Implication of weekly and diurnal $^{14}$C calibration on hourly estimates of CO-based fossil fuel CO$_2$ at a moderately polluted site in southwestern Germany

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**ABSTRACT**

A 7-year-long data set of integrated high-precision $^{14}$CO$_2$ observations combined with occasional hourly $^{14}$CO$_2$ flask data from the Heidelberg sampling site is presented. Heidelberg is located in the highly populated and industrialized upper Rhine valley in southwestern Germany. The $^{14}$CO$_2$ data are used in combination with hourly carbon monoxide (CO) observations to estimate regional hourly fossil fuel CO$_2$ ($\Delta$FFCO$_2$) mixing ratios. We investigate three different $^{14}$C calibration schemes to calculate $\Delta$FFCO$_2$: (1) the long-term median $\Delta$CO/FFCO$_2$ ratio of 14.6 ppb ppm$^{-1}$ (mean: 15.5 ± 5.6 ppb ppm$^{-1}$), (2) individual (2-)week-long integrated $\Delta$CO/FFCO$_2$ ratios, which take into account the large week-to-week variability of ±5.6 ppb ppm$^{-1}$ (1σ; interquartile range: 5.5 ppb ppm$^{-1}$), and (3) a calibration which also includes diurnal changes of the $\Delta$CO/FFCO$_2$ ratio. We show that in winter a diurnally changing $\Delta$CO/FFCO$_2$ ratio provides a much better agreement with the direct $^{14}$C-based hourly $\Delta$FFCO$_2$ estimates whereas summer values are not significantly improved with a diurnal calibration. Using integrated $^{14}$CO$_2$ samples to determine weekly mean $\Delta$CO/FFCO$_2$ ratios introduces a bias in the CO-based $\Delta$FFCO$_2$ estimates which can be corrected for with diurnal grab sample data. Altogether our $^{14}$C-calibrated CO-based method allows determining $\Delta$FFCO$_2$ at a semi-polluted site with a precision of approximately ±25%.

1. Introduction

Assessing the continental carbon balance (e.g. in Europe or North America) from atmospheric observations and inverse modelling, quantitative knowledge of anthropogenic CO$_2$ emissions from fossil fuel burning and cement production is indispensable. Recent studies show that, in particular in Europe, atmospheric signals from fossil fuel emissions are of similar size or larger than those from co-located biospheric fluxes (Levin and Karstens, 2007a). Fossil fuel mixing ratios estimated from bottom-up inventories combined with atmospheric transport modelling do, however, require careful validation. This is due to uncertainties in the underlying emissions but also in model transport parameters (Peylin et al., 2009). Using (e.g. week-long) integrated atmospheric $^{14}$CO$_2$ measurements to calculate regional fossil fuel CO$_2$ concentration offsets ($\Delta$FFCO$_2$) relative to background air is a well-established technique (Levin et al., 2003). It can be used to determine the long-term trends (Levin and Rödenbeck, 2008) and seasonal cycles of fossil fuel CO$_2$ at a site, but these measurements do not provide the temporal resolution generally required for atmospheric inversions (i.e. hourly).

As $^{14}$C analyses are still too costly to be performed on hourly resolution, surrogate tracers have been suggested to assess fossil fuel CO$_2$ variations on shorter timescales. But these tracers, CO, SF$_6$, C$_2$H$_2$ and others (Bakwin et al., 1997; Gamnitzer et al., 2006; Rivier et al., 2006; Tumbull et al., 2006) in most cases do not fully meet the requirements of a strict source relation to fossil CO$_2$ emissions or have sink mechanisms which are not well understood. A proposed purely observation-based method to estimate the hourly FFCO$_2$ offset uses weekly mean observed $\Delta$CO/FFCO$_2$ ratios based on week-long integrated high-precision $^{14}$CO$_2$ measurements and hourly CO observations (Levin and Karstens, 2007b). Applying this approach one has, however, to be aware of potential variations of the $\Delta$CO/FFCO$_2$ ratio on shorter (e.g. diurnal) time scales. Furthermore CO cannot be regarded as a conservative tracer, and may have significant sources which are not related to FFCO$_2$. 

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as well as sinks, dependent on the catchment area of the site investigated (Gamnitzer et al., 2006).

