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Estimation of the fossil-fuel component in atmospheric CO_2 based on radiocarbon measurements at the Beromünster tall tower, Switzerland

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Abstract

Fossil fuel CO_2 (CO_{2ff}) is the major contributor of anthropogenic CO_2 in the atmosphere, and accurate quantification is essential to better understand the carbon cycle. Since October 2012, we have been continuously measuring the mixing ratios of CO, CO_2 CH_4 and H_2O at five different heights at the Beromünster tall tower, Switzerland. Air samples for radiocarbon ($\Delta^{14}CO_2$) analysis have also been collected from the 212.5 m sampling inlet of the tower on a bi-weekly basis. A correction was applied for $^{14}CO_2$ emissions from nearby nuclear power plants (NPPs), which have been simulated with the Lagrangian transport model FLEXPART-COSMO. The $^{14}CO_2$ emissions from NPPs offset the depletion in ^{14}C by fossil-fuel emissions resulting in an underestimation of the fossil-fuel component in atmospheric CO_2 by about 16 %. An average observed ratio (R_{CO}) of 13.4 ± 1.3 mmol/mol was calculated from the enhancements in CO mixing ratios relative to the clean air reference site Jungfraujoch (ΔCO) and the radiocarbon-based fossil-fuel CO_2 mole fractions. This ratio is significantly higher

than both the mean anthropogenic CO/CO_2 emission ratios estimated for Switzerland from the national inventory (7.8 mmol/mol for 2013), and the ratio between in-situ measured CO and CO_2 enhancements at Beromünster over the Jungfraujoch background (8.3 mmol/mol). Differences could not yet be assigned to specific processes and shortcomings of these two methods but may originate from locally variable emission ratios as well as from non-fossil emissions and biospheric contributions. By combining the ratio derived using the radiocarbon measurements and the in-situ measured CO mixing ratios, a high-resolution time series of CO_{2ff} was calculated exhibiting a clear seasonality driven by seasonal variability in emissions and vertical mixing. By subtracting the fossil-fuel component and the large-scale background, we have determined the regional biospheric CO_2 component that is characterized by seasonal variations ranging between -15 to +30 ppm. A pronounced diurnal variation was observed during summer modulated by biospheric exchange and vertical mixing while no consistent pattern was found during winter.

1. Introduction

Fossil fuel CO_2 (CO_{2ff}) is the fundamental contributor to the increase in atmospheric CO_2, hence its precise quantification is crucial to better understand the global carbon budget. One of the major uncertainties in the projections of climate change is the uncertainty in the future carbon budget due to feedbacks between terrestrial ecosystems and climate (Heimann and Reichstein, 2008). Information on the response of the biosphere to climate variations can be obtained from atmospheric CO_2 observations, but isolating the biospheric signal in the measured CO_2 mixing ratios requires an accurate quantification of the fossil fuel component. Several methods have therefore been proposed for quantifying CO_{2ff}, which are based on observations or models. A widely employed approach is to determine CO_{2ff} with an atmospheric transport model that incorporates CO_{2ff} emissions from a bottom-up emission inventory.

Emission inventories are based on statistics of the energy-use by different sectors and the quantification of CO_{2ff} emissions by accounting for the carbon content of each fuel and its corresponding oxidation ratios (Friedlingstein et al., 2010; Le Quéré et al., 2016). When compared to other greenhouse gases, national emission inventories for CO_2 are quite accurate, but the computation of these inventories is laborious, and the quality depends on the energy statistics and reporting methods that vary strongly between countries (Marland, 2008; Marland et al., 2009). A recent study evaluating different energy statistics and cement production data estimated an uncertainty of about 5 % for the global fossil-fuel emissions of the past decade (2006 – 2015)(Le Quéré et al., 2016). At country level the uncertainties are usually below 5 % in developed countries but often exceed 10 % in developing countries (Ballantyne et al., 2015).

Additional uncertainties arise from the spatial and temporal disaggregation of national annual total emissions to the grid of the atmospheric transport model. At sub-country scales (less than 150 km), the uncertainty from bottom-up estimates can reach up to 50 % (Ciais et al., 2010). Finally, errors in the transport model and the inability to correctly represent point observations in the model may contribute substantially to the uncertainty of model simulated CO_{2ff} mixing ratios (Tolk et al., 2008; Peylin et al., 2011).

Radiocarbon measurements can be used to directly quantify CO_{2ff} in atmospheric CO_2 observations. Radiocarbon is produced in the lower stratosphere during the reaction of neutrons with nitrogen induced by cosmic rays (Currie, 2004). In addition, nuclear bomb tests in the 1960s led to large radiocarbon input into the atmosphere which was thereafter decreasing due to gradual uptake by the oceans and the terrestrial biosphere. Nowadays, the decline in atmospheric $^{14}CO_2$ is mainly driven by input from ^{14}C-free fossil fuel CO_2 (Levin et al., 2010). This decline is well detectable at background sites such as Jungfraujoch, Switzerland and Schauinsland, Germany (Levin et al., 2013). While all reservoirs exchanging

carbon with the atmosphere are relatively rich in ^{14}C, fossil-fuels (millions of years old) are devoid of ^{14}C due to its radioactive decay with a half-life of 5370 years. Hence, any fossil-fuel CO_2 emitted to the atmosphere will dilute the background ^{14}C signal, the so-called Suess effect, which can then be used to unravel recently added fossil-fuel CO_2 to the atmosphere (Zondervan and Meijer, 1996; Levin et al., 2003; Gamnitzer et al., 2006; Turnbull et al., 2006; Levin and Karstens, 2007; Turnbull et al., 2009; Turnbull et al., 2011; Lopez et al., 2013; Turnbull et al., 2014; Turnbull et al., 2015). However, this depletion can also partially be offset by CO_2 release from the biosphere which has enriched $^{14}C/^{12}C$ ratios due to the bomb tests as well as by direct ^{14}C emissions from the nuclear industries (Levin et al 2010). This technique also enables to separate between biospheric and fossil-fuel CO_2 components in atmospheric CO_2 observations, and thus to better constrain the biospheric CO_2 fluxes when coupled with inversion models (Basu et al., 2016). The uncertainty in CO_{2ff} estimated by the radiocarbon method is mainly determined by the precision in the ^{14}C measurement, the choice of background as well as the contribution from other sources of ^{14}C such as nuclear power plants (NPPs) (Turnbull et al., 2009).

