

Abstract

We present the continuous data record of atmospheric CO₂ isotopes measured by laser absorption spectroscopy for an almost four year period at the High Altitude Research Station Jungfrauoch (3580 m a.s.l.), Switzerland. The mean annual cycles derived from data of December 2008 to September 2012 exhibit peak-to-peak amplitudes of 11.0 μmol mol⁻¹ for CO₂, 0.60 ‰ for δ¹³C and 0.81 ‰ for δ¹⁸O. The high temporal resolution of the measurements also allow to capture variations on hourly and diurnal time scales. For CO₂ the mean diurnal peak-to-peak amplitude is about 1 μmol mol⁻¹ in spring, autumn and winter and about 2 μmol mol⁻¹ in summer. The mean diurnal variability in the isotope ratios is largest during the summer months too, with an amplitude of about 0.1 ‰ both in the δ¹³C and δ¹⁸O, and a smaller or no discernible diurnal cycle during the other seasons. The day-to-day variability, however, is much larger and depends on the origin of the air masses arriving at Jungfrauoch. Backward Lagrangian particle dispersion model simulations revealed a close link between air composition and prevailing transport regimes and could be used to explain part of the observed variability in terms of transport history and influence region. A footprint clustering showed significantly different wintertime CO₂, δ¹³C and δ¹⁸O values depending on the origin and surface residence times of the air masses.

Based on the experiences gained from our measurements, several major updates on the instrument and the calibration procedures were performed in order to further improve the data quality. We describe the new measurement and calibration setup in detail and demonstrate the enhanced performance of the analyser. A precision of about 0.02 ‰ for both isotope ratios has been obtained for an averaging time of 10 min.

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1 Introduction

Isotopes are ideal tracers of sources and sinks of carbon dioxide (CO₂). They provide unique information on the fluxes of CO₂ between the different pools involved in the carbon cycle. This is because the physical, chemical and biological exchange processes slightly fractionate between the different isotopes leading to characteristic isotopic signatures in the atmosphere, land and ocean. The carbon isotope composition of CO₂ ($\delta^{13}\text{C}$) is an excellent marker, for example, for partitioning oceanic and biospheric fluxes (Ciais et al., 1995; Keeling et al., 2011). Interpreting variations in the oxygen isotope composition of CO₂ ($\delta^{18}\text{O}$) is more challenging, because the $\delta^{18}\text{O}$ is affected by both the carbon and water cycles (Farquhar et al., 1993). However, the $\delta^{18}\text{O}$ has been used to estimate gross biosphere fluxes (Ciais et al., 1997; Welp et al., 2011).

Stable isotope measurements traditionally rely on flask sampling and isotope ratio mass spectrometry (IRMS), reaching precisions for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO₂ of about 0.01 ‰ and 0.02 ‰, respectively (Werner et al., 2001). A novel alternative approach for measuring isotope ratios is laser spectroscopy. This optical technique allows for in-situ measurements with high time-resolution (up to 10 Hz), and precisions up to 0.02 ‰ have been reached for $\delta^{13}\text{C}$ of atmospheric CO₂ (Richter et al., 2009). In addition to dedicated research instruments (Tuzson et al., 2008b; Richter et al., 2009), several commercial CO₂ isotope analysers have become available in the last decade. A tunable diode laser absorption spectrometer using liquid nitrogen cooled lead salt laser enabled to study isotopic carbon fluxes in terrestrial ecosystems (Bowling et al., 2003, 2005; Griffis et al., 2004, 2008). Other recent commercial instruments are based on cavity ring-down spectroscopy (Vogel et al., 2012), off-axis integrated cavity output spectroscopy (McAlexander et al., 2011), or quantum cascade laser absorption spectroscopy (Sturm et al., 2012). Another optical technique is based on Fourier transform infrared spectroscopy (Griffith et al., 2012).

Up to now, no long-term measurements of tropospheric CO₂ isotopes using laser spectroscopy have been reported. The goals for inter-laboratory compatibility defined

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mean atmospheric pressure is 654 hPa and the mean annual temperature is -7.5°C . Because of the high elevation, the year-round accessibility and the special geographical situation in the center of Europe the site is well suited for long-term monitoring of tropospheric background air but also for studying the transport of anthropogenic or biogenic tracers from the boundary layer to the free troposphere. A large number of trace gases and aerosol parameters are routinely monitored at Jungfraujoch as part of the Swiss National Air Pollution Monitoring Network (NABEL) and the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization (WMO).

2.2 Instrument setup

The quantum cascade laser absorption spectrometer has been developed at Empa in collaboration with Aerodyne Research Inc. in 2007 and has been presented in detail in Nelson et al. (2008) and Tuzson et al. (2008a). The instrument has first been used for field studies near sources (Kammer et al., 2011; Tuzson et al., 2008a) and was then deployed at Jungfraujoch (Tuzson et al., 2011). The laser spectrometer uses a pulsed near-room temperature quantum cascade laser emitting at a wavelength near $4.3\ \mu\text{m}$. The instrument is based on differential absorption spectroscopy with two identical optical paths and a pair of multi-pass absorption cells with a path length of 7.3 m each to simultaneously analyse sample and reference gas. The laser wavelength is scanned over the three main CO₂ isotopologues $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ and the transmitted light is recorded with thermoelectrically cooled infrared detectors (PVI-3TE-4.4, Vigo Systems, Poland). A dedicated, commercially available software (TDLWintel, Aerodyne Research Inc., USA) is used for spectral analysis. The laser temperature and voltage, the cell temperature and pressure as well as the automatic calibrations including data processing into preliminary calibrated values are controlled using custom written LabVIEW code.

Sample air is drawn from the heated NABEL main inlet from the roof of the Sphinx laboratory. The sampling setup from December 2008 to November 2011 was as described in Tuzson et al. (2011) with a sample pump upstream of the instrument and

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four solenoid valves for calibration. This pump was removed in November 2011 as it had a small leak due to a damaged diaphragm, and from then on the sample air was drawn through the instrument by the pump downstream of the measurement cell only.

In March 2012, several hardware components were upgraded and a new calibration and gas-handling setup was implemented (Fig. 1). In the newly developed gas handling module, a 12-port multi-position valve (EMT2SD12MWE, VICI AG International, Switzerland) selects between the sample air stream and one of several primary and working standard gases. The sample cell flow rate is about 350 mL min⁻¹. The reference cell is constantly flushed with compressed air from a cylinder at a flow rate of about 50 mL min⁻¹. The gas pressures in the reference and sample cell are measured by absolute pressure manometers and actively controlled at 80 ± 0.003 hPa by adjusting the set points of two mass flow controllers (MFC2022, Axetris AG, Switzerland). Zero air is generated by an oil-free reciprocating air compressor and a carbon dioxide absorber/dryer (MCA1, Twin Tower Engineering, USA). Zero air is used to purge the optics housing at a flow rate of 1 L min⁻¹ and occasionally to stepwise dilute a standard gas with a mass flow controller in order to correct for concentration dependence of the isotope ratios. The temperature stability of the optics was improved by adding further thermal insulation around the optical module and by using more precise PID temperature controllers (3216, Eurotherm Produkte AG, Switzerland). Thus, variations of the gas temperature in the measurement cells are typically damped by a factor of 100 compared to the laboratory air temperature variations (i.e. a 1 K change in the laboratory temperature results in a ~ 10 mK change in the cell temperature). The stability of the cell temperature is typically about ±5 mK over 24 h. Furthermore, the set point resolution of the laser temperature controller (LFI3751, Wavelength Electronics, USA) was enhanced by supplying an input voltage to the analogue input of the controller. This allows a much tighter control of the laser frequency and thus eliminates any drift in δ¹³C due to a drift of the spectral window.

