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Comparison of continuous in-situ CO₂ observations at Jungfrauoch using two different measurement techniques

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Abstract

Since 2004, atmospheric carbon dioxide (CO₂) is measured at the High Altitude Research Station Jungfraujoch by the division of Climate and Environmental Physics at the University of Bern (KUP) using a nondispersive infrared gas analyzer (NDIR) in combination with a paramagnetic O₂ analyzer. In January 2010, CO₂ measurements based on cavity ring down spectroscopy (CRDS) as part of the Swiss National Air Pollution Monitoring Network have been added by the Swiss Federal Laboratories for Materials Science and Technology (Empa). To ensure a smooth transition – a prerequisite when merging two datasets e.g. for trend determinations – the two measurement systems run in parallel for several years. Such a long-term intercomparison also allows identifying potential offsets between the two datasets and getting information about the compatibility of the two systems on different time scales.

A good agreement of the seasonality as well as for the short-term variations was observed and to a lesser extent for trend calculations mainly due to the short common period. However, the comparison revealed some issues related to the stability of the calibration gases of the KUP system and their assigned CO₂ mole fraction. It was possible to adapt an improved calibration strategy based on standard gas determinations, which lead to better agreement between the two data sets. By excluding periods with technical problems and bad calibration gas cylinders, the average hourly difference (CRDS – NDIR) of the two systems is $-0.03\text{ ppm} \pm 0.25\text{ ppm}$. Although the difference of the two datasets is in line with the compatibility goal of $\pm 0.1\text{ ppm}$ of the World Meteorological Organization (WMO), the standard deviation is still too high. A significant part of this uncertainty originates from the necessity to switch the KUP system frequently (every 12 min) for 6 min from ambient air to a working gas in order to correct short-term variations of the O₂ measurement system. Allowing additionally for signal stabilization after switching the sample, an effective data coverage of only 1/6 for the KUP system is achieved while the Empa system has a nearly complete data coverage. Additionally,

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different internal volumes and flow rates between the two systems may affect observed differences.

1 Introduction

Carbon dioxide (CO₂) is an important greenhouse gas which plays a major role for the radiative forcing of the atmosphere and therefore contributes significantly to the greenhouse effect (Arrhenius, 1896). Since natural as well as anthropogenic processes alter the mole fraction of CO₂ in the atmosphere, it is important to survey the mole fraction changes for a long time period to understand these processes and draw conclusions about the involved CO₂ fluxes (Ramonet et al., 2010; Schimel et al., 2001). Additionally, in-situ CO₂ measurements can be used in modeling studies as input parameters or to verify model output (Uglietti et al., 2011; Chevallier et al., 2010; Peters et al., 2010). Therefore it is crucial that the datasets are well calibrated and are traced back to a common reference scale as well as that the measurement systems demonstrate a high precision and accuracy. This guarantees minimal biases between different measurement sites and laboratories and improves the compatibility of the datasets. For CO₂ measurements the WMO recommends a compatibility of ±0.1 ppm for the Northern Hemisphere (WMO, 2011).

High altitude observatories such as the High Alpine Research Station Jungfraujoch (JFJ) are predestined to monitor the background mole fraction of trace gases like CO₂ because they are mostly in the free troposphere.

That is why the division of Climate and Environmental Physics of the Physics Institute, University of Bern (KUP) started measuring CO₂ with a non-dispersive infrared (NDIR) gas analyzer (Sick Maihak, Germany, model S710) embedded in a combined CO₂/O₂ analyzing system at JFJ in late 2004. At the beginning of 2010, a cavity ring down spectrometer (until July 2011 a Picarro Inc., USA, model G1301, afterwards a Picarro Inc., USA, model G2401) was installed by the Swiss Federal Laboratories for Materials Science and Technology (Empa) as part of the Swiss National Air Pollution

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Monitoring Network (NABEL) enabling a long-term performance of CO₂ measurements at Jungfraujoch by Empa. To ensure that both records can be merged smoothly, it was decided to run both systems in parallel for a significant period, not only to detect potential biases, but also to provide information about the compatibility of the two different measurement systems too, as it was done at other stations e.g at Mauna Loa (Komhyr et al., 1989; Peterson et al., 1977). Because of the year-round manned infrastructure and excellent accessibility by train, it is possible to test the compatibility of the two systems in-situ under real conditions at a background site featuring only limited atmospheric variation.

In this study we report the data of the KUP and the Empa in-situ CO₂ measurement system from January 2010 until December 2012.

2 Methods

2.1 Sampling site

The High Altitude Research Station Jungfraujoch (JFJ) is located 7°59′20″ E, 46°32′53″ N on the northern ridge of the Swiss Alps. The station itself is on a mountain saddle between the mountains Mönch (4099 m a.s.l.) and Jungfrau (4158 m a.s.l.) at an altitude of 3580 m a.s.l.. Because of the high elevation the station is most of the time above the planetary boundary layer and receives predominantly air from the free troposphere. It is therefore an ideal location to measure atmospheric background air of continental Europe (Henne et al., 2010; Zellweger et al., 2003; Baltensperger et al., 1997). Nevertheless, the station is sometimes influenced by polluted boundary layer air, especially during Föhn events (Zellweger et al., 2003) or during hot summer days, when air from the surrounding valley is thermally uplifted to Jungfraujoch (Zellweger et al., 2000; Baltensperger et al., 1997). A comprehensive in-situ measurement program with more than 70 trace gases and a large suite of aerosol properties is run

continuously at Jungfraujoch by an international consortium of research institutions. JFJ is also one of the currently 29 global GAW (Global Atmosphere Watch) stations.

