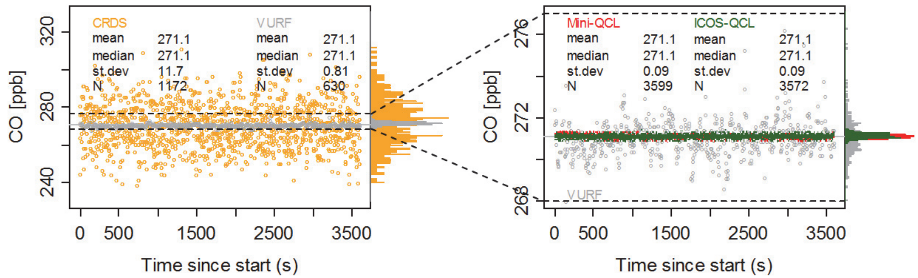

Fig. 1. Instrumental precision (noise) over a 1 h-period for the highest possible time resolution (CRDS and VURF, 3.1 s and 5.7 s, left panel) and 1 s-data (Mini-QCL and ICOS-QCL, right panel). The frequency distribution of individual measurement values is shown as a histogram on the right of each plot. The black dashed lines illustrate the different y-axis scales, and the VURF data (grey) is also shown in the right panel.

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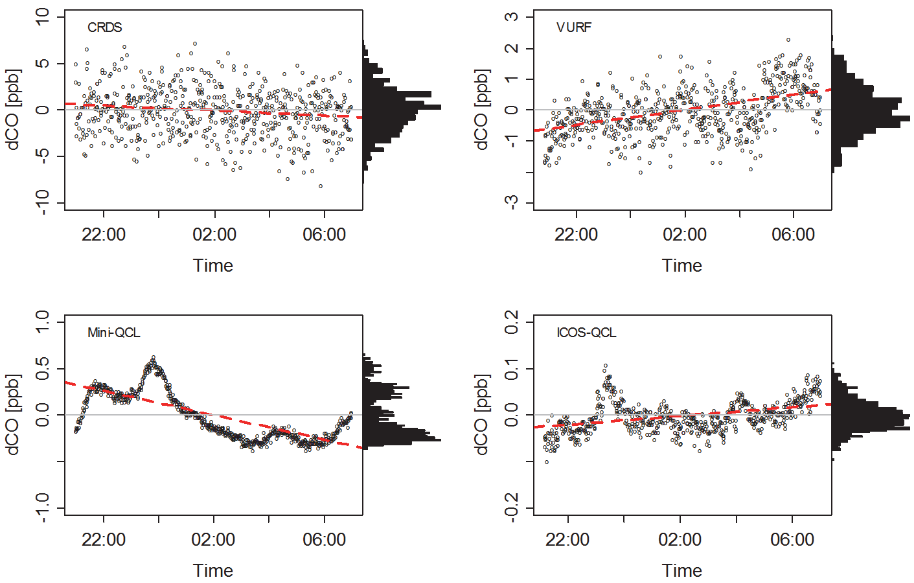

Fig. 2. Instrument drift over a 10 h-period for 1 min-data. The deviation to the mean value is shown for each data point. The red line shows the linear regression line. The frequency distribution of individual measurement values is shown as a histogram on the right of each plot. Please take note of the different y-axis scales of the different panels.