2.3 Calibration

The calibration procedure up to March 2012 was as described in Tuzson et al. (2011). Briefly, a drift standard (cylinder A) was measured every 15 min, one calibration standard (cylinder B) was measured every two hours and one calibration standard (cylinder C) every 12 h. Each calibration gas was sampled for 300 s, except the drift standard, which was sampled for 128 s. Whenever a standard (cylinder B or C) was nearly empty, a new calibration cylinder with the same CO₂ concentration and isotopic composition was prepared and analysed against the old standard cylinders, an in-house NOAA-ESRL standard (from NOAA Earth System Research Laboratory/Central Calibration Laboratory, USA, with the isotope composition analysed by INSTAAR at the University of Colorado, USA) and occasionally against other calibrated standard gases. After the new primary standards were available (see below) a backward propagation of the calibration scale resulted in more consistent values of the calibration cylinders, although the traceability of the isotope data remains a challenge for this time period. The CO₂ mole fraction of the calibration gases was measured by gas chromatography and since 2010 with a cavity ring-down spectrometer (G1301, Picarro Inc., USA) and linked to the WMO-X2007 scale using in-house NOAA-ESRL standards.

In spring 2012, an improved calibration strategy was implemented. A set of four primary standards was prepared (Table 1). Three standards were produced by mixing different amounts of CO₂ from different sources (marine carbonate and methane burning) into aluminium cylinders and then diluted with synthetic air (79.5 % N₂, 20.5 % O₂). A fourth cylinder with a $\delta^{18}\text{O}$ value closer to the atmospheric $\delta^{18}\text{O}$ contains compressed air (Messer Schweiz AG, Switzerland). Subsamples of these gases were filled into 1.5 L glass flasks and the isotopic composition relative to the VPDB-CO₂ standard was determined by isotope ratio mass spectrometry in the WMO Central Calibration Laboratory at the Max-Planck-Institute for Biogeochemistry (MPI-BGC), Jena, Germany. The CO₂ mole fraction was linked to the WMO-X2007 scale by our NOAA-ESRL standards using the cavity ring-down spectrometer. The primary standards are expected to

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last for > 20 yr and our calibration scales are linked to these four gases. Three shorter-lived secondary working standards are then used to calibrate the instrument. These working standards are measured against the primary standards at Jungfraujoch about every two months to establish the working standard scale and to check for drifts in the working standard cylinders. They have a lifetime of about 1 yr and are replaced when the cylinder pressure decreases to below 30 bar. All calibration gases are stored in 30 L aluminium cylinders (Scott-Marrin, Inc., USA), except for one primary standard consisting of compressed air, which is a 20 L stainless steel cylinder. The reference and drift gases are contained in 50 L stainless steel cylinders. The regulators are two stage high-purity brass regulators (412 Series, CONCOA, Pangas AG, Switzerland) and all tubing is either stainless steel tubing or Synflex tubing (SERTOflex 1300, Serto AG, Switzerland).

The new calibration procedure is as follows: every 30 min a drift cylinder (compressed air) is measured for 5 min. The three working standards are analysed every 6 h for 5 min each. Two working standards are used to perform a two-point calibration for the CO₂ mole fraction and the isotope ratios. The third standard is treated as a target cylinder to check the stability of the working standard calibration. One working standard with a high CO₂ mole fraction is also used to measure every 5 days the concentration dependence of the isotopes by diluting it with zero air.

2.4 Data processing

The spectral fitting of the TDLWintel software produces isotopologue mole fractions based on spectroscopic data and several data post-processing steps are necessary to obtain calibrated data. The processing procedure for the isotope ratios of the pre-March-2012 data consists of the following steps. First, a drift correction due to changes in gas temperature, laser frequency shifts, laser intensity fluctuations and gas pressure is applied. A multiple linear regression of the drift standard measurements with the four above mentioned instrument parameters is performed to remove the influence of changing instrument parameters on the isotope ratios. The magnitude of this correction

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was typically 0–3%. Since the relationship between the isotope ratios and one of the instrument parameters can change when there is a change in the system setup (i.e. new reference gas cylinder, stepwise adjustment of the laser frequency, change in the fitting parameters, etc.), raw data are analysed in blocks with constant conditions. This leads to blocks of data of a few days to a few weeks which were analysed consecutively. The residual variations still present in the drift standard measurements are used for a second drift correction. A smoothing spline is fitted through the drift standard measurements (every 15 min) and used to correct the sample and calibration measurements. The next step is the concentration dependence correction of the isotope ratios, which uses the coefficients from the last concentration dependence calibration. Finally, the actual calibration is performed using the cylinder B and/or cylinder C measurements. For most of the 2009–2011 time period a one-point (offset) calibration is applied using the results of cylinder B or C. The instrument response (slope of measured CO₂ versus WMO scale or measured isotope ratios versus VPDB-CO₂ scale, respectively) were determined from manual calibrations performed with different calibration gases and assumed to be constant. This turned out to be the more robust calibration approach compared to using a 2-point calibration, because the uncertainty of the calculated calibration slope was larger than the real variations in the slope coefficients. Furthermore, data could also be calibrated in a consistent way at times when there was only one calibration cylinder (B or C) available.

The improvements in the instrument stability implemented in spring 2012 allowed for a simplification of the data processing. In particular, the drift correction based on correlations with instrument parameters is obsolete. Instead, the drift standard measurements (every 30 min) are used in a first step to remove any drift. Next, the concentration dependence correction is applied. Third, the calibration coefficients (slope and offset) are calculated based on the 6-hourly calibration measurements. To further reduce the uncertainty in the calibration coefficients a smoothing spline is fitted to these values. The smoothed calibration coefficients are then applied to the sample data to get calibrated values. Finally, the 1 s data are averaged to 10 min mean values.

2.5 Transport simulations and footprint clustering

The Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Version 9.0) (Stohl et al., 2005) was used in backward mode to calculate source sensitivities for Jungfraujoch for the whole observation period. At each 3-hourly interval, 50 000 model particles were initialised at the location of Jungfraujoch and traced back in time for 10 days. FLEXPART considers horizontal and vertical displacements due to the mean atmospheric flow, turbulent mixing especially in the atmospheric boundary layer and vertical transport due to deep convection. Here, the model was driven by European Centre for Medium Range Weather Forecast (ECMWF) operational analysis (00:00, 06:00, 12:00, 18:00 UTC) and +3 h forecasts (03:00, 09:00, 15:00, 21:00 UTC) with 91 vertical levels and a horizontal resolution of $0.2^\circ \times 0.2^\circ$ for the Alpine area (4°W – 16°E , 39° – 51°N) and $1^\circ \times 1^\circ$ for the global domain. The limited horizontal resolution of the model does not well represent the Alpine topography and, hence, a large difference between observatory and model altitude exists. In previous studies, the optimal release height for Jungfraujoch was determined to be at 3000 m above sea level, almost halfway between the real station's altitude and the model ground (Keller et al., 2011; Brunner et al., 2012). We adopted this initial altitude in the current study as well. The simulated source sensitivities can directly be multiplied with mass releases at a source grid cell, yielding simulated mole fractions at the receptor (Seibert and Frank, 2004). Source sensitivities are given in units $\text{s m}^3 \text{kg}^{-1}$ and are also referred to as residence times or footprints. Source sensitivities were generated on a regular grid with $0.1^\circ \times 0.1^\circ$ covering Europe and a secondary grid with $0.5^\circ \times 0.5^\circ$ horizontal resolution for the Northern Hemisphere. The lowest vertical output level reached up to 100 m above model ground, which is the same as the minimal mixing height in the model.