2.2 NDIR measurements (KUP)

The KUP CO₂ measurements base on a combined system to monitor CO₂ and O₂ changes in the atmosphere. The ambient air is entering through a strongly ventilated (600 m³ h⁻¹) common inlet on the observatory's roof to a manifold, which serves many air detectors, where an aliquot of it is drawn to the KUP system. The air is cryogenically dried to a dew point of -90 °C (FC-100D21, FTS systems, USA). Temperature as well as pressure is stabilized to avoid influences caused by ambient air density fluctuations. This allows the determination of CO₂ by a NDIR spectrometer (Maihak S710) with a frequency of 1 Hz and O₂ by a paramagnetic cell under highly controlled conditions. Measurements are done in a cyclic sequence of 18 h with each gas measured for 6 min with only the last 115 s of a six minute period used for mole fraction determination, to allow for signal stabilization after changing the sample source. At the beginning of each sequence, the system is calibrated with two reference gases (high and low span). A working gas is measured between two ambient air measurements to correct for short term variations. Thus, an 18 h measurement sequence looks therefore as follows:

B – G – K – B – H – B – A – A – B – A – A – B – . . . – A – A – B

where B represents the working gas, G the high span CO₂/low span O₂, K the low span CO₂/high span O₂, H the target cylinder and A represents ambient air.

All measurements ending in a particular hour are used for the calculation of hourly mean CO₂ observations, which in our case includes therefore 6 ambient observation values per hour. Cylinder measurements (see Table 1) with a known mole fraction showed a precision better than 0.04 ppm for 1 h analysis. The CO₂ values are reported on the WMO X2007 scale. In February 2011, the Maihak analyzer was replaced with an identical Maihak device because of technical problems.

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2.3 Cavity ring down spectroscopy measurements (Empa)

From late December 2009 until July 2011 Empa was measuring CO₂ with a commercially available Wavelength-Scanned Cavity Ringdown Spectrometer (Picarro Inc., USA; G1301) coupled to a custom-built calibration/drying unit. Initially, the sample air from the manifold was dried prior to analysis by means of a Nafion dryer to a dew point of < -30 °C. Along with CO₂, the instrument also measures CH₄ and H₂O in the same sample frequency of approximately 0.5 Hz. The H₂O measurements allow for correction of the CO₂ mole fraction in case of interferences (i.e. dilution and pressure broadening) due to potential water moisture in the system. From August 2010 on, the Nafion dryer was short-cut, no water vapor removal was used anymore and CO₂ dry air mole fractions were determined after application of an empirical humidity correction.

After a system breakdown due to a faulty electronic board in July 2011, the G1301 analyzer was replaced in September 2011 by the newer G2401 model (Picarro Inc., USA) that is also capable to monitor CO mole fractions. Since then, the drying of the sample gas was again applied mainly due to beneficial effects with respect to the precision of the CO analysis. The water vapour correction functions for both instruments were determined by humidifying a dry reference gas by passing it over a water droplet in a coiled tubing (see Rella et al., 2013 for details).

Calibrations are performed every 46 h with two calibration gases (high and low span). In addition, a target gas is analyzed every 15 h to detect potential shorter term instrument sensitivity changes. The mole fractions of the calibration gases were determined by the World Calibration Center for CH₄, CO₂, CO and O₃ at Empa. Measurements of standard cylinders showed a precision better than 0.04 ppm for 15 min analysis (Table 1). Similar to the KUP, CO₂ mole fractions are also reported on the WMO X2007 scale.

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2.4 Calibration gases

The gases used to calibrate the KUP measurements are compressed outside air filled in steel cylinders delivered by Carbagas (Switzerland). Normally, each gas cylinder is first delivered to our laboratory at the University of Bern and measured for its CO₂ mole fraction and $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values by mass spectrometry and a combined Licor 7000 NDIR and Oxzilla (Sable Systems, USA) system (CO₂ and O₂). The measured values are calibrated with a sub-set of three standards from the WMO/GAW Central Calibration Laboratory (CCL) run by the National Oceanic and Atmosphere Administration (NOAA, Boulder, USA) and were used as assigned values of the KUP system at Jungfraujoch (see Table 2). The cylinders are shipped to Jungfraujoch and stored in the basement until their usage as calibration gases. To maintain a stock of calibration gases at JFJ is necessary because the KUP system has to be calibrated frequently due to O₂ measurements (Uglietti, 2008) and has a rather high gas consumption of up to 150 mL min⁻¹.

The calibration gases used by Empa consist of compressed dry natural air in aluminum cylinders filled with a modified oil-free compressor (Rix Industries, USA) at Empa. The mole fractions of the gases are determined by the World Calibration Center for CH₄, CO₂, CO and O₃ at Empa through comparison with a suite of standards from the WMO/GAW CCL (see Table 3). After measuring the calibration gases, the cylinders are shipped to JFJ.

Lists of the calibration gases used by both systems during the period of intercomparison are included in Tables 2 and 3, respectively.

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3 Results

3.1 Comparison of the two datasets

The CO₂ measurements of both systems for the period 2010–2012 are shown in Fig. 1. In general the two data sets show a good agreement. There are two longer gaps in the CRDS record during 11 June to 16 September 2011 and 5 to 18 January 2012. The first gap was caused by technical problems of the Picarro and was replaced by a new 4 channel model. In January 2012 a hard disk failure was responsible for the roughly 2 week break. The NDIR data set shows four longer gaps during 31 January to 16 February 2011; 21 to 28 December 2011; 14 to 25 April 2012 and 7 to 24 October 2012. The reasons for the gaps in the NDIR dataset were due to technical issues with the Maihak analyzer, eventually leading to a replacement of the analyzer with an identical one. Furthermore, a power failure was responsible for failure of a gas flow controller and in April and October 2012 a dysfunction of the gas drying system. Throughout the record small gaps are also present due to e.g. system crashes, failures in the regulation of the gas flows etc. The remaining hourly mean values where we have overlap for both systems (20 460 common hours) are in good agreement. The datasets show a similar seasonality as well as peaks caused by pollution events (e.g. advection of air masses from the Po basin in Italy or from Northeastern Europe).