Here we make an assessment of $^{14}$C- and CO-based estimates of hourly fossil fuel CO$_2$ in Heidelberg, a semi-polluted site located in the upper Rhine valley. These estimates are based on CO/FFCO$_2$ ratios determined by different methods and at different temporal resolutions. The first approach uses the mean CO/FFCO$_2$ emission ratio determined only from bottom-up emission inventories in the catchment area, we call this approach the ‘bottom-up CO-based’ approach. The second method uses the measured long-term mean $\Delta$CO/FFCO$_2$ ratio determined from week-long or 2-week-long integrated CO mixing ratios and $^{14}$CO$_2$-based FFCO$_2$ measurements at the site; we call this approach the ‘simple CO-based’ approach. The third approach uses individual week-long or 2-week-long $^{14}$C-based CO calibrations as suggested by Levin and Karstens (2007b); we call this approach the ‘advanced CO-based’ approach. Finally, we include in the $^{14}$C calibration of CO also diurnal variations of the $\Delta$CO/FFCO$_2$ ratio, and call this approach the ‘diurnal CO-based’ approach. Hourly $\Delta$CO/FFCO$_2$ ratios are determined from an extended data set of $^{14}$CO$_2$ measurements made on hourly grab samples collected in Heidelberg over the period of 2001–2008. CO-based FFCO$_2$ estimates are then compared with the direct $^{14}$C-based fossil fuel CO$_2$ offsets, either on the time scales of the integrated samples, that is week-long or 2-week-long, or on that of the grab samples, that is hourly. The aim of this assessment is to investigate the uncertainties of the different approaches and come up with the most accurate and, at the same time most cost-effective methodology to estimate hourly fossil fuel CO$_2$ levels at continental stations.

2. Methods

2.1. Characteristics of the Heidelberg sampling site and its catchment area

The air sampling was performed in Heidelberg from the roof of the Institut für Umweltphysik building on the University campus in the western outskirts of Heidelberg (49.417°N, 8.675°E, 116 m a.s.l.). Heidelberg is a medium-size city (145,000 inhabitants) in the densely populated upper Rhine valley located about 20 km southeast of the industrial area of Mannheim/Ludwigshafen. With a predominantly southwesterly to southeasterly airflow, the larger catchment area of the Heidelberg sampling site is the upper Rhine valley, southwestern Germany and eastern France. The topography of the Rhine valley and the Neckar valley also strongly influence the regional airflow and sometimes favour atmospheric inversions, leading to strong build-up of CO$_2$ concentrations.

An advantage conducting this study in an urban environment is that the influence of non-pollution sources of CO or possible interaction with biochemical processes (e.g. soil uptake) are expected to be quite low, while rather high local offsets of CO and FFCO$_2$ are present (Gamnitzer et al., 2006). Nonetheless, one has to be aware of the possible problems of this site/approach: (1) strong influence from very local sources and (2) highly variable CO/FFCO$_2$ emission ratios in the catchment area, depending on wind direction. Generally, the CO/FFCO$_2$ emission ratio of the mean anthropogenic source in a polluted area is strongly dependent on the dominant combustion processes. For the state of Baden–Württemberg, the main catchment area of Heidelberg, the CO/FFCO$_2$ ratios of the fossil fuel CO$_2$ sources, as determined from emission inventories range from 0.6 to 1.3 ppb CO ppm$^{-1}$ FFCO$_2$ for industrial emissions to 98–102 ppb CO ppm$^{-1}$ FFCO$_2$ for technical devices (e.g. industrial, agricultural and construction machines and military). For other important CO$_2$ sources such as residential heating and small consumers, emission ratios of 2.4 ppb CO ppm$^{-1}$ FFCO$_2$ and 5.5–6.9 ppb CO ppm$^{-1}$ FFCO$_2$ are reported. As our measurement site is located in the suburbs of Heidelberg, traffic is assumed to have a strong influence on the FFCO$_2$ levels, with a typical German fleet emission factor of 17.2–24.1 ppb CO ppm$^{-1}$ FFCO$_2$ (LUBW, 2006, 2009; Stat. Landesamt BW, 2003, 2009).