In order to distinguish different transport regimes towards Jungfraujoch, source sensitivities were used in a clustering method. A straightforward clustering approach would be to treat the simulated source sensitivities in every grid cell as an individual variable in a cluster analysis. The number of cluster variables would then be equal to the number

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of grid cells in the output grid and quickly become too large to be efficiently handled by any cluster algorithm. Hence, a reduction of the cluster variables is required. This can be achieved by aggregating grid cells with small average residence times to larger grid cells, a procedure also used in regional scale inversion studies (Keller et al., 2011; Vollmer et al., 2009). Starting from grid cells with 0.1° resolution, we allowed aggregation to grid cells with up to 3.2° horizontal resolution, if the total residence time in the aggregated cells remained below a certain threshold. This threshold was iteratively deduced so that the total number of aggregated grid cells did not exceed 100. Only the European output domain was considered for the clustering, which will focus the separation of flow regimes more onto the regional scale transport and to a lesser degree onto inter-continental transport.

The clustering was performed on the time series of residence times of the aggregated surface grid cells only. Since these variables were not normally or log-normally distributed, we chose an alternative distance measure to obtain the dissimilarity matrix, \mathbf{D} with elements $d_{i,j}$, that is used in the clustering process. Absolute distances between the ranks of the surface sensitivities over time were calculated according to

$$d_{i,j} = \sum_{k=1}^N |\text{rank}(\tau_k)_i - \text{rank}(\tau_k)_j|, \quad (1)$$

where the source sensitivities are indicated as τ and the index k runs over all aggregated grid cells N , while i and j refer to the time. The matrix \mathbf{D} is symmetric and contains zeros in the diagonal. The off-diagonal elements contain the distance between two transport simulations at different times. Finally, based on the dissimilarity matrix the clustering was calculated using k-medoids clustering (Kaufman and Rousseeuw, 1990), which was previously successfully used for cluster analysis of single trajectory simulations (Henne et al., 2008). The number of selected clusters was obtained using the silhouette technique (Kaufman and Rousseeuw, 1990) by choosing the number of clusters (in the range 2 to 20) for which the average silhouette widths showed a local maximal. In the present case, a local maximum was obtained for 8 clusters with an

average silhouette width of 0.16. A similar technique for clustering source sensitivities as obtained from LPDM calculations was presented by Hirdman et al. (2010). However, they aggregated residence times to larger regions defined by continental or country borders and Euclidean distances between these were used to derive the dissimilarity matrix.

To display the different flow regimes, average residence time maps per cluster were generated by summation over all cluster members and division by the number of clusters. For all clusters these show maximal values close to the site. In order to emphasize the differences between the individual clusters, the difference of cluster average and over-all average residence times was computed and normalised by the mean of cluster and over-all average (residence times by cluster normalised: RTCN). In this way, differences can be displayed in a linear and symmetric fashion, with RTCN values ranging from -2 to 2 . Areas with RTCN larger than 0 indicate areas with greater than average surface contact and values larger than 1 indicate areas with 3 times larger residence times.

3 Results and discussion

3.1 Precision

The precision and stability of the updated instrument was characterized by the two-sample standard deviation (Werle et al., 1993) and is shown in Fig. 2. Tank air with a CO_2 mole fraction of $401 \mu\text{mol mol}^{-1}$ was continuously measured for 5 h. The two sample standard deviation with 1 s data acquisition is about 0.4‰ for both isotope ratios. The best precision of about 0.02‰ is reached for an averaging time of about 10 min. This improvement compared to our previously reported values (Tuzson et al., 2011) is a result of the better temperature, pressure and laser frequency stability. As a consequence, the interval for the drift standard measurements was increased from 15

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to 30 min. The precision of the CO₂ mole fraction measurement is 0.16 μmol mol⁻¹ at 1 s and 0.01 μmol mol⁻¹ at 10 min averaging time.

The half hourly cylinder air measurements are still well correlated with the laboratory temperature (correlation coefficients of 0.6 to 0.8 for CO₂ and δ¹³C and -0.4 to -0.7 for δ¹⁸O). Thus, temperature variations remain the major source for the drift on time scales longer than about 15 min, although it is not clear whether this is due to optical or electronic components that may both respond to temperature fluctuations.

A comparison of the precision before and after the instrument upgrades is shown in Fig. 3. It should be noted that the instrument has been running for more than two years almost unattended and without major revisions leading to some reduction in performance. During the selected time period of six days in June 2011 and June 2012 the CO₂ mole fraction was relatively constant between 390 and 396 μmol mol⁻¹ and consequently the variations in the isotope ratios are small. The lower noise level in the 10 min averaged data for June 2012 is obvious and demonstrates the benefits of the instrument upgrades. Averaging to hourly mean values (solid lines in Fig. 3) greatly reduces the noise, in particular for the data before the upgrade. This is significant because data of background monitoring sites are usually reported as hourly mean values or even aggregated to longer intervals when compared with model output (e.g. from FLEXPART, see Sect. 3.4).

Four months of target cylinder measurements after the instrument upgrade are shown in Fig. 4. The assigned values of the target cylinders have been determined using the primary standards and the uncertainty ranges ($\pm 1\sigma$) are depicted as shaded areas in Fig. 4. Each single target cylinder measurement consists of a 120 s average and the standard deviation of the isotope ratio data of 0.06–0.07 ‰ roughly corresponds to the measurement precision at 120 s averaging time (Fig. 2). Analyzing the target cylinder for more than 120 s would, therefore, most likely lead to an even smaller spread in the target cylinder data.

Figure 5 shows the instrument response from the analysis of the four primary standards. The residuals of the linear fit between the measured and the assigned values

indicate the linearity and accuracy of the instrument. The standard deviation of the residuals from Fig. 5 is $0.12 \mu\text{mol mol}^{-1}$ for CO_2 , 0.06‰ for $\delta^{13}\text{C}$ and 0.13‰ for $\delta^{18}\text{O}$, respectively, which are typical values for the measurement of the four primary standards.