Despite its importance as a fossil-fuel tracer, measurements of ^{14}C are still sparse. The measurements are expensive and laborious, which so far has prevented frequent sampling and has motivated researchers to combine ^{14}C measurements with additional tracers such as CO to enhance spatial and temporal coverage (Gamnitzer et al., 2006; Levin and Karstens, 2007; Vogel et al., 2010; Lopez et al., 2013; Turnbull et al., 2014; Turnbull et al., 2015). The CO-method relies on using high frequency CO measurements and regular calibration of the temporally changing $\Delta CO:\Delta CO_{2ff}$ ratios based on weekly or bi-weekly ^{14}C measurements. Despite its advantage of providing a proxy for continuous CO_{2ff} data, the method introduces additional uncertainties due to diurnal and seasonal variability in the CO sink, and the presence of multiple non-fossil CO sources such as oxidation of hydrocarbons or wood and

biofuel combustion (Gamnitzer et al., 2006). Spatial variations in the $\Delta CO:\Delta CO_2$ ratio across Europe due to different source compositions and environmental regulations, which affects the measured ratios due to changes in air mass origin (Oney et al., In review) are the main reason for the temporally changing $\Delta CO:\Delta CO_{2ff}$ ratio for a given measurement site.

In Switzerland, CO_2 contributes about 82 % of the total greenhouse gas emissions according to the Swiss national emission inventory for 2013, and fossil-fuel combustion from the energy sector contributes more than 80 % of the total CO_2 emission (FOEN, 2015b). In order to validate such bottom-up estimates, independent techniques based on atmospheric measurements are desirable. In addition, as mentioned above, the biospheric CO_2 signals can only be estimated with a good knowledge of CO_{2ff}. In this study, we present and discuss $^{14}CO_2$ measurements conducted bi-weekly between 2013 and 2015 at the Beromünster tall tower in Switzerland. From these samples in combination with background CO, CO_2 and $^{14}CO_2$ measurements at the high-altitude remote location Jungfraujoch, Switzerland, ΔCO to ΔCO_{2ff} ratios (R_{CO}) are derived. These ratios are then combined with the in-situ measured ΔCO mixing ratios to estimate a high-resolution time series of atmospheric CO_{2ff} mixing ratios, and by difference, of the biospheric CO_2 component. The influence of ^{14}C emissions from nearby NPPs and correction strategies are also discussed.

2. Methods

2.1. Site description and continuous measurement of CO and CO_2

A detailed description of the Beromünster tall tower measurement system as well as a characterization of the site with respect to local meteorological conditions, seasonal and diurnal variations of greenhouse gases, and regional representativeness can be obtained from previous publications (Oney et al., 2015; Berhanu et al., 2016; Satar et al., 2016). In brief, the tower is located near the southern border of the Swiss Plateau, the comparatively flat part of Switzerland between the Alps in the south and the Jura mountains in the northwest (47° 11′

23″ N, 8° 10’ 32″ E, 797 m a.s.l.), which is characterized by intense agriculture and rather high population density (Fig. 1). The tower is 217.5 m tall with access to five sampling heights (12.5 m, 44.6 m, 71.5 m, 131.6 m, 212.5 m) for measuring CO, CO_2, CH_4 and H_2O using Cavity Ring Down Spectroscopy (CRDS) (Picarro Inc., G-2401). By sequentially switching from the highest to the lowest level, mixing ratios of these trace gases were recorded continuously for three minutes per height, but only the last 60 seconds were retained for data analysis. The calibration procedure for ambient air includes measurements of reference gases with high and low mixing ratios traceable to international standards (WMO-X2007 for CO_2 and WMO-X2004 for CO and CH_4), as well as target gas and more frequent working gas determinations to ensure the quality of the measurement system. From two years of data a long-term reproducibility of 2.79 ppb, 0.05 ppm, and 0.29 ppb for CO, CO_2 and CH_4, respectively was determined for this system (Berhanu et al., 2016).

2.2. Sampling and CO_2 extraction for isotope analysis

Air samples for $^{14}CO_2$ analysis were collected every second week from the highest inlet usually between 9:00 to 13:00 UTC. During each sampling event, three samples were collected over a 15-minute interval in 100 L PE-AL-PE bags (TESSERAUX, Germany) from the flush pump exhaust line of the 212.5 m sampling inlet, which has a flow rate of about 9 L min^{-1} at ambient conditions. The sampling interval was chosen to ensure radiocarbon sample collection in parallel with the continuous CO and CO_2 measurements by the CRDS analyzer at the highest level. Each bag was filled at ambient air pressure for 6 to 8 minutes and a total air volume of 50 to 70 L (at STP) was collected.

CO_2 extraction was conducted cryogenically in the laboratory at the University of Bern usually the day after the sample collection. During the extraction step, the air sample was first pumped through a stainless steel water trap (-75 °C), which was filled with glass beads (Rashig rings, 5 mm, Germany). A flow controller (Analyt-MTC, Aalborg, USA) with

flow totalizer tool was attached to this trap to maintain a constant flow of air (1.2 L min^{-1}) towards the second trap (trap 2), a spiral-shaped stainless steel tube (1/4") filled with glass beads (~ 2 mm) and immersed in liquid nitrogen to freeze out CO_2. When the flow ceased, trap 2 was isolated from the line and evacuated to remove gases which are non-condensable at this temperature. Then, trap 2 was warmed to room temperature, and eventually immersed in slush at -75 °C to freeze out any remaining water. Finally, the extracted CO_2 was expanded and collected in a 50 mL glass flask immersed in liquid nitrogen.

Sample extraction efficiency was calculated by comparing the amount of the cryogenically extracted CO_2 with the CO_2 measured in-situ by the CRDS analyzer during the time of sampling. The amount of CO_2 extracted is determined first by transferring the extracted CO_2 cryogenically to a vacuum line of predetermined volume. Then, based on the pressure reading of the expanded gas, and the total volume of air collected determined by the mass flow controller with a totalizer function attached to trap 1, CO_2 mixing ratios were calculated.

At the end of 2014 we noticed that there was a leakage from the sampling line exhaust pumps, which resulted in unrealistically high CO_2 mixing ratios (usually more than 500 ppm). Therefore, we repalced all the exhaust pumps and the leakage problem was solved. Seven samples, which were suspected to be contaminated due to this issue, were consequently excluded. The sample extraction efficiency since then has usually been better than 99 %. We also made a blank test to check the presence of any leaks or contamination during sample processing but did not observe any of these issues.