The average seasonality of the monthly mean values, spanning 36 months, are 10.01 ± 0.33 ppm and 10.05 ± 0.37 ppm for the CRDS and the NDIR data set, respectively. Due to missing data one monthly value in each dataset had to be interpolated. For the complete datasets, the CRDS data show an annual increase of 1.89 ± 0.01 ppm year⁻¹ whereas the NDIR data show a slope of 1.69 ± 0.01 ppm year⁻¹, the uncertainties correspond to the error of the linear increase fitted to the data. Selecting only data points where both systems have overlapping data points, the difference in the slopes decreases slightly as documented by values of the annual increase of CO₂ of 1.91 ppm year⁻¹ (CRDS) and 1.72 ppm year⁻¹ (NDIR). A correlation plot of the CRDS dataset against the NDIR dataset reveals a very high correlation with a slope

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of 0.991 ppm/ppm, an intercept 3.662 ppm and a R^2 of 0.9909 (Fig. 2, grey points). It can be seen in Fig. 3 (grey points), that the differences of the two data sets are very stable over the three year period of the comparison. The average of the difference between the CRDS dataset and the NDIR dataset is 0.04 ± 0.40 ppm (Fig. 3, grey points), negative and positive differences equal out to almost zero. During periods of rapid CO₂ changes, the standard deviation of the differences is larger than during stable periods and significantly exceeds the precision of both instruments. This point can be emphasized by zooming in to higher resolution data (115 s averages). For this exercise, the high-resolution CRDS data were aggregated to 115 s averages corresponding to the averaging intervals of the NDIR system. There it can be clearly seen, that the difference becomes noisier with fast changes (e.g. during the late afternoon in Figs. 4 and 5) and decreases again with more stable conditions (e.g. during the night time in Figs. 4 and 5).

The behavior of short-term variations is different for both systems as shown by a change of statistical characteristics when discarding values for which the change rate is above a certain threshold (Table 4). These changes in system behavior are most probably due to different volumes and gas flows resulting in different residence times and leading to dispersion effects. For example the NDIR system uses a water trap with a large volume, potentially dampening the CO₂ signal despite the high flow rate, compared to the rather small Nafion dryer of the CRDS system. The cutoff criteria of the change rate was set to 0.75 ppm h^{-1} , values with a higher change rate were discarded. Below 0.75 ppm h^{-1} there is still an improvement of the agreement, but the loss in data points is too high. Additionally, the standard error starts to increase again below a change rate of 0.75 ppm h^{-1} because a lot of data points are omitted by this criteria. By setting the threshold to 0.75 ppm roughly 20 % of the common data points are omitted. The correlation between the remaining data for both systems gets a bit closer to the ideal 1 : 1 function with a slope of 0.996 ppm, an intercept of 1.5696 ppm/ppm and a R^2 of 0.9924 (Fig. 3, black points). Also the differences between the CRDS and the NDIR dataset are smaller considering only the data points of the more stable

conditions (Fig. 3, black points), the average of the difference remains almost zero, namely $0.05 \text{ ppm} \pm 0.32 \text{ ppm}$.

However, there are problematic features worth mentioning. By replacing the working gas B26 with B27 and B28 with B29 (see Table 2) small shifts occurred, which are most likely caused by an inaccurate assignment of the CO_2 values of the working gases (Fig. 3). By excluding the periods of the cylinders B27 and B29 11038 common data points are remaining, the average of the differences, however, stays almost the same, namely -0.03 ppm but with reduced standard deviation of 0.25 ppm .

In late 2010, the difference between the two datasets increased significantly, because of technical issues (see Sect. 3.1). After replacing the analyzer, the difference was again very small and stable (Fig. 3). Furthermore, with the exchange of the Picarro in summer 2011, a small jump in the difference between the two systems occurred (Fig. 3). Since the replacement happened during a single working gas period of the KUP system (B27), the offset was probably caused by the change of the Picarro analyzer.

3.2 Drift of calibration gases and their corrections

In case of regular periodic calibrations, the pressure of a calibration gas cylinder decreases relatively linearly considering a longer timescale than its decanting frequency. Because steel cylinders show pressure dependent adsorption and desorption effects of gases such as CO_2 or H_2O (Langmuir, 1918), CO_2 continuously desorbs from the cylinder walls and increases the CO_2 mole fraction of the calibration gas during its usage. To avoid a large drift of the CO_2 mole fraction in calibration gases, Keeling et al. (1998) recommended using calibration gas cylinders only to a remaining pressure of 25 to 30 bar. The adsorption of CO_2 to the cylinder wall can be calculated according to Langmuir (Langmuir, 1918) and corrected for by the formula:

$$\text{WG}_{\text{corr}}(t) = \text{WG}_{\text{meas}}(t) - \left(\frac{a \cdot b \cdot p_0}{b \cdot p_0 + 1} - \frac{a \cdot b \cdot p(t)}{b \cdot p(t) + 1} \right) \quad (1)$$

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where WG_{meas} corresponds to the measured CO₂ value of the working gas [ppm], a and b are constants (related to the Avogadro constant, the number of elementary spaces of the surface, the molecular mass and the temperature), p_0 is the start pressure and $p(t)$ is the pressure at the time of the measurement. This enrichment of CO₂ is more pronounced at lower pressures compared to high pressures as seen from Eq. (1). For example at 100 bar cylinder pressure, the correction is only about 0.05 ppm, whereas at 30 bar it is already up to 0.3 ppm (with $a = 5\,715\,797$ and $b = 568\,897$, a and b values were derived from measurements of cylinder B23). In steel cylinders, present water vapor would cause an even more pronounced desorption effect. However, all cylinders used here contained dry gas. In Leuenberger et al. (2014) an in-depth discussion of this adsorption/desorption influence of gases on steel and aluminium cylinders is presented based on dedicated experimental results in our laboratory as well as in a climate chamber.