2.2. Quasi-continuous CO$_2$, CO and $^{14}$CO$_2$ measurements in Heidelberg

Two air intake lines at the southwestern and southeastern corner of the Institute’s roof top at ~30 m above local ground are constantly flushed and air sampling to our gas chromatographic system (Combi-GC) is performed quasi-continuously two to four times within 30 min. The air is analysed for its CO$_2$, CO, CH$_4$, N$_2$O, SF$_6$ and H$_2$ mixing ratios. For the present analysis, we use hourly mean values from both intake lines. For details of the measurement technique, see Gamnitzer et al. (2006) and Hammer et al. (2009). Typical measurement precision for CO$_2$ is better than ±0.15 ppm and for CO better than ±2.5%. Air sampling for the week-long integrated $^{14}$CO$_2$ samples is taken from the southwesterly inlet line. Atmospheric CO$_2$ for $^{14}$CO$_2$ analysis is absorbed in CO$_2$-free sodium hydroxide solution. Samples are collected only during nighttime (from 1900 to 0700 local time) to reduce the influence from very local traffic close to the sampling site during the day (Levin et al., 2003). From the analysis of the diurnal cycles of the $\Delta$CO/FFCO$_2$, we learned that the night-time mean lies systematically above the daily average ratio by about 2–6% (with the stronger influence during summer time), thus this selective sampling does not significantly alter our results. $^{14}$C analysis of the integrated samples is performed in the Heidelberg Radiocarbon Laboratory by conventional counting. Details of the sampling and analysis techniques can be found in Levin et al. (1980) and Kromer and Münich (1992). The typical $^{14}$CO$_2$ measurement precision of individual samples is $\Delta^{14}$C = ±2–3‰. As described by Levin et al. (2003), we make a correction of the integrated samples for a small but significant influence of $^{14}$CO$_2$ emissions from a nearby nuclear power plant. Due to the uncertainty of this correction, the uncertainty
of corrected \( \Delta^{14}C \) values is increased to \( \pm 3\%e \). From January 2002 until March 2003 as well as from July 2005 until April 2006 samples were integrated over 2 weeks. For the rest of the study period, week-long integrated samples were collected.

2.3. Grab samples

For our study it is especially important to assess variations of the \( \Delta CO/\Delta FFCO_2 \) ratio on short (diurnal) timescales. Therefore, an automated flask sampling system (Neubert et al., 2004) was used to fill grab samples. Twenty 2.5-l glass flasks are flushed continuously, consecutively one after the other in hourly intervals. After a so-called diurnal event consisting of 10–20 individual flasks has been collected, automated sampling is stopped and the air is analysed at the Combi-GC for trace gas mixing ratios and later on the CO\(_2\) is cryogenically extracted for \( ^{14}C \) analysis. Most of the samples collected during 2001–2005 were analysed by AMS technique at the Groningen Radiocarbon laboratory with a typical measurement uncertainty of \( \pm 5–10\%e \) (Gammitzer et al., 2006). The samples collected from 2005 onwards were analysed at the AMS laboratory of the Max-Planck-Institute for Biogeochemistry in Jena, Germany, with a typical measurement uncertainty of \( \pm 2–3\%e \).

2.4. Calculating regional fossil fuel CO\(_2\) offsets

Calculation of the regional fossil fuel CO\(_2\) offset \( \Delta FFCO_2 \) is based on the assumption that the measured (meas) CO\(_2\) mixing ratio consists of three components, (1) the background (bg), (2) a regional biogenic (bio) and (3) a regional fossil fuel (\( \Delta FFCO_2 \)) CO\(_2\) component, with all three components having characteristic \( \Delta^{14}C \) values. \( \Delta FFCO_2 \) can then be estimated from eq. (1) [the derivation can be found in Levin et al. (2008)] to

\[
\Delta FFCO_2 = \frac{CO_{2bg} (\Delta^{14}C_{bg} - \Delta^{14}C_{meas}) - CO_{2meas} (\Delta^{14}C_{meas} - \Delta^{14}C_{bio})}{\Delta^{14}C_{bio} + 1000}
\]

(1)