2.3. Measurement of $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{14}C$

Prior to radiocarbon measurement, the extracted CO_2 was analyzed for the stable isotopes $\delta^{13}C$ and $\delta^{18}O$ using the Isotope Ratio Mass Spectrometer (Finnigan MAT 250) at the Climate and Environmental Physics Division of University of Bern, which has an accuracy

and precision of better than 0.1 ‰ for both $\delta^{13}C$ and $\delta^{18}O$ (Leuenberger et al., 2003). ^{14}C analysis of the extracted CO_2 was performed with an accelerator mass spectrometer (AMS) MICADAS (MIni CArbon DAting System) at the Laboratory for the Analysis of Radiocarbon (LARA) at the Department of Chemistry and Biochemistry of the University of Bern (Szidat et al., 2014). An automated graphitization equipment (AGE) was used to prepare solid target gas (Nemec et al., 2010) from the extracted CO_2 stored in 50 mL glass flasks. A measurement series consisted of up to 15 air samples converted to 30 solid graphite targets (duplicates), together with four and three targets from CO_2 produced by combustion of the NIST standard oxalic acid II (SRM 4990C) and fossil CO_2 (Carbagas, Gümligen), respectively, which were used for the blank subtraction, standard normalization, and correction for isotopic fractionations. Data reduction was performed using the BATS program (Wacker et al., 2010). As $^{14}C/^{12}C$ from Beromünster was measured at the LARA laboratory in Bern, whereas the corresponding background samples from Jungfraujoch were analyzed at the Institute of Environmental Physics, Heidelberg University, the datasets needed to be adjusted to each other. A recent interlaboratory compatibility test estimated a small bias of 2.1 ± 0.5 ‰ (Hammer et al., 2016) between the two institutes, which was subsequently subtracted from the ^{14}C measurements of the Beromünster samples.

2.4. Determination of the fossil fuel CO_2 component

2.4.1. The $\Delta^{14}C$ technique

For the determination of the CO_{2ff} component we followed the method developed by Levin and co-workers (Levin et al., 2003; Levin and Karstens, 2007). The measured CO_2 is assumed to be composed of three major components: the free troposphere background (CO_{2bg}), the regional biospheric component (CO_{2bio}) comprising photosynthesis and respiration components, and the fossil-fuel component (CO_{2ff}):

$$CO_{2meas} = CO_{2bg} + CO_{2bio} + CO_{2ff} \quad (1)$$

Each of these components has a specific $\Delta^{14}C$ value described as $\Delta^{14}C_{meas}$, $\Delta^{14}C_{bg}$, $\Delta^{14}C_{bio}$ and $\Delta^{14}C_{ff}$. In analogy to Eq. (1), a mass balance equation can also be formulated for ^{14}C as:

$$CO_{2meas}\,(\Delta^{14}C_{meas} + 1000\ ‰) = CO_{2bg}\,(\Delta^{14}C_{bg} + 1000\ ‰) + CO_{2bio}\,(\Delta^{14}C_{bio} + 1000\ ‰) + CO_{2ff}\,(\Delta^{14}C_{ff} + 1000\ ‰) \qquad (2)$$

Note that non-fossil fuel components such as biofuels are incorporated into the biospheric component in Eq. (1). The fossil-fuel term in Eq. (2) is zero as fossil fuels are devoid of radiocarbon ($\Delta^{14}C_{ff}$ = -1000 ‰). Replacing the biospheric CO_2 component in Eq. (1) by a formulation derived from Eq. (2), the fossil fuel CO_2 component is derived as:

$$CO_{2ff} = \frac{CO_{2bg}\left(\Delta^{14}C_{bg} - \Delta^{14}C_{bio}\right) - CO_{2meas}\,(\Delta^{14}C_{meas} - \Delta^{14}C_{bio})}{\Delta^{14}C_{bio} + 1000‰} \qquad (3)$$

Equation (3) can be further simplified by assuming that $\Delta^{14}C_{bio}$ is equal to $\Delta^{14}C_{bg}$ (Levin et al., 2003) as:

$$CO_{2ff} = \frac{CO_{2meas}\,(\Delta^{14}C_{bg} - \Delta^{14}C_{meas})}{\Delta^{14}C_{bg} + 1000‰} \qquad (4)$$

Hence, the fossil fuel CO_2 component can be determined using the CO_{2meas} and $\Delta^{14}C_{meas}$ values measured at the site as well as $\Delta^{14}C_{bg}$ obtained from the Jungfraujoch mountain background site in the Swiss Alps.

However, the CO_{2ff} determined using Eq. (4) incorporates a small bias due to the non-negligible disequilibrium contribution of heterotrophic respiration while the contribution from autotrophic respiration can be approximated by $\Delta^{14}C_{bg}$. Turnbull et al. (2006) showed that this effect will lead to an underestimation of CO_{2ff} on average by 0.2 ppm in winter and 0.5 ppm in summer, respectively, estimated for the northern hemisphere using a mean terrestrial carbon residence time of 10 years. To account for this bias, a harmonic function varying seasonally between these values was added to the derived CO_{2ff} values. However, variation of respiration fluxes on shorter timescales cannot be accounted for by this simple correction.

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2.4.2. Simulation of $^{14}CO_2$ from nuclear power plants

Radiocarbon is produced by nuclear reactions in NPPs and primarily emitted in the form of $^{14}CO_2$ (Yim and Caron, 2006), except for Pressurized Water Reactors (PWR), which release ^{14}C mainly in the form of $^{14}CH_4$. Previous studies have shown that such emissions can lead to large-scale gradients in atmospheric $\Delta^{14}C$ activity and offset the depletion from fossil-fuel emissions (Graven and Gruber, 2011). At Heidelberg in Germany, an offset of 25 % and 10 % of the fossil-fuel signal was observed during summer and winter, respectively, due to emissions from a nearby plant (Levin et al., 2003). Similarly, Vogel et al. (2013) determined the influence of NPPs for a measurement site in Canada, and estimated that about 56 % of the total CO_{2ff} component was masked by the contribution from NPPs. In Switzerland, there are five NPPs and the closest plant is located about 30 km to the northwest of Beromünster (Fig. 1). Furthermore, air masses arriving at Beromünster are frequently advected from France, which is the largest producer of nuclear power in Europe.

To estimate the influence of NPPs on $\Delta^{14}C$ at Beromünster, we used FLEXPART-COSMO backward Lagrangian particle dispersion simulations (Henne et al., 2016). FLEXPART-COSMO was driven by hourly operational analyses of the non-hydrostatic numerical weather prediction model COSMO provided by the Swiss weather service MeteoSwiss at approximately 7 x 7 km^2 resolution for a domain covering large parts of Western Europe. For each 3-hour measurement interval during the three-year period, a source sensitivity map (footprint) was calculated by tracing the paths of 50'000 particles released from Beromünster at 212 m above ground over 4 days backward in time. The source sensitivities were then multiplied with the $^{14}CO_2$ emissions of all NPPs within the model domain. Thereby, the emission of a given NPP was distributed over the area of the model grid cell containing the NPP. Source sensitivities were calculated for three different vertical layers (0-50 m, 50-200 m, 200-500 m). Since the height of ventilation chimneys of the Swiss NPPs

is between 99 m and 120 m, only the sensitivity of the middle layer was selected here as it corresponds best to the effective release height.