3.2 Long-term data record

An overview of the data record from December 2008 to September 2012 is shown in Fig. 6. Hourly averaged data for CO_2 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ as well as fitted background curves are plotted. Two different methods have been used to calculate the long-term background values. The first method decomposes the signal into a long-term trend, a yearly cycle and short-term variations (Thoning et al., 1989). This curve fit consists of a combination of a polynomial (second order) and annual harmonics ($n = 4$) functions and the residuals from this fit are then smoothed using a low pass filter (80 days cut-off). The second method uses local regression (60 days window) to extract the baseline signal (Ruckstuhl et al., 2012). This is a non-parametric and thus very flexible approach and accounts for a possibly asymmetric contamination of the background signal (e.g., in winter local pollution always leads to a positive deviation from the background CO_2 concentration). The mean difference of the baseline values between the local regression and the smoothed curve fit are $-0.66 \pm 0.56 \mu\text{mol mol}^{-1}$ for CO_2 , $0.04 \pm 0.04 \text{‰}$ for $\delta^{13}\text{C}$ and $0.06 \pm 0.05 \text{‰}$ for $\delta^{18}\text{O}$, respectively. Thus, both methods give very similar results and highlight the seasonal dynamics of the carbon dioxide and its isotopic composition in the atmosphere.

The gap in the time series in autumn 2011 was due to a pump failure. The diaphragm of the sample pump, which was originally installed upstream of the instrument, was broken. This resulted in a small leak and the influence of laboratory air could be seen as a small increase in the CO_2 mole fraction when people were present in the room. Data periods when the sample air was contaminated with laboratory air were removed based on a comparison with CO_2 data from another trace gas analyser (G2401, Picarro Inc., USA), which uses the same air inlet. Data were flagged as contaminated

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by lab air, when the difference in the CO₂ mole fraction exceeded 2 μmol mol⁻¹. This is a conservative limit with regard to the isotope ratios, which were also affected by this contamination. Assuming that the CO₂ mole fraction in the well ventilated lab increases from 400 μmol mol⁻¹ to 1000 μmol mol⁻¹ due to the presence of people in the laboratory and the δ¹³C of the respired CO₂ is -23 ‰ (Epstein and Zeiri, 1988), one would expect a δ¹³C of the laboratory air of about -17 ‰ (compared to -8 ‰ of the background CO₂). A contribution of 2 μmol mol⁻¹ CO₂ from laboratory air would then in turn lead to a change in the measured δ¹³C of 0.045 ‰ at the most. This is less than the overall measurement uncertainty at that time. Using this procedure, 8 % of the data were removed during the period with the leak. Additionally, from 11 July 2011 to 16 September 2011 all data has been removed from further analysis because no CO₂ data from the trace gas analyser was available during this period and as a result the data could not be screened for contamination.

We compared our laser based data with IRMS values from an intercomparison programme of δ¹³C flask measurements (van der Laan-Luijkx et al., 2012). These samples were taken at Jungfraujoch between December 2007 and August 2011 and analysed by three different IRMS laboratories. They revealed average differences between the laboratories of -0.02 to -0.03 ‰. The standard deviation of the individual differences was between 0.20 and 0.30 ‰. They conclude that the WMO goal for the measurement compatibility of δ¹³C (±0.01 ‰) (WMO, 2011) is not yet reached within this flask sampling program. If we compare our hourly averaged values which correspond to the flask sampling times with the flask results from the MPI-BGC laboratory then the average difference is -0.03 ‰ with a standard deviation of 0.19 ‰. This is similar to the differences between the flask samples and indicates that our data compare well with the flask data and within the inter-laboratory uncertainty of different isotope ratio mass spectrometry labs. For δ¹⁸O, the average difference to the MPI-BGC flask data is -0.31 ‰ with a standard deviation of 0.26 ‰ (W. Brand, personal communication, 2012). This substantial difference can be explained by the larger uncertainty in our δ¹⁸O calibration scale, mainly because the δ¹⁸O value of our standard gases (-24

to -10‰) did not span the range of the measured $\delta^{18}\text{O}$ values ($\sim 0\text{‰}$). Flask data for comparison are not yet available for the period since March 2012, but we expect that both the precision and the accuracy have been improved by the instrument and calibration upgrades. Nevertheless, continuing efforts are needed to evaluate the uncertainties and ensure the high accuracy and the traceability of the data, which are required at background monitoring sites like Jungfraujoch.

3.3 Mean seasonal and diurnal cycles

Mean annual cycles derived from the monthly bin-averaged data as well as from the annual harmonic part of the smooth curve fit are shown in Fig. 7. The averaged data have been detrended using the long-term trend derived from the smooth curve fit. The peak-to-peak amplitude of the seasonal variation is $11.0\ \mu\text{mol mol}^{-1}$ for CO_2 , 0.60‰ for $\delta^{13}\text{C}$ and 0.81‰ for $\delta^{18}\text{O}$. This is in good agreement with the seasonality obtained from independent flask measurements where amplitudes of $10.54\ \mu\text{mol mol}^{-1}$ for CO_2 and 0.54‰ for $\delta^{13}\text{C}$ have been observed for the period between December 2007 and August 2011 (van der Laan-Luijkx et al., 2012).

The seasonality in CO_2 and $\delta^{13}\text{C}$ is dominated by the land biosphere and the relative contribution of photosynthesis and respiration (net ecosystem CO_2 exchange). The minimum in CO_2 mole fraction in August nearly coincides with the maximum in $\delta^{13}\text{C}$ and is due to peak net ecosystem CO_2 uptake. The CO_2 maximum and $\delta^{13}\text{C}$ minimum is reached around March when ecosystem respiration is dominating. In contrast to the seasonal cycle of CO_2 and $\delta^{13}\text{C}$, the seasonality of $\delta^{18}\text{O}$ is more complex. The $\delta^{18}\text{O}$ seasonal cycle is out of phase with CO_2 and $\delta^{13}\text{C}$ and shows its maximum in June and its minimum in December. This is a result of the interplay between the isotopic fluxes of photosynthesis and soil respiration (Peylin et al., 1999). Because of the isotopic equilibration with water, the $\delta^{18}\text{O}$ of CO_2 is strongly influenced by the oxygen isotopic composition of the leaf and soil water with which it is in contact. Therefore, the different seasonal phases of leaf discrimination, soil respiration and the oxygen

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isotope composition of precipitation are reflected in the seasonal cycle of atmospheric $\delta^{18}\text{O}$ (Yakir, 2003).

One distinct advantage of the high-time resolution measurements, compared to the traditional flask sampling, is that not only seasonal variations and long-term trends can be assessed, but also variations on hourly and diurnal time scales. This allows for combining the measurements with meteorology and interpret them in terms of atmospheric dynamics. The mean diurnal cycles of CO_2 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the different seasons are shown in Fig. 8. Generally, the mean diurnal changes are small. For CO_2 , the maximum occurs during the day with a peak-to-peak amplitude of about $1 \mu\text{mol mol}^{-1}$ in spring, autumn and winter. In summer, the mean amplitude is larger with the maximum at midday and a subsequent drop of the CO_2 mole fraction of about $2 \mu\text{mol mol}^{-1}$ in the afternoon, most likely due to uplift of boundary layer air, which is depleted in CO_2 because of photosynthetic uptake. These observations are in line with the PBL influence that was established for other parameters. The diurnal variations of aerosol parameters and other gaseous compounds measured at Jungfraujoch show almost no diurnal cycle in winter and a larger PBL influence in summer mostly due to thermally induced vertical transport (Zellweger et al., 2003; Collaud Coen et al., 2011). The diurnal variability is also seen in the isotope ratios with a maximum variation in the summer months of about 0.1‰ both in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and a smaller or no discernible diurnal cycle during the other seasons.