Besides mean CO\(_2\) and \( \Delta^{14}C \) measured at the sampling site, this requires knowledge of the background mixing ratios of CO\(_2bg\) and its \( \Delta^{14}C_{bg}\). For Heidelberg, we use the continental clean-air site Jungfraujoch measurements as background for \( ^{14}C \). The background CO\(_2\) data were taken from the Atlantic station Mace Head (Messager et al., 2008; GLOBALVIEW-CO\(_2\), 2009) as no adequate time-series from the Jungfraujoch are available for the whole period of investigation. Using different sites as background for CO\(_2\) and \( ^{14}C \) introduces an inevitable additional but small error to our estimate. A comparison of the \( ^{14}CO_2 \) measurements from Jungfraujoch and Mace Head, however, suggest a mean FFCO\(_2\) surplus at Jungfraujoch of about 0.5 ppm compared to the marine background at Mace Head (Levin et al., 2010). As in Levin et al. (2008), \( \Delta^{14}C_{bio}\) of the biogenic CO\(_2\) component was estimated from model calculations by Levin et al. (2010) for mid latitudes of the northern hemisphere; we hereby assumed that half of the biospheric component originates from heterotrophic respiration while the other half is from autotrophic respiration which can be approximated by atmospheric background \( \Delta^{14}C_{bg}\). With these assumptions, \( \Delta^{14}C_{bio}\) changes from approximately 100\%e in 2002 to \~70\%e at the end of 2008.

The sensitivity of our estimate to the chosen biospheric \( \Delta^{14}C \) is rather small: Assuming that biosphere and atmosphere are in equilibrium would yield a mean bias of \(-0.45\) ppm \( \Delta FFCO_2 \) for our observation period, typically varying between \(-0.1\) and \(-0.8\) ppm.

2.5. Calculating weekly \( \Delta CO/\Delta FFCO_2 \) ratios and subsequent ‘simple’ and ‘advanced’ hourly CO-based \( \Delta FFCO_2 \)

The regional weekly mean CO offset at the sampling site is calculated here as the difference between Jungfraujoch CO data (Zellweger et al., 2009) [smoothed with a harmonic regression fitting routine by Nakazawa et al. (1997)] and the measured hourly CO mixing ratio. All values were then averaged over the integration period of the \( ^{14}C \) sample (week-long or 2-week-long), and \( \Delta CO/\Delta FFCO_2 \) ratios are calculated. Note that for the Heidelberg measurements the integrated \( ^{14}C \) sampling is night-time selected to avoid a bias from very local pollution during daytime. The long-term mean from 2002 to 2009 of the individual ratios is then used to estimate the simple CO-based hourly FFCO\(_2\) offsets from hourly \( ^{14}CO_2 \) data according to

\[
\Delta FFCO_2^{\text{hourly}} = \frac{\Delta CO^{\text{hourly}} (\Delta FFCO_2^{^{14}C\text{-based}}/\Delta CO^{\text{manny}})_{\text{mean 2002–2009}}}{\Delta CO^{\text{hourly}} (\Delta FFCO_2^{^{14}C\text{-based}}/\Delta CO^{\text{manny}})_{\text{smoothed}}}
\]

(2)

In the advanced CO-based approach, we use the individual ratios of \( \Delta CO/\Delta FFCO_2 \) for calibration instead of the long-term mean to derive hourly \( \Delta FFCO_2 \) from hourly \( \Delta CO \) according to Levin and Karstens (2007b)

\[
\Delta FFCO_2^{\text{hourly}} = \Delta CO^{\text{hourly}} (\Delta FFCO_2^{^{14}C\text{-based}}/\Delta CO^{\text{manny}})_{\text{weekly smoothed}}
\]

(3)

When applying eq. (3) ratios are smoothed using a binomial filter, which is the mathematical representation of the fact, that changes of the \( \Delta CO/\Delta FFCO_2 \) ratio are expected to take place rather continuously over time and not abruptly from week to week, which would lead to discontinuities in the calculated hourly \( \Delta FFCO_2 \) record.