The release of ^{14}C both in inorganic (CO_2) and organic form (CH_4) is routinely measured at all Swiss NPPs. The corresponding data have been kindly provided by the Swiss Federal Nuclear Safety Inspectorate (ENSI) and the Berner Kraftwerke (BKW) operating the NPP Mühleberg at temporal resolutions ranging from annual (Benznau 1 & 2), to monthly (Leibstadt, Gösgen), and bi-weekly (Mühleberg), and we assumed constant emissions over the corresponding periods. For Beznau 1, the emissions of 2015 were distributed over the first 3 months of the year due to the shut-down of the plant in March 2015. The largest sources of $^{14}CO_2$ in Switzerland are the two Boiling Water Reactors (BWP) Mühleberg and Leibstadt (Loosli and Oeschger, 1989). Beznau 1 & 2 and Gösgen are PWRs emitting about one order of magnitude less $^{14}CO_2$. For NPPs outside Switzerland, the emissions were estimated from energy production data reported to the International Atomic Energy Agency (IAEA) and NPP type-specific emission factors following Graven and Gruber (2011). The enhancement in $\Delta^{14}C$ caused by nuclear emissions at Beromünster ($\delta\Delta_{nuc}$) was then computed according to Graven and Gruber (2011) as:

$$\delta\Delta_{nuc} = \frac{\delta A_{nuc} \times 1000‰}{R_S(C_R + \delta C_{ff})} \qquad (5)$$

where δA_{nuc} and δC_{ff} are the enhancements in $^{14}CO_2$ and CO_2 relative to a reference site with a background CO_2 mixing ratio C_R, respectively. R_S represents the modern day $^{14}C/^{12}C$ ratio of 1.176×10^{-12}.

2.4.3. Calculation of R_{CO}, $\Delta CO/\Delta CO_2$ and high resolution CO_{2ff}

A ΔCO to ΔCO_{2ff} ratio (R_{CO}) was calculated as the slope of the geometric mean regression (model II), with ΔCO being the corresponding CO enhancement over a background measured at Jungfraujoch, and the CO_{2ff} values determined above. The CO measurements at

Jungfraujoch were conducted using a CRDS analyzer (Picarro Inc., G-2401) with a measurement precision of ±1 ppb for 10-minute aggregates (Zellweger et al., 2012).

As CO is usually co-emitted with CO_2 during incomplete combustion of fossil and other fuels, we have also computed a tracer ratio designated as $\Delta CO/\Delta CO_2$ from the enhancements in the in-situ measured CO and CO_2 mixing ratios over the Jungfraujoch background (Oney et al., 2016, In review). CO_{2bg} values were obtained by applying the robust extraction of baseline signal (REBS) statistical method to the continuous CO_2 measurements at the high altitude site Jungfraujoch (Schibig et al., 2016) with a band width of 60 days. Note that while R_{CO} strictly refers to the ratio of ΔCO to fossil fuel CO_2 emissions, the $\Delta CO/\Delta CO_2$ ratio can be influenced by biospheric contribution as well as CO_2 emissions from non-fossil sources such as biofuels and biomass burning.

In order to construct the high resolution CO_{2ff} time series, we combined the in-situ measured CO enhancements at the Beromünster tower with the radiocarbon-derived ratios R_{CO}, and estimated CO_{2ff}^{CO} for the three-year dataset as:

$$CO_{2ff}^{CO} = \frac{CO_{obs} - CO_{bg}}{R_{CO}} \qquad (6)$$

where CO_{obs} is the hourly averaged CO measurements at the tower. CO_{bg} is the background CO values derived from measurements at the High Alpine Research Station Jungfraujoch, estimated in the same way as CO_{2bg} by applying the REBS statistical method (Ruckstuhl et al., 2012) with a bandwidth of 60 days to eliminate the influence of short-term local variability occasionally observed at Jungfraujoch.

3. Results and Discussions

3.1. $\Delta^{14}CO_2$ and CO_{2ff}

Figure 2a shows the in-situ measured hourly mean CO_2 dry air mole fractions at Beromünster (black) from the 212.5 m sample inlet matching at hours when air samples were

collected for radiocarbon analysis and the corresponding background CO_2 at Jungfraujoch (blue). During the measurement period, we have recorded CO_2 mixing ratios between 389 ppm and 417 ppm. Spikes of CO_2 were observed mainly during winter, associated with weak vertical mixing and enhanced anthropogenic emissions while lower CO_2 mixing ratios were recorded during summer due to strong vertical mixing and photosynthetic uptake (Berhanu et al., 2016; Satar et al., 2016).

Isotopic analysis of the air samples yielded $\Delta^{14}C_{meas}$ between -12.3 ‰ and +22.8 ‰, with no clear seasonal trend, after correction for the model-simulated contribution from NPPs (Fig. 2b). Based on the simulations described in section 2.4.2, we have calculated a mean enhancement in $\Delta^{14}C$ of +1.6 ‰ and a maximum of +8.4 ‰ due to NPPs. This agrees qualitatively with the coarse resolution simulations of Graven and Gruber (2011), which suggest a mean enhancement of +1.4 ‰ to +2.8 ‰ over this region (Graven and Gruber, 2011). While about 70 % of this contribution is due to Swiss NPPs, the remaining contribution is of foreign origin. About 75 % of the contribution from the Swiss NPPs is due to Mühleberg, which is located west of Beromünster and hence frequently upstream of the site, due to the prevailing westerly winds (Oney et al., 2015). Note that each data point represents a mean value of the triplicate samples collected consecutively with a standard error of 2 ‰ among triplicates. During this period, the background $\Delta^{14}C$ values measured at Jungfraujoch varied between 15 ‰ and 28 ‰. Regional depletions in $\Delta^{14}C$ due to fossil-fuel emissions, i.e. differences between Beromünster and the clean air reference site Jungfraujoch, were in the range of -0.7 ‰ to -29.9 ‰ with a mean value of -9.9 ‰.

Figure 2c shows the corresponding CO_{2ff} determined after correcting for radiocarbon emissions from NPPs. The typical uncertainty in CO_{2ff} is 1.1 ppm calculated from a mean $\Delta^{14}C$ measurement uncertainty of 2.0 ‰ in both the sample and the background values. A mean fossil-fuel CO_2 contribution of 4.3 ppm was calculated from these samples. Few cases,

notably the sample from 27 March 2014, showed a higher CO_{2ff} and a strong depletion in $\Delta^{14}C_{meas}$, consistent with the high CO_2 mixing ratio shown in the top panel. This can be due to a strong local fossil-fuel contribution or a polluted air mass transported from other regions of Europe coinciding with the grab samplings. As this event occurred during a period with moderate temperatures (mean temperature of 6.8 °C measured at the highest level of the Beromünster tower between March and May), strong fossil fuel CO_2 emissions due to heating are not expected. The FLEXPART-COSMO transport simulations for this event suggest an air mass origin from southeastern Europe. Periods with winds from the east, colloquially known as Bise, are well known to be associated with very stable boundary layers and correspondingly strong accumulation of air pollutants during the cold months of the year between autumn and spring. Air masses reaching Beromünster from Eastern Europe have recently been reported to contain unusually high levels of CO during late winter and early spring periods, coinciding with this sampling period (Oney et al., 2016, In review).