3.4 Footprint clustering

The clustering algorithm described in Sect. 2.5 resulted in eight distinct clusters of air mass origins for Jungfraujoch and for the time period of January 2009 to April 2012. Figure 9 shows maps of the normalised residence time near the surface (footprint maps) obtained from the Lagrangian particle dispersion model FLEXPART. Clusters 1, 2 and 6 represent air masses with surface contact predominantly over South, East and North European land masses, respectively. Clusters 3 and 5 belong to flow regimes for which the surface sensitivities are extended to more distant and south-easterly and

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south-westerly directions, respectively. The clusters with the shortest residence time over ground are numbers 4, 3, 7 and 8. Cluster 4, in particular, seems to be representative of free tropospheric air without significant surface contact in Europe within the last 10 days before arriving at Jungfraujoch. Mainly North Atlantic influence can be attributed to cluster 7 and, with some additional contribution from the British Isles, to cluster 8.

To address the question whether the different transport regimes are reflected in our observations of CO₂ and its isotopic composition, we have aggregated the data into 3-hourly averages corresponding to the time steps of the model output. The data can then be grouped according to the eight different clusters (Fig. 10). The background concentrations derived from the local regression (Sect. 3.2) were subtracted from the CO₂, δ¹³C and δ¹⁸O values to obtain the short-term deviations from the background (ΔCO₂, Δδ¹³C and Δδ¹⁸O). In order to minimize the influence of local transport processes (thermally-induced transport), which are often not fully resolved in the transport model, only winter time data (December to February) were selected in Fig. 10. In winter, the Jungfraujoch is primarily situated in the free troposphere and much less influenced by thermal convection of local boundary layer air as compared to the summer months (Zellweger et al., 2003). Including all data into this analysis would result qualitatively in the same picture with significant differences between clusters, although the differences are not as pronounced as for winter data only. The reason for this might be that apart from the thermally induced transport events also the spacial and temporal source and sink patterns are more complex in summer due the stronger biospheric activity.

The different concentrations and isotopic compositions between the clusters can be explained by the different residence times of the air within the surface layer and the different CO₂ emission rates and sources depending on the region. Figure 11 shows the median values per cluster as a function of the mean surface residence time. Generally, the longer the air masses stay within the lowest 100 m above ground, the higher the CO₂ mole fraction and the lower the isotope ratios are. However, air parcels from clusters 2 and 6 have a smaller surface residence time by about 30 % compared to

cluster 1, but rather higher concentrations. This indicates that emission rates are higher for clusters 2 and 6 than for cluster 1, which has the footprint area partially over the Mediterranean.

The two clusters with the most pronounced differences in the measured ΔCO_2 concentrations and isotope ratios are clusters 4 and 6. Cluster 4 has the lowest median ΔCO_2 value and correspondingly the highest values in $\Delta\delta^{13}\text{C}$ and $\Delta\delta^{18}\text{O}$. This agrees well with the footprint map showing no recent contribution from potentially polluted air masses. In contrast to cluster 4, cluster 6 has the highest ΔCO_2 concentrations, lowest $\Delta\delta^{18}\text{O}$ and second lowest $\Delta\delta^{13}\text{C}$ (after cluster 1). This can be explained by the relatively long surface residence time and the strong impact of air masses influenced by anthropogenic emissions from North-Western Europe including the high emission regions in the German Ruhr area and the Netherlands. The other clusters with high CO_2 concentrations are clusters 1 (Italy), 2 (East Europe) and partially 8 (UK), which agrees well with the high anthropogenic emissions expected from these influence regions. A pairwise comparison using the Wilcoxon rank sum test indicates that cluster 6 is significantly ($p < 0.001$) different from clusters 3, 4, 5 and 7 for ΔCO_2 and both isotope ratios. Cluster 4, in turn, is significantly ($p < 0.001$) different from clusters 1, 2, 6 and 8 for all three species. Thus, the CO_2 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures measured at Jungfraujoch distinctly vary according to the different transport patterns.

4 Conclusions

We present a high time resolution record of the isotopic carbon dioxide composition in the atmosphere measured at the background monitoring site Jungfraujoch from December 2008 to September 2012 by laser absorption spectroscopy. In spring 2012 the data quality has been further improved by minimizing instrumental drift and by optimizing the calibration setup.

The mean annual cycles derived from almost four years of data revealed peak-to-peak amplitudes of $11.0 \mu\text{mol mol}^{-1}$ for CO_2 , 0.60‰ for $\delta^{13}\text{C}$ and 0.81‰ for $\delta^{18}\text{O}$.

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A major benefit of the high-time resolution measurements compared to the traditional flask sampling is that, in addition to seasonal variations and long-term trends, also variations on hourly and diurnal time scales can be captured. This allows for a combination with transport models for inverse emission estimation. The mean diurnal cycles of CO₂ and its isotopic composition are small at Jungfraujoch. For CO₂, the mean diurnal peak-to-peak amplitude is about 1 μmol mol⁻¹ in spring, autumn and winter, and about 2 μmol mol⁻¹ in summer. The mean diurnal variability in the isotope ratios shows a maximum of about 0.1 ‰ both in the δ¹³C and δ¹⁸O in the summer months, and a smaller or no discernible diurnal cycle during the other seasons. The day-to-day variability, however, can be much larger depending on the origin of the air masses arriving at Jungfraujoch. Backward Lagrangian particle dispersion model simulations revealed a close link between air composition and prevailing transport regimes and were able to explain part of the observed variability in terms of transport history and influence region. The footprint clustering, which was applied to the model output, showed significantly different wintertime CO₂, δ¹³C and δ¹⁸O values depending on the air mass origin and surface residence times.

Long-term, high resolution measurements of CO₂ isotopes and tracing the observed variabilities back to their origin will improve the understanding of the carbon cycle. For example, estimates of global photosynthesis based on atmospheric δ¹⁸O rely on estimates of the CO₂ hydration efficiency, i.e. the percentage of CO₂ molecules entering a leaf or the soil that isotopically equilibrate with plant and soil water. This CO₂ hydration efficiency is still a substantial source of uncertainty (Wingate et al., 2009; Welp et al., 2011) and high time resolution data records such as the time series presented here, combined with an atmospheric transport model and a terrestrial biosphere model of δ¹⁸O (Cuntz et al., 2003) will be valuable for further constraining such estimates.

Another very useful tracer in this context are radiocarbon (¹⁴C) observations in order to separate biospheric fluxes from fossil fuel CO₂ emissions (Levin et al., 2003). Up to now, ¹⁴CO₂ measurements were too costly to be performed on hourly time scales. However, with further advances in laser spectroscopy, continuous high-resolution

$^{14}\text{CO}_2$ measurements might become feasible in the future (Galli et al., 2011). This would allow a direct determination of fossil fuel derived CO_2 and complement the information that can be obtained with continuous stable isotope measurements.

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Table 1. Primary standards with the assigned values on the WMO-X2007 scale for CO₂ and the VPDBCO 2 scale for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ as determined in spring 2012.