2.6. Including diurnal variations in the hourly fossil fuel CO\(_2\) estimates

Equation (3) implies a constant ratio of \( \Delta CO/\Delta FFCO_2 \) over a whole week. This assumption is well in line with time-curves from emission inventories describing day to day variations. For weekdays, the \( \Delta CO/\Delta FFCO_2 \) ratio is assumed constant in up-to-date emission models (Friedrich et al., 2003; IER, 2008), and the mean \( \Delta CO/\Delta FFCO_2 \) ratio only differs
slightly on weekends. Hence the mean emission ratio changes from day to day should be rather small. Yet from emission ratio data it is reasonable to assume significant variations of the \( \Delta CO/\Delta FFCO_2 \) ratio on the diurnal timescale. To comprise this variability in the hourly FFCO\(_2\)-algorithm, we determined the mean diurnal variation from grab samples (Section 2.3). From these data we can deduce an average hourly correction function \( \omega(t) \), recurring after 24 h, whereby \( \omega(t) \) is given as \( \text{Ratio}_{\text{diurnal}} \text{mean} / \text{Ratio}_{\text{diurnal}} \text{meas} (t) \). The daily mean ratio was found to be about 2–6% lower than the ratio determined for nighttime only. Thus, \( \omega(t) \) would have a mean value of 1.02–1.06. This bias is larger in summer than in winter, but as this correction is small compared to other effects, we are only using \( \omega(t) \) to rescale the diurnal cycle and intentionally keep the same mean, that is the diurnal mean of \( \omega(t) \) is set to 1. The measured mean diurnal ratios for every hour \( \text{Ratio}_{\text{diurnal}} \text{meas} \) are given in Fig. 3. The hourly \( \Delta FFCO_2 \) is calculated according to

\[
\Delta FFCO_2^{\text{hourly}} (t) = \Delta CO^{\text{hourly}} (t) \left( \frac{\Delta FFCO_2^{14C\text{-based}}}{\langle \Delta CO^{\text{hourly}} \rangle_{\text{smoothed}}} \right) \omega(t).
\] (4)

We call this approach *diurnal CO-based approach*.

3. Results and discussion

3.1. Long-term observations of the fossil fuel CO\(_2\) mixing ratio and the \( \Delta CO/\Delta FFCO_2 \) calibration ratio

Estimates of \( ^{14}C\)-based fossil fuel CO\(_2\) have been made in Heidelberg since 1986, and monthly mean values were reported earlier by Levin et al. (2003, 2008). Here we present the individual measurements, together with the observed mean CO offsets and \( \Delta CO/\Delta FFCO_2 \) ratios [Fig. 1, compare also Gammnitzer et al. (2006) for the first part of the data set]. There is a striking similarity between fossil fuel CO\(_2\) offsets and CO offsets in Heidelberg (Figs. 1a and b), however, as already noted by Gammnitzer et al. (2006), individual \( \Delta CO/\Delta FFCO_2 \) ratios still show large variations from week to week. For the time period shown in Fig. 1, the mean ratio is 15.5 ppb CO ppm\(^{-1}\) FFCO\(_2\) (median 14.6 ppb ppm\(^{-1}\)) with a standard deviation of all data of 5.6 ppb ppm\(^{-1}\) (interquartile range of 5.5 ppb ppm\(^{-1}\)). The standard deviation of the periods with 2-week-long integration is smaller, as variations on short time scales are smoothed in the integrated samples. Our observed ratio is close to the CO/FFCO\(_2\) ratios of emissions in the district of Heidelberg for the years 2004 and 2006, which are 14.8 and 13.6 ppb ppm\(^{-1}\), respectively (LUBW, 2006, 2009). The large standard deviation of weekly \( \Delta CO/\Delta FFCO_2 \) ratios of 5.6 ppb ppm\(^{-1}\) which is most probably due to the large heterogeneity of emissions with a large range of CO/FFCO\(_2\) emission ratios (Section 2.1), was the reason why Levin and Karstens (2007b) suggested using individually observed ratios and not a long-term mean ratio to calculate hourly fossil fuel CO\(_2\) offsets according to eq. (3).