By subtracting the background and fossil-fuel CO_2 contributions from the measured mixing ratios, CO_{2bio} values were also determined ranging between +11.2 ppm and -12.4 ppm (Figure 2d). Even if there is no clear seasonal trend, the lowest CO_{2bio} values were recorded during summer implying net photosynthetic CO_2 uptake while most of the values in winter are positive or close to zero due to respiration. Two of the samples in June and July 2015 showed a rather large positive CO_{2bio} contribution, in contrast to the expected summertime minimum. Reasons for such high values can be biomass harvesting or enhanced respiration by plants and soil, associated with warmer temperature which will lead to enhanced CO_2 emissions (Oney et al., 2016, In review).

3.2. R_{CO} values from radiocarbon measurements

From the simultaneous CO and radiocarbon measurements, we calculated an R_{CO} of 13.4 ± 1.3 mmol CO/mol CO_2 with a correlation coefficient (r^2) of 0.7, and a median value of

11.2 mmol CO/mol CO_2. If we split the data seasonally, R_{CO} values of 12.5 ± 3.3 mmol CO/mol CO_2 and 14.1 ± 4.0 mmol CO/mol CO_2 were obtained during winter and summer, respectively. The slightly lower R_{CO} during winter is due to larger CO_{2ff} share during this period from domestic heating. Our estimate is well within the range of values from previous studies (10-15 mmol/mol) observed at other sites in Europe and North America (Gamnitzer et al., 2006; Vogel et al., 2010; Turnbull et al., 2011). To test the sensitivity of this ratio to the selection of background site, we additionally calculated R_{CO} using background values estimated with the REBS method from the in-situ CO measurements at Beromünster instead of Jungfraujoch. The value obtained in this way (12.7 ± 1.2, r^2 = 0.6) is only slightly lower than the value obtained using Jungfraujoch as background site. Considering the persistent decrease in CO emissions (Zellweger et al., 2009) in response to the European emission legislation, our estimated R_{CO} is surprisingly high.

3.3. ΔCO/ΔCO_2 from continuous measurements

Figure 3 shows the seasonally resolved ΔCO to ΔCO_2 correlations derived from in-situ measured CO and CO_2 enhancements over the background observed at Jungfraujoch, and we have estimated a tracer ratio of 8.3 ± 0.1 mmol/mol (r^2 = 0.5) for the entire measurement period. From measurements during winter, when the two species are most strongly correlated, a ΔCO/ΔCO_2 ratio of 7.3 ± 0.1 mmol/mol (r^2 = 0.9) is obtained, while barely any correlation is observed in summer and weak correlations (r^2 < 0.4) during spring and autumn. Recently, Oney et al. (2016) reported a higher wintertime ratio of 8.3 mmol/mol for the same combination of measurements at Beromünster and Jungfraujoch but for a different time period. If we consider only winter 2013 as in their data, we obtain essentially the same value, while much lower ratios of 6.5 mmol/mol and 6.4 mmol/mol were calculated for 2014 and 2015, respectively. The higher ratios in winter 2013 are likely related to the unusually cold conditions and extended periods of air mass transport from Eastern Europe. Note that these

enhancement ratios also include emissions from non-fossil sources such as biofuels and biomass burning in contrast to R_{CO}. The national inventory attributes about 15 % of total CO_2 emissions in 2014 to non-fossil fuel sources (FOEN, 2015b). If we correct for these sources assuming a constant contribution throughout the year, the winter time $\Delta CO/\Delta CO_2$ ratio for the three year data becomes 8.7 mmol/mol. This ratio is roughly consistent with the anthropogenic CO to CO_2 emission ratio of 7.8 mmol/mol calculated from Switzerland's greenhouse gas inventory report for 2013 (FOEN, 2015b, a). The slightly higher value points towards an underestimation of the CO emissions by the inventory.

This wintertime $\Delta CO/\Delta CO_2$ ratio of 8.7 mmol/mol is still about 30 % lower than the R_{CO} estimate for the same period (12.5 mmol/mol) shown as a black line in Fig. 3. This suggests that despite the strong correlation between ΔCO and ΔCO_2 in winter the regional CO_2 enhancements are not only caused by anthropogenic emissions but include a significant biospheric CO_2 component. This also implies that the observed correlation is not only due to spatially and temporally correlated sources but is caused to a large extent by meteorological variability associated with more or less accumulation of trace gases in the boundary layer irrespective of their origin. This interpretation is supported by the fact that a strong correlation ($r^2 > 0.7$) was also observed between CO and CH_4 during winter at the same tower site (Satar et al., 2016) despite their sources being vastly distinct. In Switzerland about 80 % of CH_4 emissions are from agriculture (mainly from ruminants) while more than 85 % of CO emissions are from the transport sector and residential heating (FOEN, 2015a).

As a consequence, the true ratio of CO to anthropogenic CO_2 may be significantly larger than the observed $\Delta CO/\Delta CO_2$ ratio of 8.7 mmol/mol, which in turn would imply that the molar ratio of the Swiss emission inventory of 7.8 mmol/mol is too small.

3.4. High resolution time series of CO_{2ff} and CO_{2bio}

Figure 4 shows the hourly mean CO mixing ratios at Jungfraujoch and Beromünster between 2013 and 2015. CO mixing ratios as high as 480 ppb were recorded at Beromünster while generally lower CO values were recorded at the more remote site Jungfraujoch. A pronounced seasonality in CO can be observed at Beromünster with higher values in winter and lower values during summer due to stronger vertical mixing and chemical depletion of CO by OH (Satar et al., 2016). The hourly mean CO_{2ff} time series calculated using these continuous CO measurements and the seasonally resolved R_{CO} values derived using the radiocarbon measurements are displayed in Fig. 4c. A seasonal trend in the calculated CO_{2ff} is observed with frequent spikes of CO_{2ff} during winter while summer values show less variability. We calculated a monthly mean amplitude (peak-to-trough) of 6.3 ppm with a maximum in February and a minimum in July. During the measurement period, we have observed CO_{2ff} mixing ratios ranging up to 27 ppm coinciding with cold periods and likely from enhanced anthropogenic emissions due to heating. Instances of slightly negative CO_{2ff} contributions, which occurred during less than 5 % of the time, were associated with negative enhancements in CO (i.e. $\Delta CO < 0$). This could be simply due to an overestimation of background values by the REBS function during these periods.