In April 2010, the working gas tank B23 run completely empty due to a faulty pressure reader and showed therefore such an enrichment effect. Hence the CO₂ values of the NDIR calibrated with the uncorrected working gas are underestimated compared to the CRDS measurements. By recalculating the measurements of the working gas using only the low and the high span (Fig. 6, black points), it is possible to approximate the evolution of the working gas CO₂ enrichment (Fig. 6, grey points) and correct for it (Fig. 7). The NDIR data were in much better agreement with the CRDS measurements after applying this correction. Comparing the uncorrected values of the B23 period to the corrected period, the R^2 of the NDIR values against the CRDS values is increased from 0.89 to 0.99 (Fig. 8). The remaining working gases cylinders were recalculated in the same manner, too. Most of them showed a similar behavior as B23, even when they were replaced at around 25 bar remaining pressure. The only difference was the intensity of the enrichment, which was weaker than with B23, because they did not run empty completely. Note that for B23 we used the time instead of the pressure as the dependent variable, because the pressure reader did not work properly during this

period. Although not preferred, this is possible because the pressure decreases linearly on long-term.

3.3 Polynomial correction of the NDIR Maihak measurements

NDIR spectrometers are nonlinear in response and hence require a correction of the data – generally of polynomial form. Ideally, the analyzer response function is implemented by the producer, mostly for a restricted mole fraction range. This is also the case for the Maihak system. The Maihak measurements at JFJ are done in differential mode, hence the reference cell is always flushed with gas of known CO₂ mole fraction and compared to the cell containing the sample. To set the polynomial function to overcome the nonlinearity of the device, the mole fraction of the reference gas has to be entered into the analyzer's system.

In fall 2011, eleven used calibration gas cylinders of the KUP system were measured with the CRDS system and remeasured with the NDIR system. The remeasuring of these cylinders revealed that the polynomial function of the Maihak was insufficient. The second order polynomial of the difference between CRDS (Empa) – NDIR (KUP) vs. CRDS (Empa) yielded a R^2 of 0.86. A very similar polynomial dependence is found between the assigned values NDIR (KUP) vs. assigned values according to Table 2, when discarding two cylinders with low remaining pressure (Table 1). We preferred the first polynomial because the cylinders might have faced already desorption effects due to changing pressure between the assignment measurement in Bern (> 2 years before) and the remeasurement at JFJ whereas the comparison with the CRDS took place within a few days. Since the cavity ring down technique is linear in the considered mole fraction range, the factors of the polynomial were used to correct the measurement values of the NDIR system removing this dependence completely (Fig. 9 and Table 1). The correction was only applied to the data measured by the NDIR analyzer actually in use at Jungfraujoch. The data of the first NDIR analyzer, which had to be replaced in the beginning of 2011 due to technical problems, remained unaltered, since the working points of the two NDIR instruments were different. There is also no possibility to

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correct the data of the older NDIR analyzer properly, because at the time there were no comparable measurements with a nearly linear measurement system. However, values in the center of this span, where most of the ambient CO₂ mole fractions are measured, should not be affected strongly, roughly 75 % of all NDIR values are affected less than 0.1 ppm by the polynomial correction. The accuracy of the standard measurements is estimated to be 0.12 ppm over the working range from 350 ppm to 450 ppm based on the CRDS-NDIR comparison including both instrumental uncertainties.

4 Discussion

Long periods of overlapping measurements are helpful to assess the compatibility of different analyzers. In this study we analyzed two different data sets which were measured at the same station over three years (the simultaneous measurements are still ongoing) to determine the compatibility and quantify differences and biases. The compatibility is challenging since the Empa uses the cavity ring down technique (Picarro Inc.) and the KUP a non-dispersive infrared spectrometer (Maihak) to measure the CO₂ mole fraction of the air. Also the calibration procedure is, given by the two used techniques, different and therefore has to be investigated.

The seasonality based on monthly measured averages (10.01 ± 0.33 ppm and 10.05 ± 0.37 ppm for the CRDS and the NDIR data set) between the two data sets agree nicely and are also in good agreement with results of flask measurements done at JFJ (10.54 ± 0.18 ppm) (van der Laan-Luijkx et al., 2013). The trend calculation (1.89 ppm year⁻¹ and 1.69 ppm year⁻¹) for the complete and the common data periods deviate by 0.2 ppm year⁻¹ which we mainly attribute to uncertainties in the assigned values for the working gases. The annual CO₂ increase of the CRDS data set is in good agreement with the average global CO₂ trend of 1.97 ppm year⁻¹ for 2003–2012 (Tans, 2014), whereas the NDIR trend is a bit too low. Nevertheless, is important to mention that for proper trend analysis the period of three years is too short. The CO₂ trend of the whole NDIR data set from the end of 2004 until the end of 2013 is

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1.99 ppm year⁻¹ which is in much better agreement with the global trend of the same period of 2.03 ppm year⁻¹ (Tans, 2014).

Despite the fact that it is common knowledge to use well assigned standard cylinder values for accurate measurements, we found larger offsets for two calibration cylinders, namely B27 and B29 used by the KUP. Thereby the calculated CO₂ values of the KUP data set are a bit too high for these two periods. This effect would have been undetected without the comparison measurements, at least for the B27 cylinder, since the offset is only around 0.2 ppm which is quite small compared to a seasonality of roughly 10 ppm and even more compared to the daily variations of up to 25 ppm in extreme cases. Experiences of ongoing international comparison on travelling cylinders highlight similar issues (Zellweger et al., 2011). Therefore, a thorough check of assigned values of calibration and working cylinders is crucial.