Tank no.	Mixture	CO ₂ ($\mu\text{mol mol}^{-1}$)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
CB08984	CO ₂ + syn. air	383.40	−3.54	−14.11
CB08970	CO ₂ + syn. air	394.43	−8.00	−17.38
CB08999	CO ₂ + syn. air	388.36	−12.01	−20.52
3076	compressed air	429.06	−10.57	−7.65

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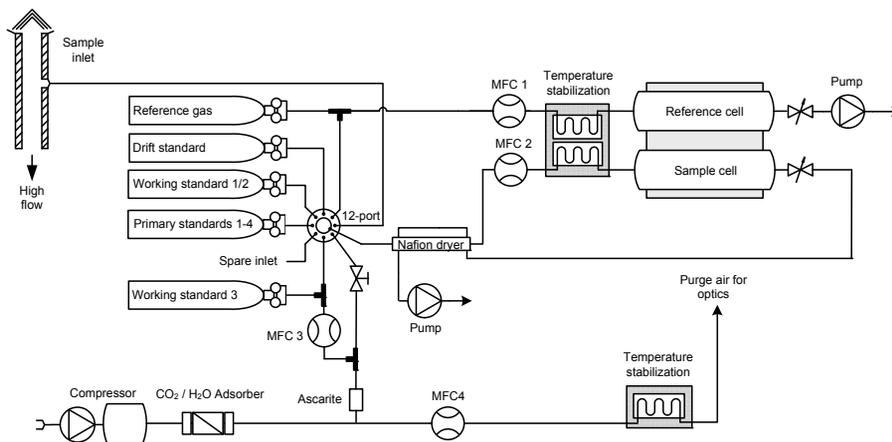


Fig. 1. Gas handling setup.

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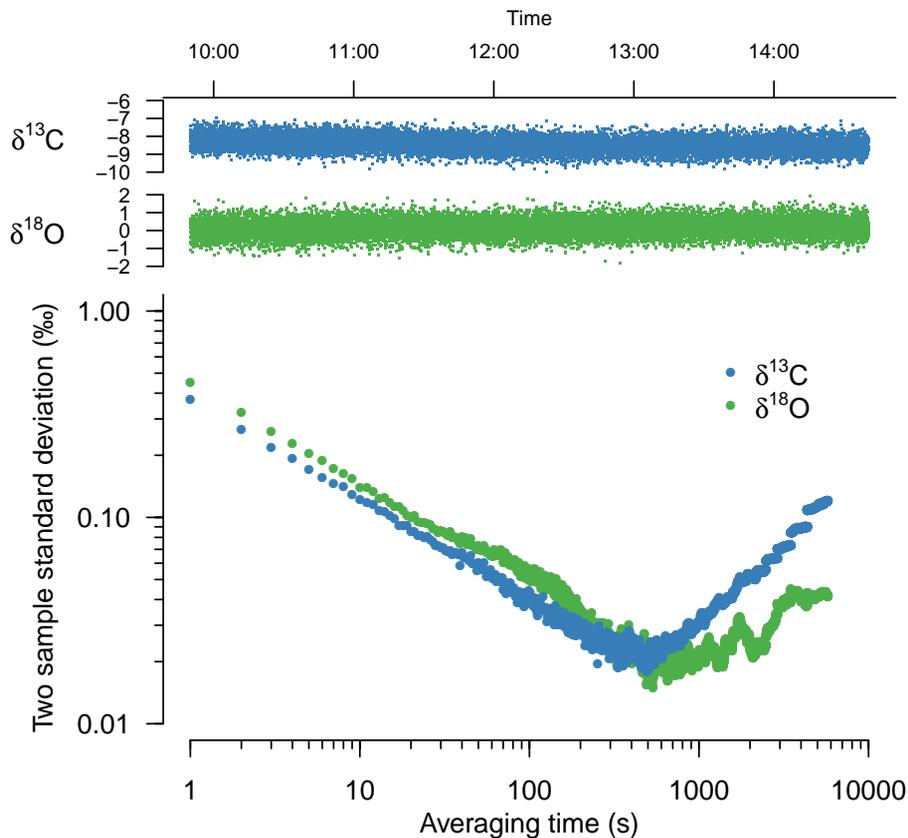


Fig. 2. Two sample standard deviation (Allan deviation) of cylinder air measurements for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. At 1 s averaging time the Allan deviation is about 0.4 ‰ and the minimum of about 0.02 ‰ is reached after ~ 10 min averaging for both isotope ratios.

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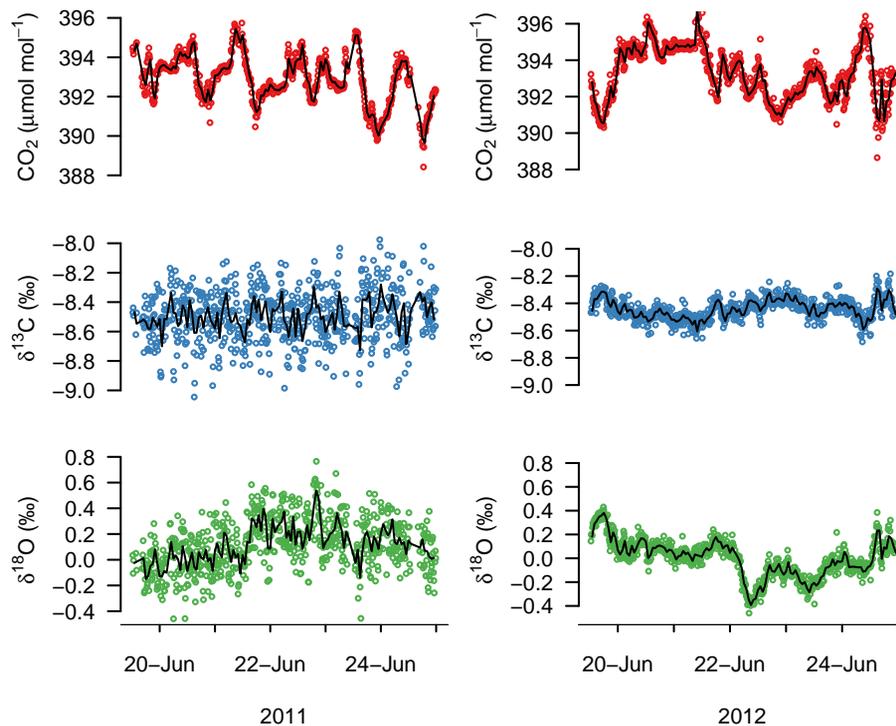


Fig. 3. Comparison of 10 min averaged data for six days in June 2011 and 2012, i.e. before and after the instrument upgrades. The solid lines are the 1 h-averaged data.