Figure 5a shows the hourly averaged residual CO_{2bio} values which exhibit a clear seasonal cycle but also a considerable scatter in all seasons ranging from -13 ppm to +30 ppm. During winter, most values were close to zero or positive, implying a dominance of respiration fluxes. In summer, conversely, pronounced negative and positive excursions were observed mostly due to the diurnal cycle in net CO_2 fluxes, which are dominated by photosynthetic uptake during daytime and respiration at night. Another factor contributing to such variations may be the application of a constant emission ratio neglecting any diurnal variability (Vogel et al., 2010).

It should also be noted that any non-fossil fuel CO_2 sources such as emissions from biofuels would be incorporated into the CO_{2bio} term since CO_{2ff} in Eq. (1) represents the fossil-fuel sources only, adding more variability to the data set. In order to reduce the influence of these diurnal factors, we have looked into afternoon CO_{2bio} values (12:00 - 15:00 UTC), when the CO_2 mixing ratios along the tower are uniform (Satar et al., 2016) and R_{CO} variability is minimal. Similar to the seasonal pattern in Fig. 5a, a clear seasonal cycle in biospheric CO_2 can be observed (Fig. 5b) in agreement with biospheric exchange, but both positive and negative extremes are less frequently observed (-12 ppm to +22 ppm).

The variation in CO_{2bio} during afternoon (12:00 – 15:00 UTC) was recently estimated at this site to a range of -20 ppm to +20 ppm by combining observations and model simulations for the year 2013 (Oney et al., 2016, In review). Our estimates are more positive when compared to their study, due to the higher R_{CO} which results in lower CO_{2ff} and correspondingly higher CO_{2bio} values.

Biospheric CO_2 shows a seasonally dependent diurnal variation as shown in Fig. 6. During winter (Dec - Feb), the biospheric CO_2 component remains consistently positive (+2 to +5 ppm) throughout the day, implying net respiration fluxes. In summer, a clear feature with increasing CO_{2bio} values during the night peaking between 07:00 and 08:00 UTC (i.e. between 08:00 and 09:00 local time) can be observed. This buildup during the night can be explained by CO_2 from respiration fluxes accumulating in the stable and shallow nocturnal boundary layer. Then, after sunrise, the early morning CO_{2bio} peak starts to gradually decrease due to a combination of onset of photosynthesis and enhanced vertical mixing due to the growth of the boundary layer. At Beromünster, a decrease in CO_2 mixing ratios from both processes is visible more or less at the same time at the 212.5 m height level, while at the lowest inlet level (12.5 m) the photosynthetic uptake signal is observed about an hour earlier (Satar et al., 2016). Between 12:00 and 15:00 UTC, when the daytime convective boundary

layer is fully established, the biospheric CO_2 continues to become more negative implying net photosynthetic uptake, which eventually stabilizes for 3 - 5 hours until nighttime CO_{2bio} accumulation starts.

4. Conclusions

From continuous measurements of CO and CO_2 and bi-weekly radiocarbon samples at the Beromünster tall tower, we have estimated a ΔCO to ΔCO_{2ff} ratio (R_{CO}) which was subsequently used to construct a 3-years long high-resolution CO_{2ff} time series. We have corrected the ratio for an offset of about 16 % caused by ^{14}C emissions from nearby NPPs. This bias was calculated by comparing the simulated mean enhancement in $\Delta^{14}C$ (1.6 ‰) due to NPPs with the measured mean depletion in $\Delta^{14}C$ due to fossil fuel CO_2 (9.9 ‰). The radiocarbon-based R_{CO} derived in this study during winter is significantly higher than the $CO:CO_2$ enhancement ratios estimated from continuous CO and CO_2 measurements during the same period, suggesting a significant biospheric contribution to regional CO_2 enhancements during this period.

The obtained CO_{2ff} time series shows a clear seasonality with frequent spikes during winter associated with enhanced anthropogenic emissions and weak vertical mixing while summer values are mostly stable.

By subtracting the estimated CO_{2ff} and CO_{2bg} from CO_{2meas}, we have also calculated the biospheric CO_2 component, which ranges between -15 ppm and +30 ppm. Considering only afternoon data (12:00 – 15:00 UTC) when the convective boundary layer is fully established, CO_{2bio} showed its minimum in summer coinciding with net photosynthetic uptake but still with frequent positive excursions possibly due to biomass burning or enhanced soil/plants exhalation. During winter, CO_{2bio} becomes nearly zero or positive, implying respiration fluxes.

A pronounced diurnal variation in CO_{2bio} was observed during summer modulated by vertical mixing and biospheric exchange while this variation disappears during winter. However, the variation in CO_{2bio} may also be influenced by the uncertainty of the CO_{2ff} estimate especially due to applying a constant emission ratio while calculating CO_{2ff}. Hence, it will be important in the future to include seasonally and diurnally resolved R_{CO} values from high-frequency radiocarbon measurements to better estimate CO_{2ff}. Additionally, including independent tracers such as Atmospheric Potential Oxygen (APO) estimates based on concurrent CO_2 and O_2 measurements will be very useful to validate fossil-fuel emission estimates from the radiocarbon method. This technique is also advantageous as the fossil fuel CO_2 estimate is unaltered by contribution from NPPs as well as it accounts for the contribution from biofuels.

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Table 1. Ratios (R_{CO}) determined using radiocarbon measurements after correcting for influence from NPPs and applying model II regression, and ratios derived from continuous CO and CO_2 measurements by the CRDS analyzer as enhancements ($\Delta CO:\Delta CO_2$) using Jungfraujoch background measurements. R_{CO} values are given in mmol/mol with standard uncertainties of the slope and r^2 values in brackets and n represents the number of samples for the radiocarbon method. Note that according to the Swiss emission inventory report for greenhouse gas emissions in 2013, the annual anthropogenic CO/CO_2 emission ratio for the national estimate is 7.8 mmol/mol.

	R_{CO} ($\Delta CO:\Delta CO_{2ff}$) (radiocarbon)	Number of samples (*n*)	$\Delta CO:\Delta CO_2$ (CRDS)
Winter (Dec-Feb)	12.5 ± 3.3 (0.6)	8	7.3 (0.9)
Summer (Jun-Aug)	14.1 ± 4.0 (0.3)	14	13.4 (0.02)
All data	13.4 ± 1.3 (0.6)	45	8.3 (0.5)

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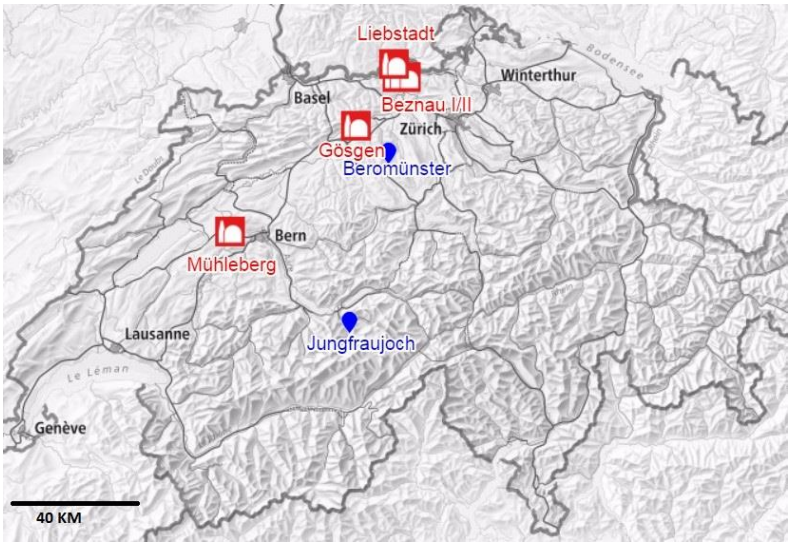

Figure 1. The geographical map of Beromünster and Jungfraujoch measurement sites (blue) as well as the five NPPs in Switzerland (red).