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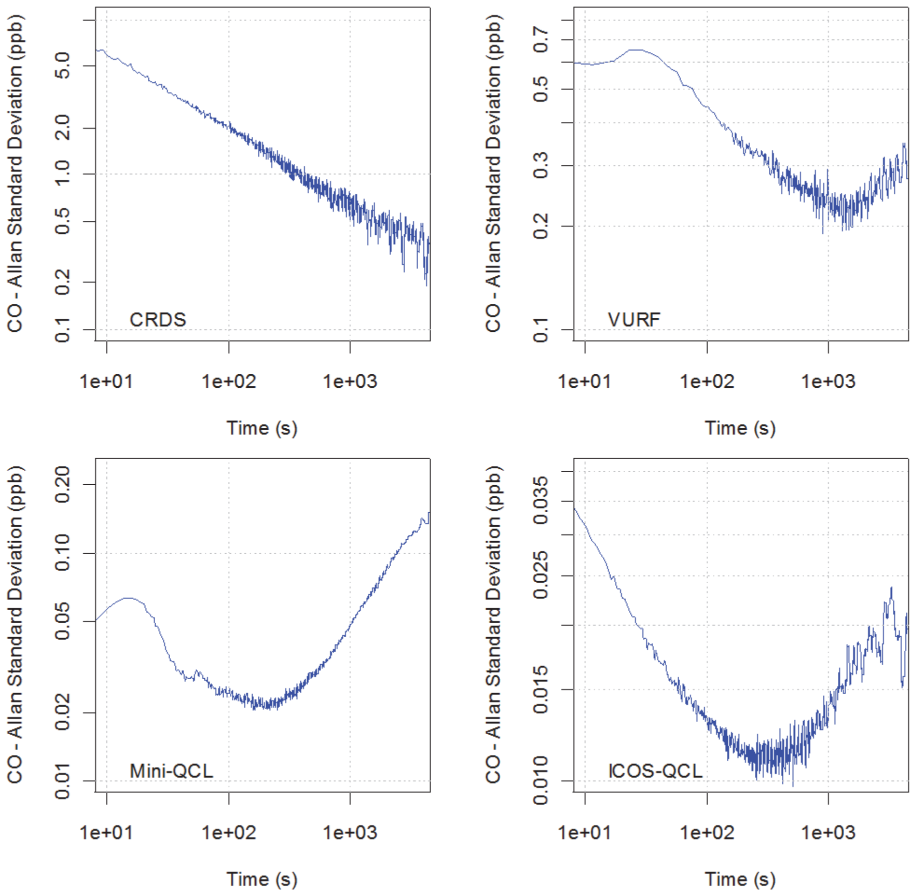

Fig. 3. Allan standard deviation plots for all tested instruments. The lowest Allan standard deviation indicates the optimum averaging time. Please take note of the different y-axis scales of the different panels. The x-axis (in logarithmic scale) spans 60 min.

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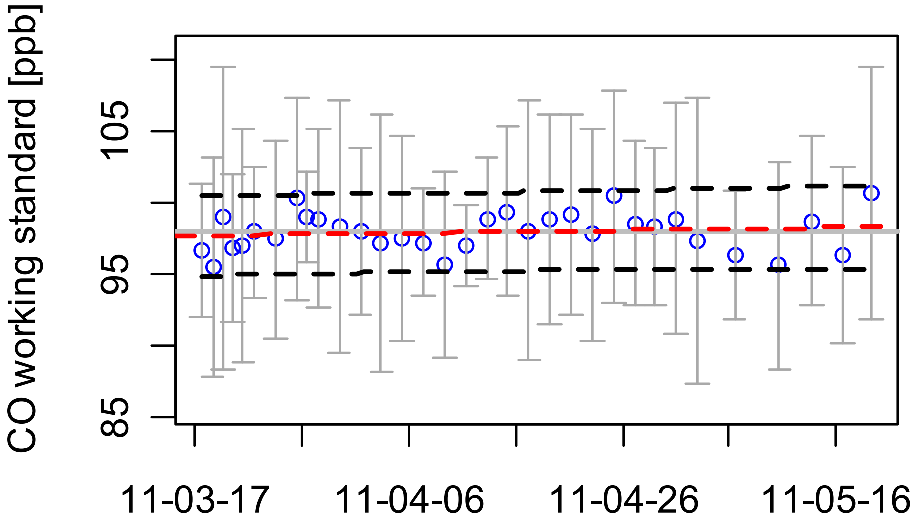

Fig. 4. Reproducibility of a 97.9 ppb working standard measured with a CRDS instrument over the period of 2 months. The individual error bars indicate the uncertainty of these measurements ($k = 2$); the red dotted line is the linear regression over time, and the black dotted lines are the 95 % confidence bands of the linear regression.