Another problem concerning the calibration cylinders is their CO₂ mole fraction. Ideally the low span is lowest in CO₂ mole fraction, the working gas intermediate, preferably close to the expected value of the specimen, and the high span accordingly highest. But in some periods (e.g. B26, B27, B29) the CO₂ mole fraction of the working gas was higher than the CO₂ mole fraction of the high span or it was very close to the high span (e.g. B28) and therefore not ideal to calibrate the measurements with a very high accuracy. However, because of logistic problems these cylinders had to be used as working gases.

Also the stability of the CO₂ mole fraction in the calibration cylinders is very important. Adsorption/desorption effects occur when the pressure of steel cylinder drops under 20 to 30 bar (2 to 3 MPa) (Keeling et al., 1998), leading to an enrichment of CO₂ in the cylinder and therefore to a CO₂ value different from the assigned. Hence, cylinders shouldn't be used until they are empty. A recalculation of the working gas cylinders with a two point calibration using the low and the high span showed that the effect starts already at roughly 80 to 90 bar (8 to 9 MPa) and had to be corrected for. This finding is supported by Leuenberger et al. (2014). At higher pressures the effects are still very small, but with decreasing pressure the difference between the measured

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CO₂ mole fraction of the calibration gas and the assigned value increases and thus leading to a worsening of the accuracy of the calculated CO₂ values.

By applying corrections mentioned above (see 3.2 and 3.3), discarding two periods of badly assigned working gases (B27 and B29) and excluding periods of fast CO₂ changes, the average difference of the hourly values decreases to -0.03 ± 0.25 ppm. Whereas the average values of almost zero is very good, the standard deviation is still high in comparison to the WMO goal of 0.1 ppm and the precision of each individual system that is roughly five times better. The rather high standard deviation is probably caused by different averaging intervals of the hourly values, by dispersion of the air parcels in the two systems due to different volumes and flow rates of the air.

Both systems obtain the outside air from the same air inlet at Sphinx observatory at Jungfraujoch, but the air is led to the two systems by separate tubing. Due to different flow rates and volumes of the two systems, the origin of an air parcel measured at a certain time is not necessarily exactly the same. For example, the volume of the NDIR drying unit leads to a residence time of three minutes, significantly longer than for the CRDS system. Therefore, the NDIR system records slightly dampened ambient signals. Furthermore, it is possible that the according air parcels are shifted a little bit and thereby leading to small differences of the CO₂ values of the two systems. This could be the reason for the observed larger differences between the two datasets during fast CO₂ mole fraction changes of the outside air.

Over all, the CO₂ mole fraction measured by the two systems shows the same pattern, not only during stable periods, but also during extreme events and even in the high resolution data. Most of the noisier periods can be accounted to specific technical problems, whereas systematic shifts are most probably caused by badly assigned calibration gases or drifts of the CO₂ mole fraction in the cylinders due to adsorption/desorption effects. While it was possible to correct for the pressure dependent drifts of the calibration gases mathematically, it is harder to correct for the shifts caused by badly assigned calibration gases, since there are not a lot of independent comparison measurements which can be used for correction.

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5 Conclusion

The CO₂ data sets of two different CO₂ measurement systems, a nondispersive infrared analyzer and a cavity ring down spectrometer, running parallel at the High Altitude Research Station Jungfraujoch were compared. The comparison showed, that the two systems are generally in good agreement, but revealed (i) adsorption/desorption effects in the calibration gas steel cylinders used by NDIR system and (ii) insufficient nonlinearity correction of the NDIR analyzer (iii) periods of small biases because of badly assigned calibration gas cylinders. Adsorption effects can be correct for by monolayer adsorption equation (Langmuir, 1918). Nonlinearity of the NDIR analyzer was constrained with a 2nd order polynomial, resulting in a better agreement between the two data sets, in particular for values strongly deviating from the average. More research in adsorption/desorption effects of calibration gas cylinders has been done at the KUP and is reported in Leuenberger et al. (2014).

Finally, we like to emphasize that using steel cylinders is not adequate for high precision trace gas determinations due to gas adsorption/desorption. Therefore, we conclude that all laboratories using steel cylinders for calibration purposes should switch to calibration gases stored in aluminium cylinders to minimize gas composition changes and to allow an improved assignment of the cylinder.

It is helpful to continue this comparison exercise for another couple of years to show that once aluminium cylinders are in use for both systems the compatibility will improve further.

Acknowledgements. This work was financially supported by the Swiss National Science Foundation (SNF-Project 200020_134641) and the Federal Office of Meteorology and Climatology MeteoSwiss in the framework of Swiss GCOS. Empa’s CO₂ measurements are part of the Swiss National Air Pollution Monitoring network, a joint responsibility of Empa and the Swiss Federal Office for the Environment. We like to thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG), especially the custodians Martin Fischer, Felix Seiler and Urs Otz for changing the calibration gases cylinders and other maintenance work on the measurement systems. Additionally the authors like to thank Peter Nyfeler

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for his precious work and help in maintaining and repairing the systems in the Laboratory in Bern and also at Jungfrauoch.

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Table 1. KUP calibration cylinders and their measured CO₂ values on the NDIR and the CRDS system. These values were used to calculate the polynomial of second degree to correct the nonlinearity of the Maihak system (See also Fig. 9).