3.2. The influence of weekly calibration on CO-based \( \Delta FFCO_2 \) estimates

Our time series, which is over 7 years long allows estimating the effect of weekly \( ^{14}C \) calibration of the advanced CO-based \( \Delta FFCO_2 \) estimates compared to using a mean ratio of \( \Delta CO/\Delta FFCO_2 \), either obtained from \( ^{14}C \) measurements over a certain period of time (simple CO-based approach), or obtained from bottom-up inventory data (as, e.g. Potosnak et al., 1999). Using a constant emission ratio from inventory data to calculate \( \Delta FFCO_2 \) from \( \Delta CO \) includes two additional errors compared to using a measured mean ratio: (a) the emission ratios are not perfectly known and can cover a wide range, depending on the inventory used (IER, 2008; EDGAR, 2009) and (b)
the catchment area or footprint contributing to the measured signals is generally not well known. The latter effect is illustrated in Fig. 2. Although we have been using the measured median value of 14.6 ppb CO ppm$^{-1}$ FFCO$_2$, we find large deviations of the weekly mean simple CO-based fossil fuel CO$_2$ offset from the true values (i.e. those individually calculated from the measured $^{14}$CO$_2$). The underestimation of FFCO$_2$ for offsets larger than 15 ppm is due to the effect that the mean weekly $^{14}$CO/FFCO$_2$ ratio and the mean weekly FFCO$_2$ mixing ratio are not completely independent. We find a mean $^{14}$CO/FFCO$_2$ ratio of only 12.9 ppb ppm$^{-1}$ for periods with measured FFCO$_2$ offsets larger than 15 ppm. These periods are most frequent during cold winter days, characterized by suppressed mixing of the (shallow) boundary layer. During these (cold winter) situations, we have enhanced emissions from domestic heating, while traffic emissions are not severely affected by ambient temperature (IER, 2008). As domestic heating emissions have lower $^{14}$CO/FFCO$_2$ ratios than the long-term mean emission ratio in Heidelberg (Section 2.1), this causes a covariance of the $^{14}$CO/FFCO$_2$ ratio and total FFCO$_2$, which is linked to temperature and atmospheric mixing conditions. Knowing this it is advisable to use the median of the distribution rather than the mean, as the median is less sensitive to outliers and (small) covariances occurring in extreme situations. Using the long-term mean $^{14}$CO/FFCO$_2$ ratio of 15.5 ppb ppm$^{-1}$ for the simple CO-based FFCO$_2$ determination would cause an underestimation of about 6% here.

### 3.3. The mean diurnal cycle of $^{14}$CO/FFCO$_2$

Besides the variations of the weekly $^{14}$CO/FFCO$_2$ ratio discussed earlier, we aim here at evaluating its behaviour on smaller time-scales. As both biospheric and anthropogenic CO$_2$ (and CO) fluxes are subject to strong diurnal variations, this time-scale is potentially of great importance. The observed mean diurnal cycle of $^{14}$CO/FFCO$_2$ for the winter period (November–February) was calculated from 89 grab samples and from 83 samples for summer (March–October) collected during pollution events (Fig. 3). The grab sample data from different events were pooled to obtain an hourly resolved record; the error bars in Fig. 3 denote the standard error of the mean. The fitted curves are derived using a Fast Fourier Transform filter, without error weighting. As there is no physical model that fully describes these diurnal variations, the only purpose of the curves is to obtain a smooth, continuous diurnal cycle which allows determining the coefficients $\omega_i$ (eq. 4) and correct the continuous FFCO$_2$ record for diurnal variations of the $^{14}$CO/FFCO$_2$ ratio.

The slightly smaller mean excess ratio of the winter time of $^{13.6 \pm 2.7}$ ppb CO ppm$^{-1}$ FFCO$_2$ compared to the summer value of $^{15.1 \pm 2.4}$ ppb ppm$^{-1}$ can be explained by the larger share of FFCO$_2$ from domestic heating and small consumers (emission ratio of 2.4–6.9 ppb ppm$^{-1}$) during winter time. Generally, the energy consumption in winter is more constant throughout the day than in summer, while traffic emissions are comparable in summer and in winter (Friedrich et al., 2003). Both diurnal $^{14}$CO/FFCO$_2$ courses show rather constant levels during the early morning and a rising ratio after 08:00 local time, which is in line with the statistics of the traffic sector, which also significantly increases in the early morning (Kühlwein et al., 2002). We find a time shift between emission changes and the response in the observed ratio, which may be interpreted as a reservoir effect, that is the observed ratio shows up as the integral of preceding emissions. During winter, the $^{14}$CO/FFCO$_2$ ratio rises...
smoothly after 08:00 local time, reaching its maximum around 18:00. We attribute the decline afterwards to the increased emissions from residential heating and the energy sector, which have cleaner combustion processes and thus have lower CO/FFCO₂ emission ratios; furthermore, the emissions of the traffic sector show a strong decrease in the evening hours.