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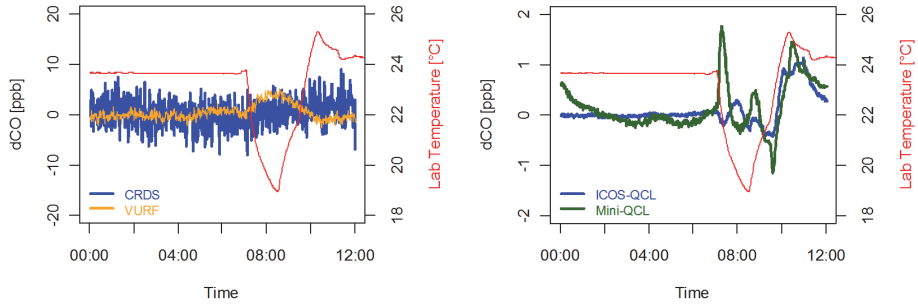

Fig. 5. Influence of the temperature on CO measurements. Left panel: VURF and CRDS, right panel: Mini-QCL and ICOS-QCL, all 1 min-data. The deviation of CO (dCO) to the mean value during the period with constant temperature (00:00–07:00 UTC+2) is shown on the right axis, and the lab temperature (red) is shown on the left axis.

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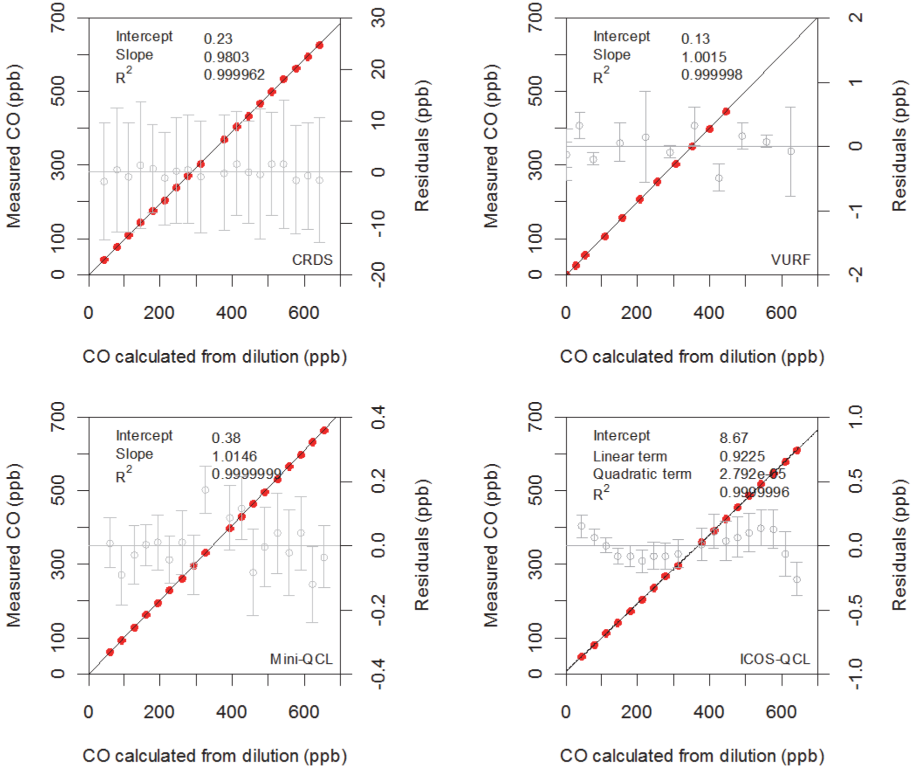

Fig. 6. Linearity plots for all instruments, including a fitted regression line and the regression residuals (open grey circles, right axis). Linear fits were applied for all techniques except of ICOS-QCL (quadratic fit). Please take note of the different right-hand y-axis scales for the different panels.

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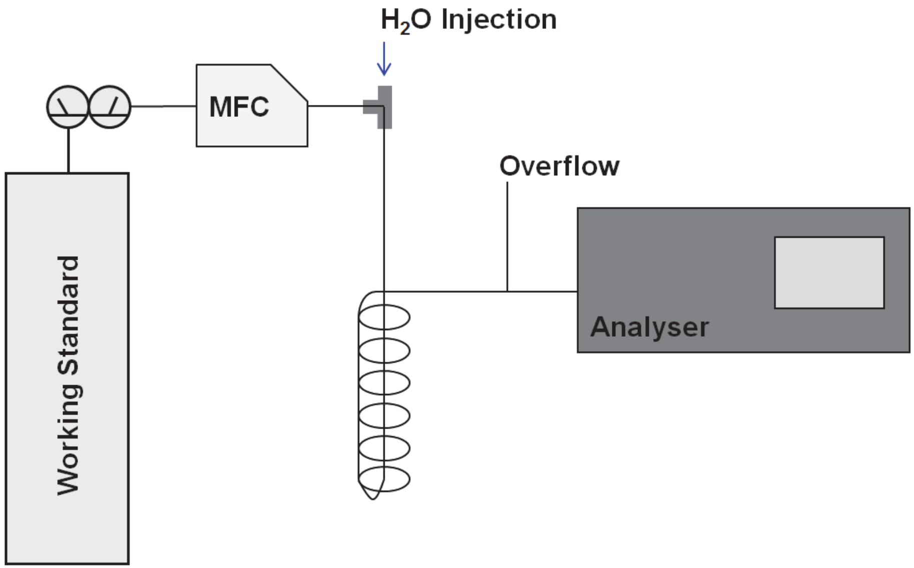