Cylinder number	Used before as	CO ₂ Picarro [ppm]	CO ₂ Maihak [ppm]	ΔCO ₂ (Picarro – Maihak) [ppm]	Pressure [bar]
LK542510	G1	431.99 ± 0.02	431.74 ± 0.04	0.25	22.1
LK94521	K5	360.57 ± 0.07	459.96 ± 0.05	0.61	23.8
LK570931	B20	438.01 ± 0.02	437.73 ± 0.04	0.28	21.9
LK542204	B21	385.09 ± 0.02	384.87 ± 0.04	0.22	26.8
LK3137	B22	384.99 ± 0.02	387.71 ± 0.05	0.28	16.1
LK3077	B24	418.68 ± 0.08	418.78 ± 0.03	−0.06	14.1
LK542469	B26	432.06 ± 0.03	431.87 ± 0.02	0.19	23.7
LK564848	B27	448.40 ± 0.03	447.83 ± 0.02	0.57	22.7
LK570916	B29	437.66 ± 0.07	437.43 ± 0.05	0.23	185

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Table 2. List of calibration gas cylinders used by the NDIR system in the period 2010 to 2012, K, G, H and B corresponds to the usage as low span, high span, target and working gas, respectively.

Cylinder number	Used as	From	To	Assigned CO ₂ [ppm] WMO X2007
LK94521	K5	10 Mar 2009	31 Dec 2010	360.31 ± 0.50
LK541816	K6	31 Dec 2010	6 Nov 2012	380.77 ± 0.25
LK542332	K7	6 Nov 2012	now	384.41 ± 0.07
LK542217	G2	23 Jul 2009	now	429.02 ± 0.25
LK542119	B23	11 Dec 2009	27 Apr 2010	379.90 ± 0.25
LK542171	H1	8 Sep 2010	now	440.16 ± 0.25
LK3077	B24	27 Apr 2010	7 Sep 2010	416.60 ± 0.10
LK541869	B25	7 Sep 2010	9 Feb 2011	416.79 ± 0.10
LK542469	B26	9 Feb 2011	17 Jun 2011	431.76 ± 0.25
LK564848	B27	17 Jun 2011	19 Oct 2011	448.04 ± 0.25
LK557112	B28	19 Oct 2011	23 Feb 2012	425.35 ± 0.05
LK570916	B29	23 Feb 2012	3 Jul 2012	437.55 ± 0.10
LK564850	B30	3 Jul 2012	5 Oct 2012	395.62 ± 0.01
LK542463	B31	5 Oct 2012	23 Jan 2013	390.34 ± 0.05

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Table 3. List of calibration gas cylinders used for the CRDS system in the period 2010 to 2012.

Cylinder number	Used as	From	To	Assigned CO ₂ [ppm] WMO X2007
D621867 (E062)	Cal. Gas 1	18 Dec 2010	now	394.11 ± 0.03
CA06290 (E063)	Cal. Gas 2	18 Dec 2010	now	429.72 ± 0.02
CB555583	Target	18 Dec 2010	now	426.04 ± 0.04

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Table 4. The statistics of different cutoff criteria of rapid CO₂ mole fraction changes and their influence on the number of points remaining, the average of the hourly differences of the NDIR and the CRDS system, the standard deviation of the differences and the according standard errors. The differences between the different cutoff criteria are most probably caused by different volumes and flow rates of the systems and thereby introduced small time lags. The measurement precision of each system is about ten times better than the standard deviation of the differences.

Cutoff criteria [ppm h ⁻¹]	Number of points	Average of differences [ppm]	Standard deviation [ppm]	Standard error [ppm]
All	19 779	0.038	0.401	0.0028
< 2	19 260	0.044	0.363	0.0026
< 1	17 474	0.049	0.336	0.0025
< 0.75	16 094	0.053	0.322	0.0025
< 0.5	13 602	0.056	0.312	0.0027
< 0.25	8666	0.060	0.295	0.0032

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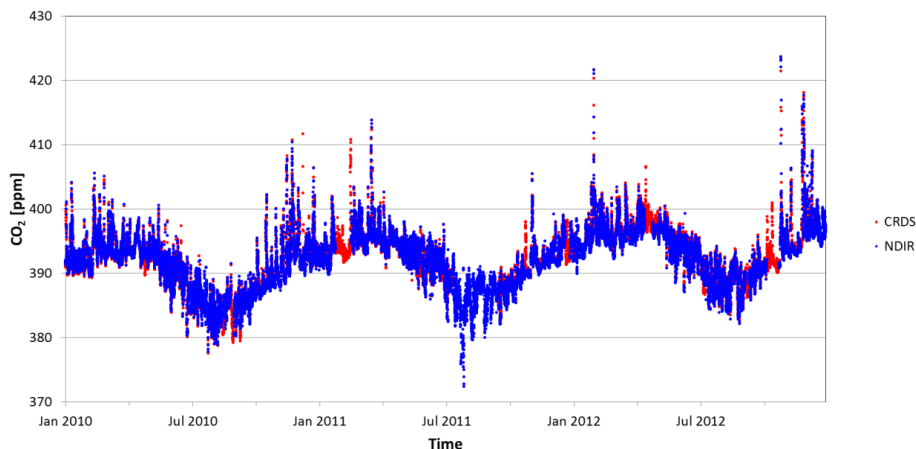


Figure 1. CO₂ measurements at Jungfraujoch of the CRDS system (red points) and the NDIR system (blue points) against time. The values represent the hourly averages of the two measurement systems.