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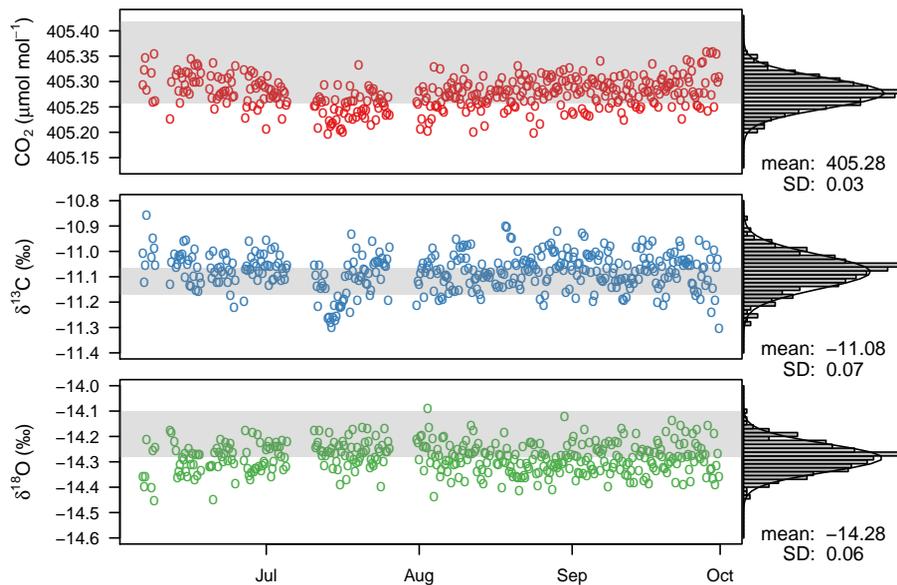


Fig. 4. Target gas measurements during four months (June 2012 to September 2012). The histograms show the distribution of the data with the respective mean and standard deviation. The shaded areas are the assigned values with the uncertainty (1σ) derived from the primary standard calibrations.

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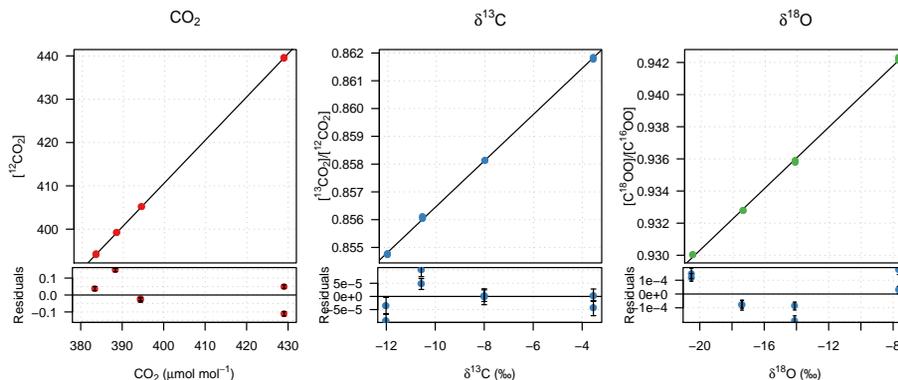


Fig. 5. Instrument response versus assigned values of the four primary standards as determined on 25 May 2012. The solid lines are weighted linear least squares fits to the data. The residuals from the fit are shown in the lower panels with the error bars representing the standard error of the mean.

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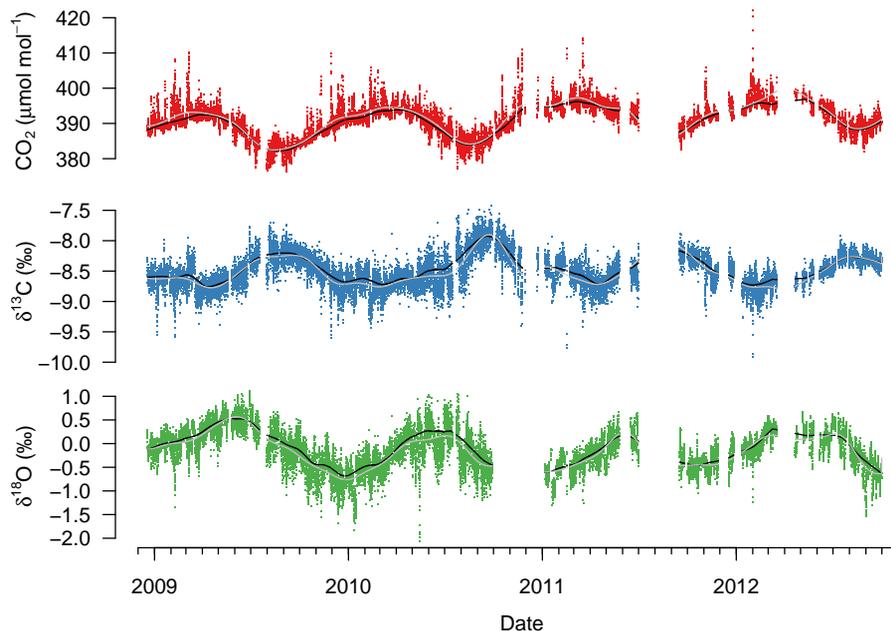


Fig. 6. Overview of the data record from December 2008 to September 2012. Hourly averaged data of CO₂ (red), δ¹³C (blue) and δ¹⁸O (green) as well as fitted background curves (black: local regression, grey: smooth curve fit, see text for explanation) are shown.

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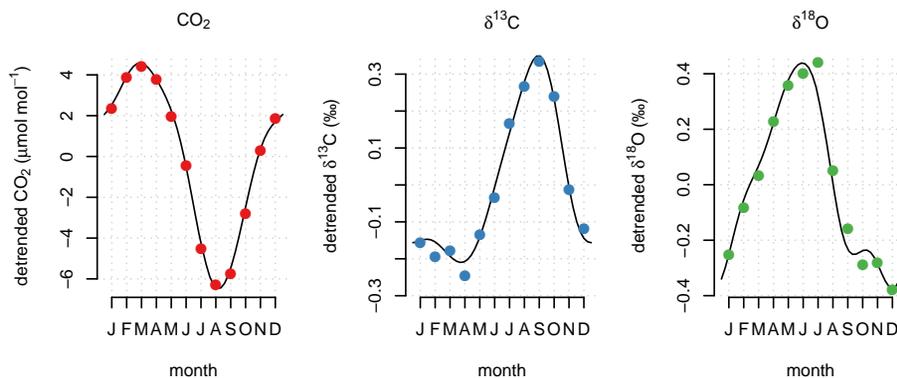


Fig. 7. Mean seasonal cycles from detrended and monthly bin-averaged data (points) and the annual harmonic part of the smoothed curve fit (lines).

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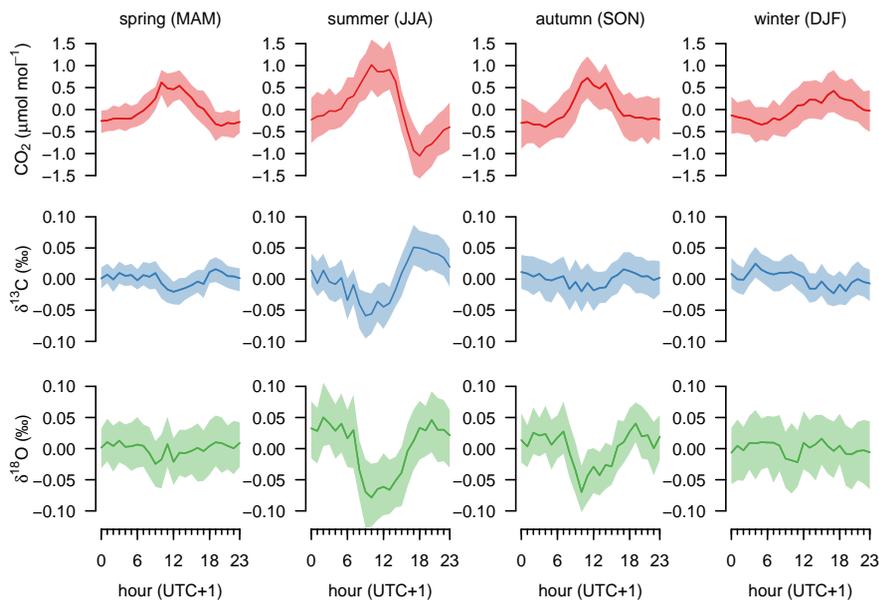


Fig. 8. Mean diurnal cycles as a difference to the daily mean for the different seasons. The shaded area is the 95 % confidence interval of the hourly mean derived from bootstrap resampling.