Fig. 7. Experimental set-up for the determination of the water vapour interference.

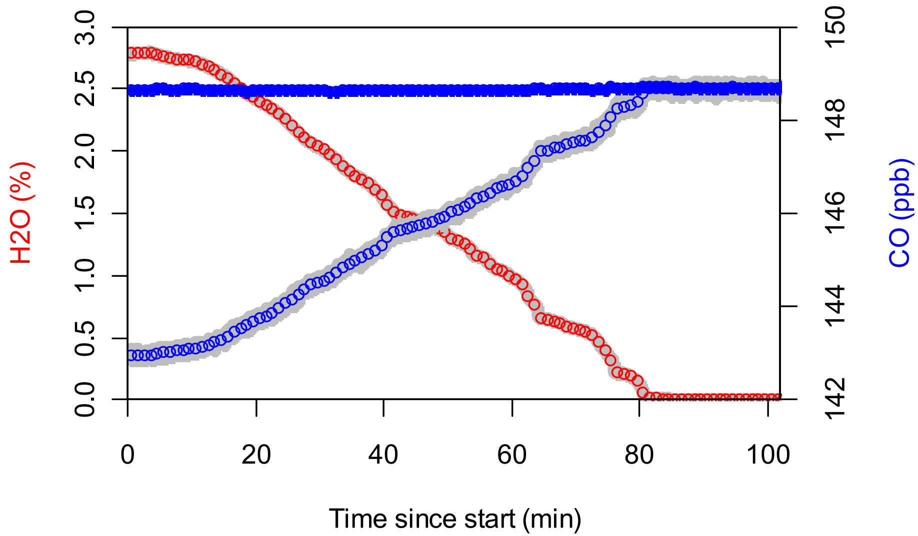

Fig. 8. Example of CO and H_2O time series during the water vapour interference experiment with the ICOS-QCL analyser. Grey circles are 1s-raw data, open circle are 1 min-averages. The filled blue circles are water vapour corrected 1 min CO data based on this experiment.

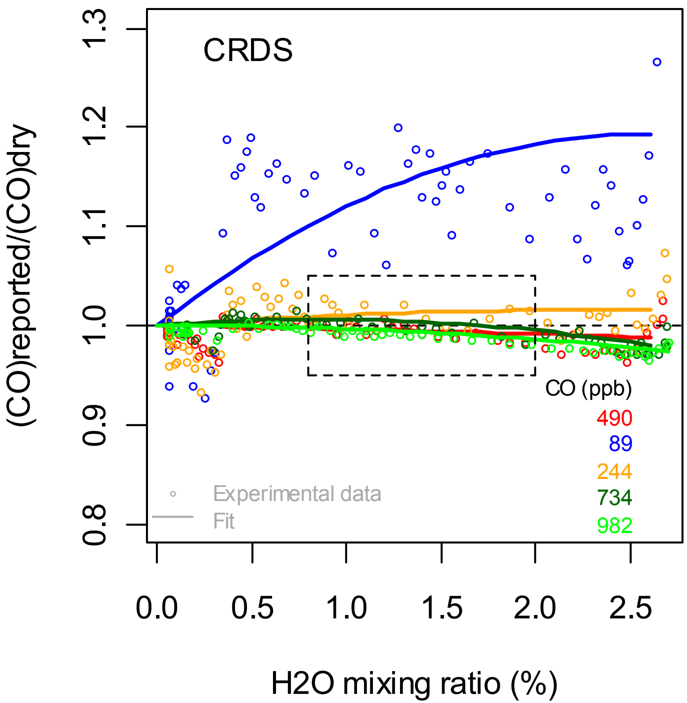

Fig. 9. Ratios of $CO_{reported}/CO_{dry}$ mole fractions vs. water vapour mixing ratios of the CRDS instrument for different CO levels. The black dotted line indicates a perfect correction of the reported CO mole fraction. The box denotes to conditions as encountered during the ambient air comparison (see below).