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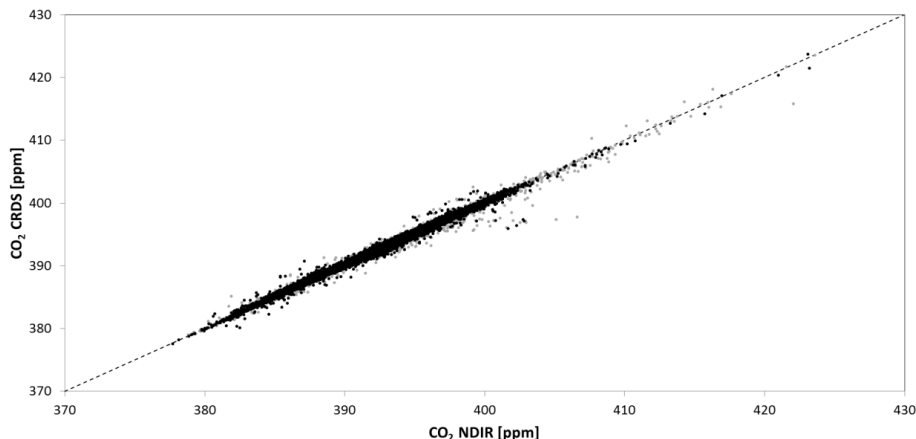


Figure 2. The hourly averages of the CRDS CO₂ measurements vs. the hourly averages of the NDIR CO₂ measurements (grey points) and the CRDS CO₂ measurements vs. the hourly averages of the NDIR CO₂ measurements without periods of rapid mole fraction changes (black points) over the whole period of comparison. The dashed diagonal represents the ideal 1 : 1 agreement. Considering all data points the R^2 is 0.9909 with a slope of 0.9908 ppm/ppm and an intercept of 3.6623 ppm. By excluding periods with a rapid mole fraction changes the agreement of the two datasets is slightly better with a R^2 of 0.9924, a slope of 0.9961 ppm/ppm and an intercept 1.5696 ppm.

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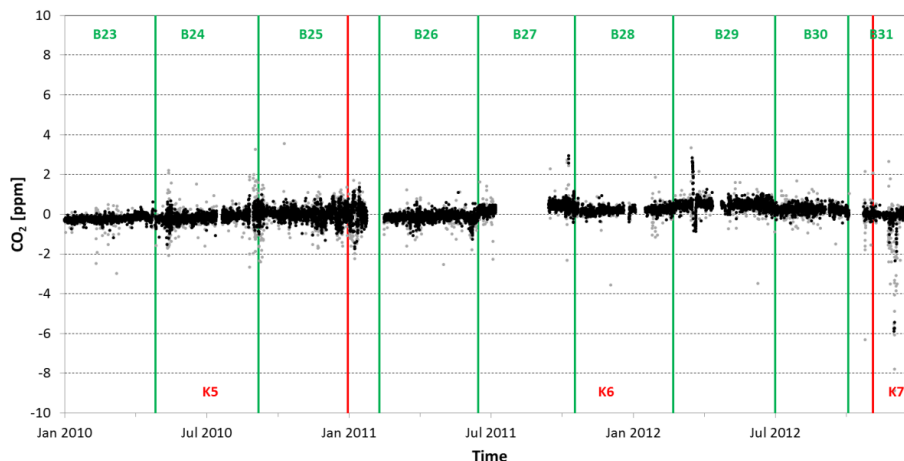


Figure 3. The difference of the CRDS – NDIR CO₂ measurements of all common hourly data points (grey points), and only during stable periods with a CO₂ change of less than 0.5 ppm h⁻¹ (black dots) against time. The green bars represent changes of the working gases of the KUP system with the green number indicating the according cylinder, the red bars indicate the changes of the low span with the according number, also in red. The high span was not replaced in the entire period.

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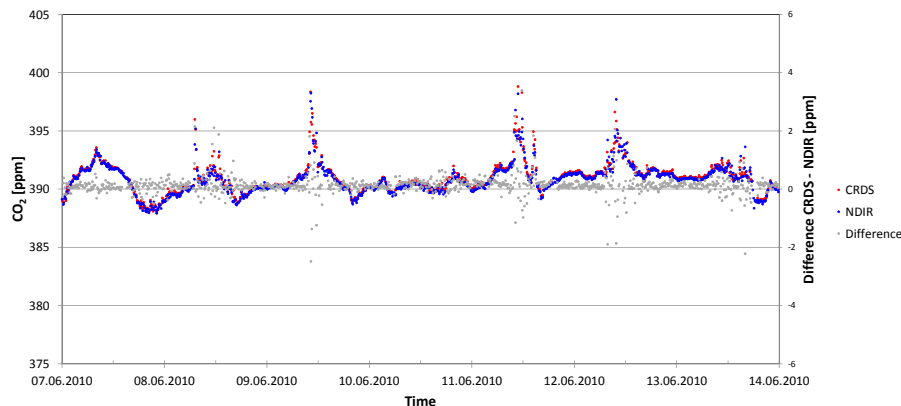


Figure 4. Time series of 115 s averages CO₂ mole fractions measured with CRDS (red) and NDIR (blue) at Jungfraujoch (left-hand y axis scale) and difference between the two systems against time (grey points) (right-hand y axis scale) for one week in June 2010.

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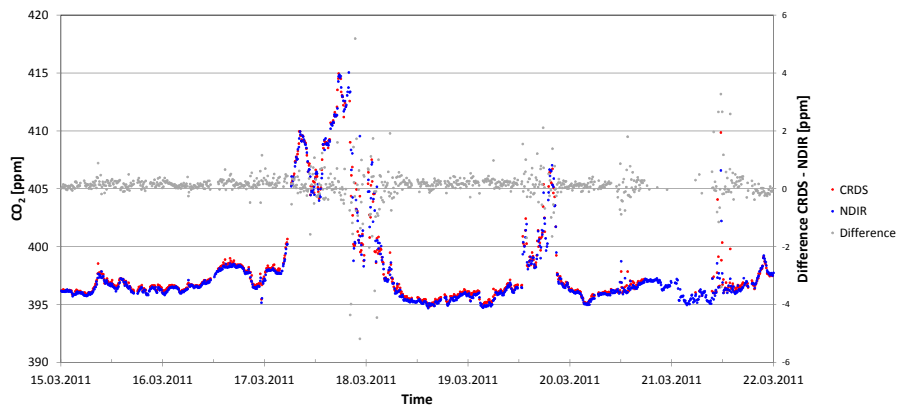


Figure 5. Time series of 115 s averages CO₂ mole fractions measured with CRDS (red) and NDIR (blue) at Jungfraujoch (left-hand y axis scale) and difference between the two systems against time (grey points) (right-hand y axis scale) for one week in March 2011.