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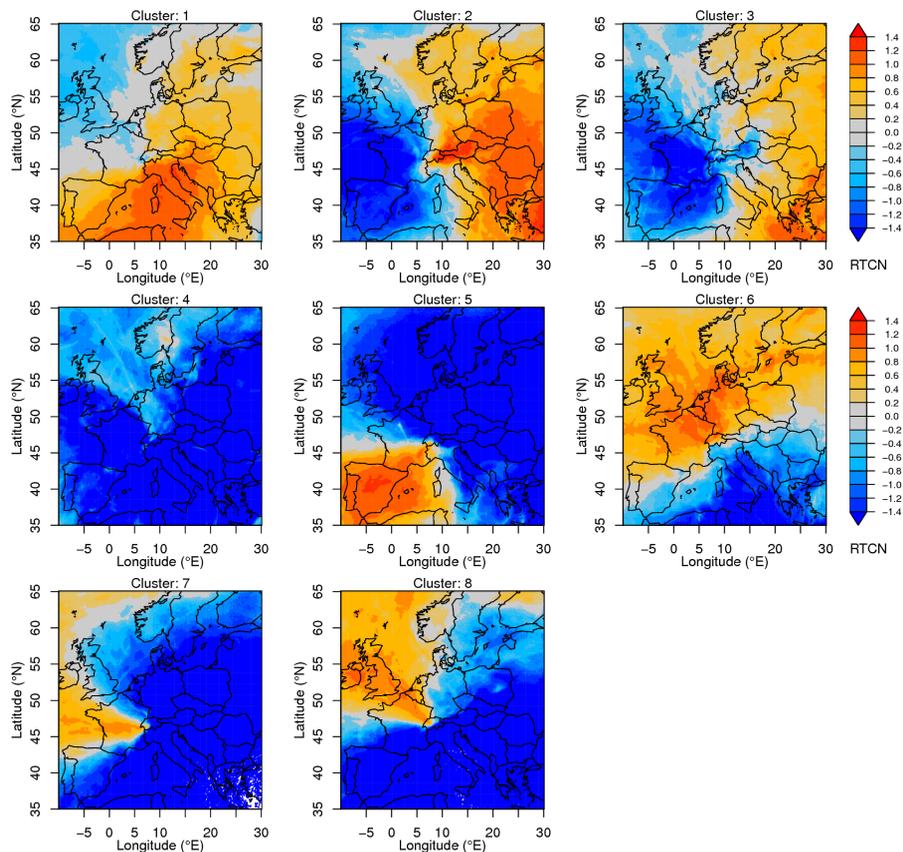


Fig. 9. Normalised residence time maps for different transport clusters for Jungfraujoch from January 2009 to April 2012 as obtained from FLEXPART simulations and footprint clustering. The color code indicates the cluster average source sensitivities at the surface relative to the overall footprint (RTCN: residence times by cluster normalised, see text for further explanation).

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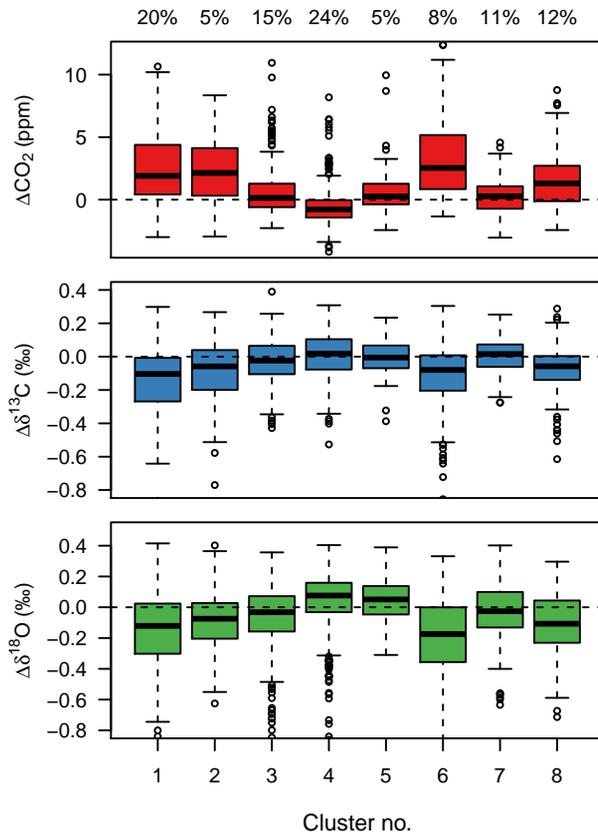


Fig. 10. Boxplots of CO₂, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ deviations from the background concentrations (Δ) for the winter months (December to February) classified by the different footprint clusters. The boxes show the interquartile range and the whiskers extend to the most extreme data point which is no more than 1.5 times the interquartile range away from the box. The percentages at the top indicate the cluster frequencies.

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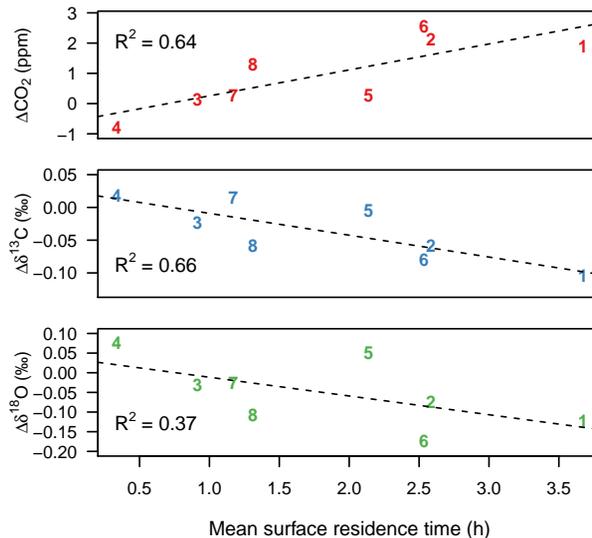


Fig. 11. Median ΔCO_2 , $\Delta\delta^{13}\text{C}$ and $\Delta\delta^{18}\text{O}$ of the eight footprint clusters as a function of the mean residence time within a layer of 100 m above ground for the winter months (December to February). The coloured numbers indicate the cluster index and the dashed lines are the ordinary least squares regression lines.