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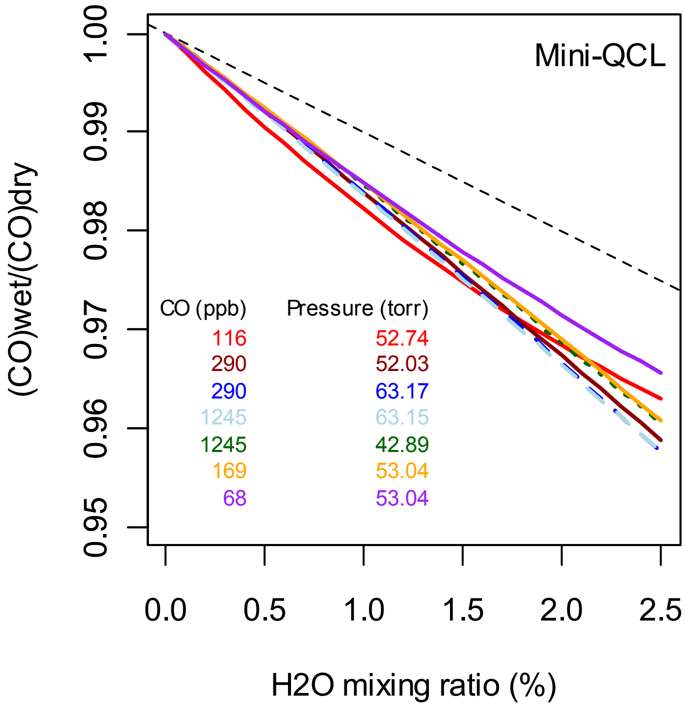

Fig. 10. Water vapour correction function for different CO mole fractions and operating pressures of the Mini-QCL instrument (coloured lines) and the effect of dilution (black dashed line).

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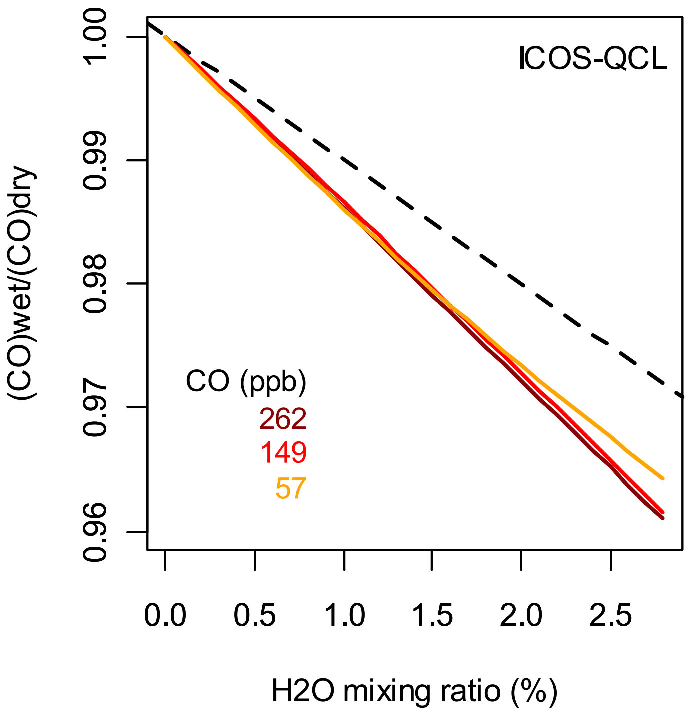

Fig. 11. Water vapour correction function for different CO mole fractions of the ICOS-QCL instrument (coloured lines) and the effect of dilution (black dotted line).