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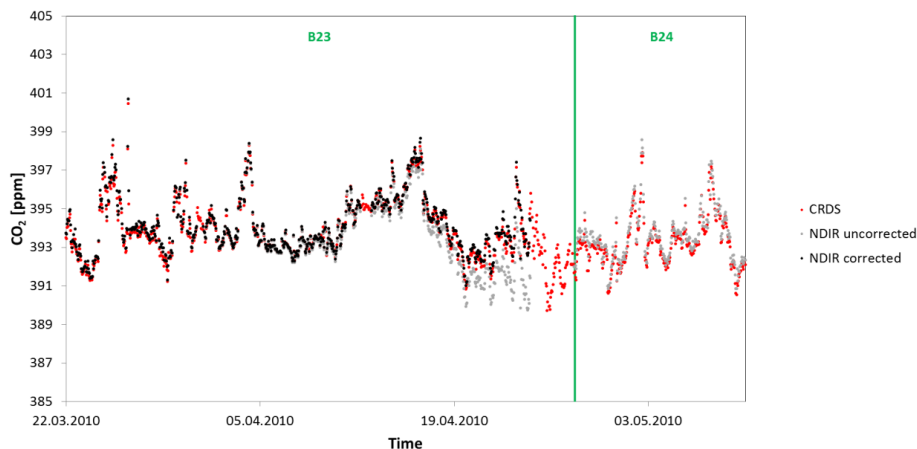


Figure 7. Time series of the CO₂ mole fractions determined with CRDS (red points) and NDIR (uncorrected in grey, after correction in black). The desorption corrected NDIR CO₂ values show a much better agreement with the CRDS CO₂ values than the uncorrected which are towards the end of the B23 period severely underestimated. After replacement of the working gas cylinder B23 with B24, the uncorrected NDIR CO₂ values show a much better agreement with the CRDS CO₂ values.

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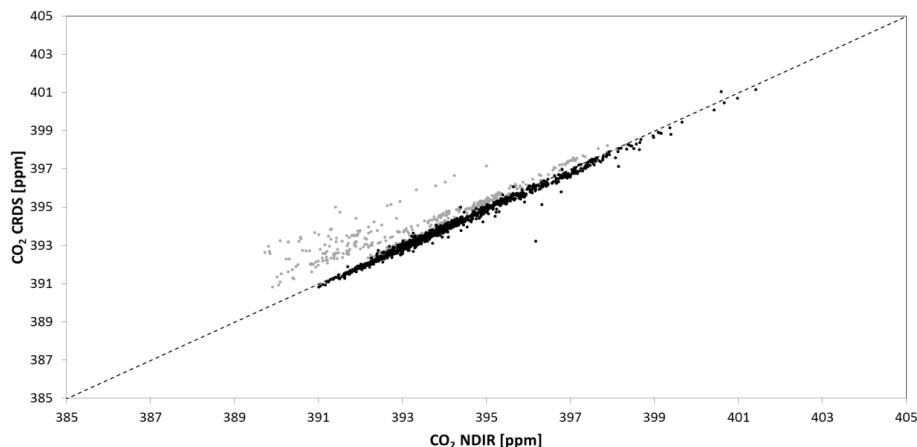


Figure 8. Correlation of ambient CO₂ mole fraction measured by CRDS vs. the uncorrected CO₂ mole fraction of the NDIR-instrument (grey points) and the desorption corrected CO₂ NDIR mole fractions (black points), respectively during the period of the working gas cylinder B23. The diagonal represents the ideal 1 : 1 agreement. Due to the CO₂ enrichment in the working gas cylinder B23 the uncorrected NDIR values seem to be much lower than the CRDS values. By applying the correction, the values of the two systems are in a much better agreement.

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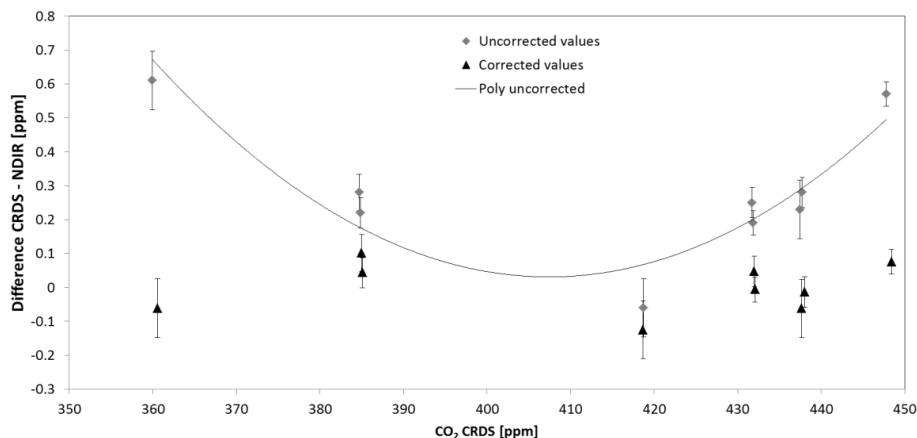


Figure 9. The difference of the CO₂ values against the CRDS values of old KUP calibration cylinders. The data show a polynomial dependency (grey diamonds), by correcting the data points with the according polynomial of second degree, the difference between the two systems varies slightly around zero (black triangles). The vertical error bars represent the combined standard deviation of both systems whereas the horizontal error bars represent only the standard deviation of the CRDS system. Because of the scale the horizontal error bars are not visible.

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