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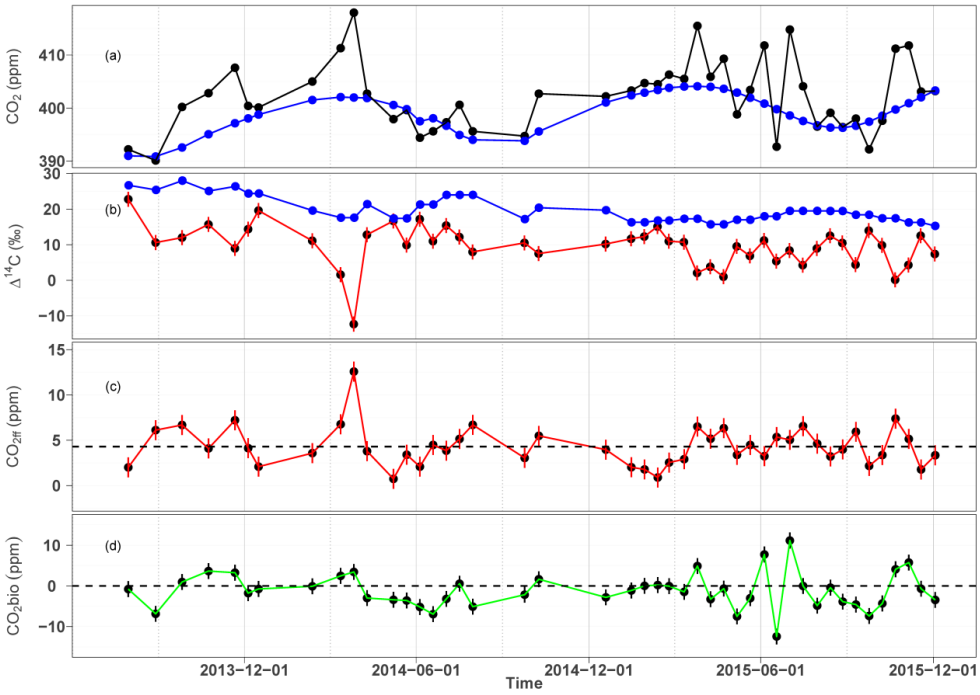

Figure 2. CO_2 mixing ratios (hourly averages) at Beromünster (black) from the sample inlet at 212.5 m and from background measurements at Jungfraujoch (blue) filtered using the REBS function for periods when ^{14}C sampling was conducted (a), $\Delta^{14}C$ determined from the bi-weekly point samplings at the site (red) and from 14-days integrated samplings at Jungfraujoch (blue) (b), CO_{2ff} determined during this period applying Eq. (4) with a mean CO_{2ff} value of 4.3 ppm (dashed line) (c), and the biospheric CO_2 determined by simple subtraction of CO_{2bg} and CO_{2ff} from the CO_{2meas} (d). Error bars in (b) and (c) indicate the mean uncertainty in $\Delta^{14}C$ measurement (± 2.1 ‰) and calculated CO_{2ff} (± 1.1 ppm), averaged for the triplicate samples while error bar in (d) is obtained from error propagation of the components in (a), (b) and (c). CO_2 mixing ratios in the top panel are only shown from times matching the radiocarbon sampling at Beromünster tower.

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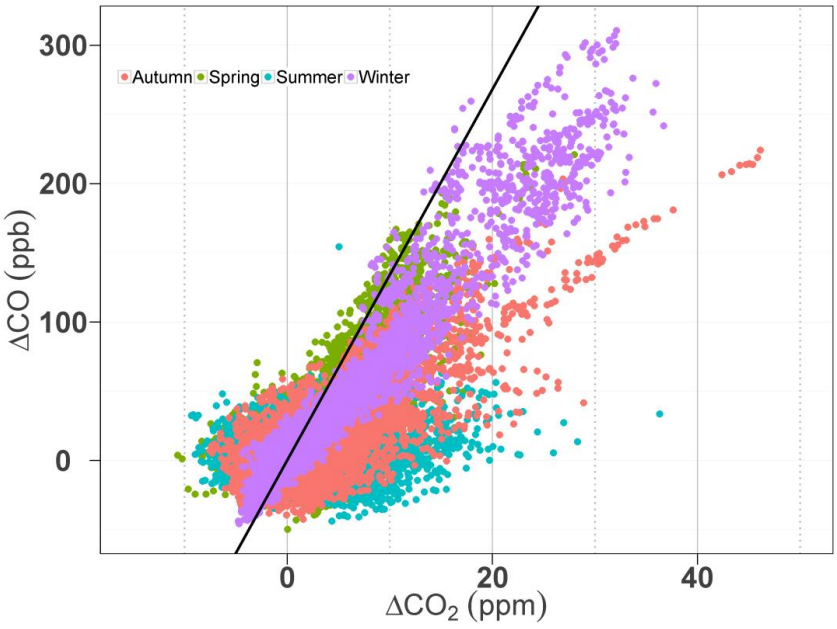

Figure 3. The correlation between enhancements in CO and CO_2 at Beromünster over Jungfraujoch background for the different seasons. The black solid line shows the wintertime R_{CO} derived from radiocarbon measurements.