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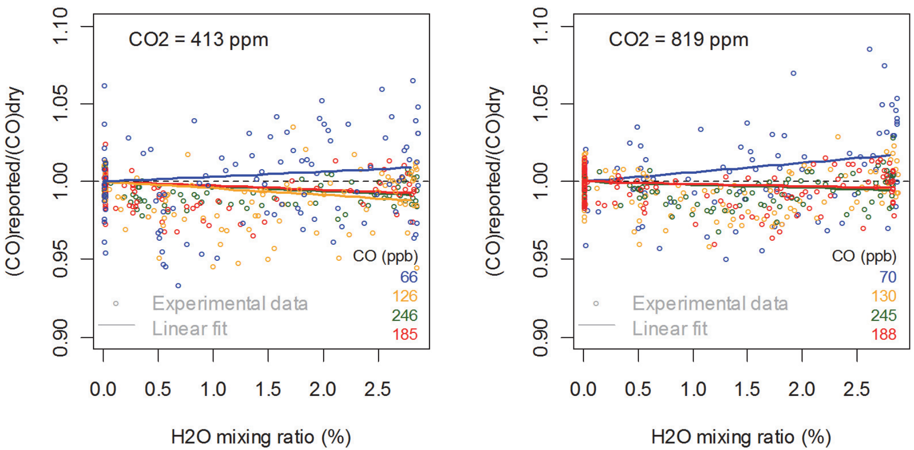

Fig. 12. Ratios of $CO_{reported}/CO_{dry}$ mole fractions vs. the water vapour mixing ratios of a Picarro G2401 CRDS instrument with optimised water vapour correction function for different CO levels. The experiment was made at two different CO_2 mole fractions (left: 413 ppm CO_2, right: 819 ppm CO_2).

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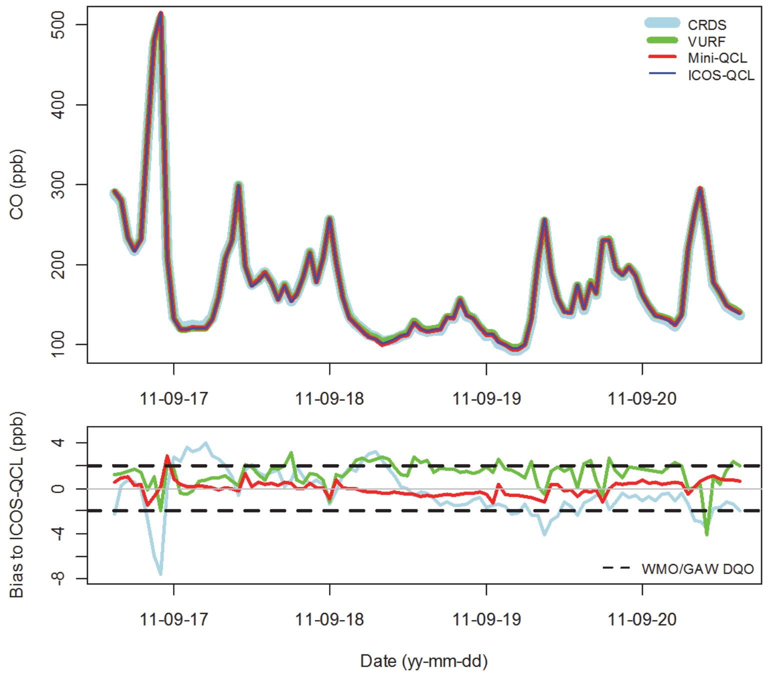

Fig. 13. Ambient air CO mole fractions measured with four different CO analysers from Friday, 16 September until Tuesday, 20 September 2011 (upper panel) and difference to the ICOS-QCL analyser (lower panel). 1 h-averages are shown.

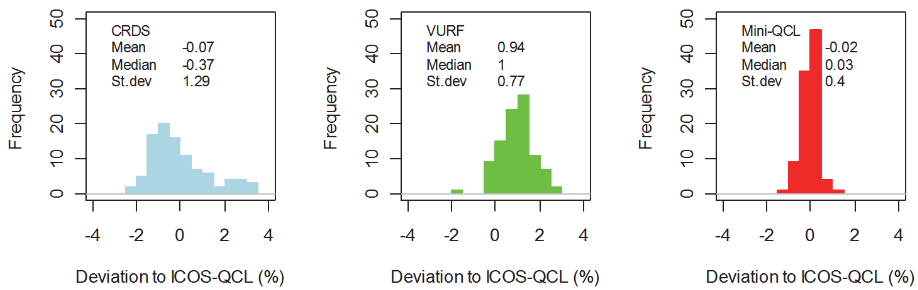

Fig. 14. Histogram of the deviations of the different instrument relative to the ICOS-QCL in per cent during the ambient air measurements.

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