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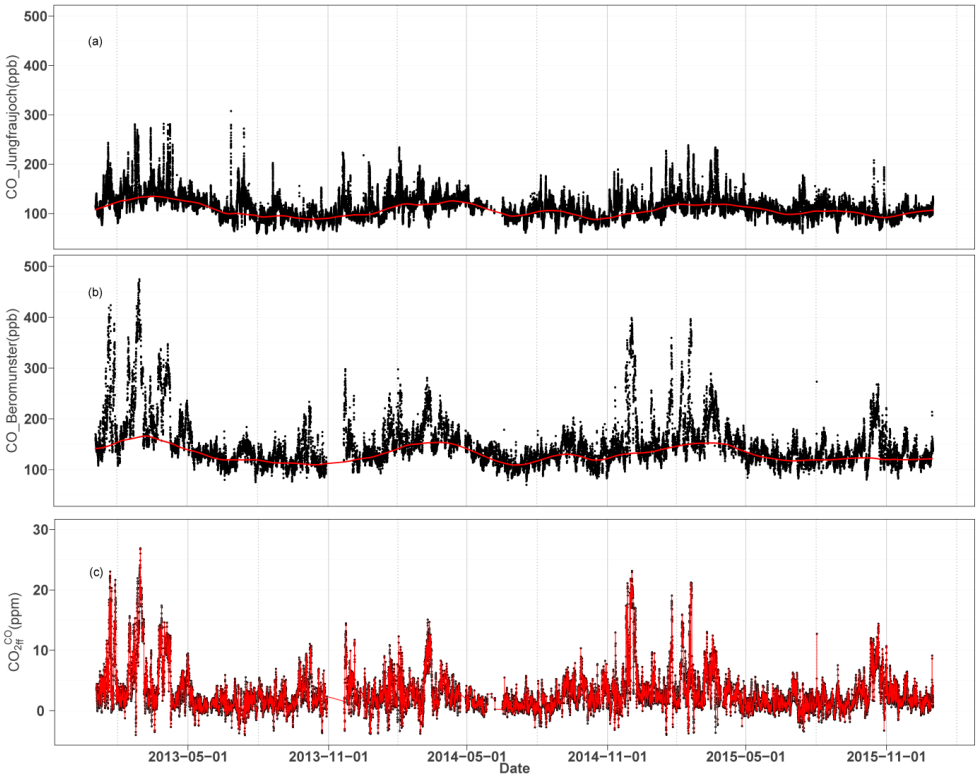

Figure 4. Time series of hourly mean CO mixing ratios measured at Jungfraujoch (a) and Beromünster (b) sites with the red curve showing the estimated background values using the REBS method with 60 days window. Panel (c) shows the hourly mean CO_{2ff} time series calculated using the emission ratios determined from radiocarbon measurements, and the CO enhancements at Beromünster over the Jungfraujoch background based on Eq. (6).

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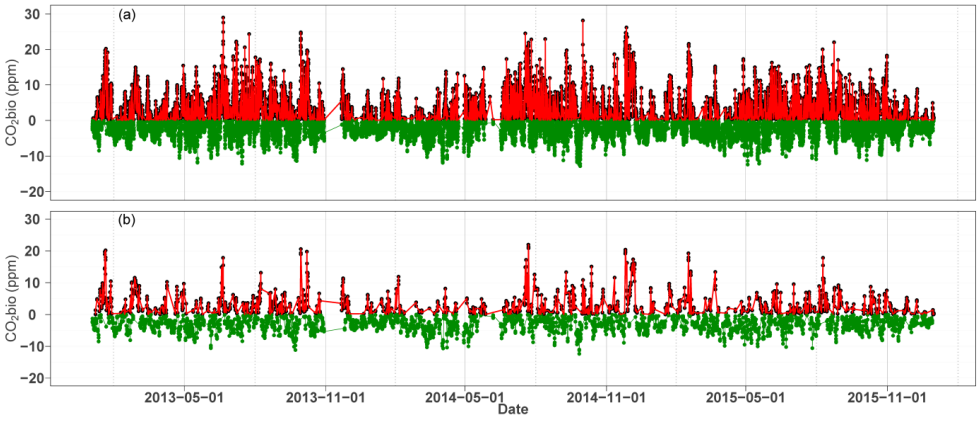

Figure 5. Time series (hourly resolution) of the biospheric CO_2 derived as a residual of the difference between the total CO_2, CO_{2bg} and CO_{2ff} for all data (a), and only afternoon data from 12:00-15:00 UTC (b). The green lines show negative CO_{2bio} implying uptake while red ones represent positive CO_{2bio}. The average uncertainty of CO_{2bio} amounts ±1.3 ppm calculated from error propagation.

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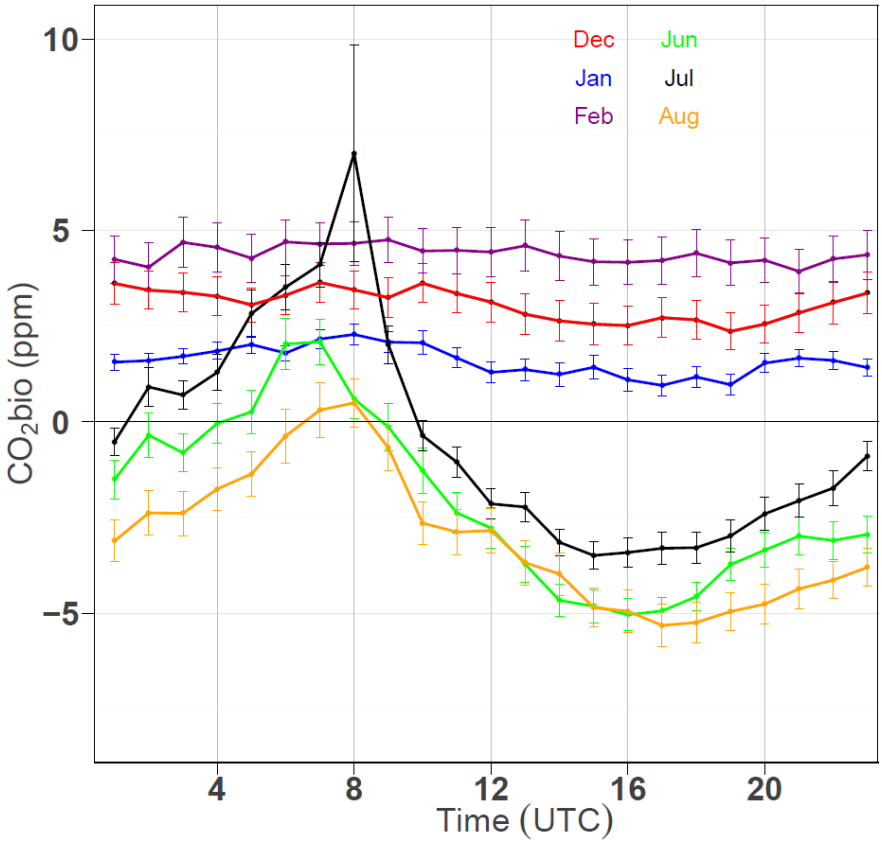

Figure 6. Hourly variations of monthly averaged biospheric CO_2 during summer (Jun – Aug) and winter (Dec – Feb). While winter values dominated by respiration are constant throughout a day, summer values show a significant diurnal variation induced by photosynthesis and vertical mixing. The error bars are the standard deviations of the hourly averaged CO_{2bio} values for each month.

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