In summer (which is actually a mean of measurements in spring, summer and autumn), we find high ΔCO/ΔFFCO₂ ratios in the early afternoon. Also assuming a large share from sources with high CO/FFCO₂ emission ratios can hardly explain values above 20 ppb ppm⁻¹ as there still should be a significant share of FFCO₂ emissions from industrial sources with low emission ratios. One reason for this surprisingly elevated ratio may be a possible contribution of ¹⁴C-enriched CO₂ from heterotrophic respiration, which shows a strong temperature dependency and thus maximum fluxes in the afternoon (Subke et al., 2003; Bernhardt et al., 2006). Although the mean contribution from biospheric CO₂ has been corrected for in the weekly fossil fuel concentrations and also when calculating hourly fossil fuel CO₂ mixing ratios (eq. 1), diurnal variations of the isotope flux (i.e. compensating CO₂ fluxes from photosynthesis and respiration which may cancel each other but still may cause a net ¹⁴C signal in the atmosphere) are not accounted for. As ΔFFCO₂ is calculated from the depletion of ¹⁴C between Heidelberg and a reference site (in our case Jungfraujoch), this additional ¹⁴CO₂ from the biosphere will ‘artificially’ reduce the offset, hence reducing the calculated local FFCO₂ excess and thus increasing the ΔCO/ΔFFCO₂ ratio. Another important reason for this elevation beyond the expected range could be additional CO from the decomposition of Volatile Organic Compounds, which other studies also found to be important in urban environments and contributing up to 20 ppb of additional CO during the afternoon hours (Griffin et al., 2007).

### 3.4. Comparing the advanced and diurnal CO-based with ¹⁴C-based ΔFFCO₂ estimates from grab sample data

The diurnal CO-based hourly ΔFFCO₂ estimates calculated taking into account the diurnal cycle of the ratio [according to eq. (4)] and the advanced CO-based hourly ΔFFCO₂ estimates, calculated according to eq. (3) without diurnal cycle, are compared in Fig. 4 with the results of the ΔFFCO₂ mixing ratios calculated from direct ¹⁴CO₂ measurements of grab samples. The advanced CO-based estimates are generally in good agreement with the ¹⁴C-based grab sample results, although systematically lower. Including the diurnal variations of ΔCO/ΔFFCO₂ the slope increases from 0.80 to 0.85. Also the correlation coefficient R² slightly increases from 0.86 to 0.89 in this case, and the sum of the root mean square differences decreases, indicating that applying this correction helps to better estimate the true ΔFFCO₂. Both x and y errors were accounted for in calculating the slope and R² using a weighted total least-squares algorithm from Krystek and Anton (2007). That both estimates are significantly lower by up to 20% than ΔFFCO₂ directly calculated from ¹⁴C measurements in the flask samples can partly be attributed to the fact, that we are here comparing grab samples collected over a few minutes only with hourly smoothed data that generally show a smaller variability. However, a more important issue we have to address here is that our integrated sampling could lead...
to a substantial bias in the ΔCO/ΔFFCO₂ ratio. As the ratios are weighted by the total ΔFFCO₂ the weekly mean will be biased towards times with high ΔFFCO₂. Comparing the mean weekly ratio of 15.5 ± 0.3 ppb ppm⁻¹ determined from the week-long integrated sampling with the mean ratios obtained from the 172 flask samples of 14.1 ± 0.5 ppb ppm⁻¹ we find a significant difference of 10±6%. This overestimation of the ΔCO/ΔFFCO₂ ratio from the integrated sampling compared to the flasks translates to a systematic underestimation of the derived ΔFFCO₂ (eq. 3) by 10 ± 6%. The general problem of the representativeness of any integrated approach and possible biases of the ratio of weekly mean ΔCO and ΔFFCO₂ from the true value, that is the weekly mean of hourly ΔCO/ΔFFCO₂ ratios, cannot be fully solved from observational data alone. To exactly quantify possible biases introduced by integration would need an accompanying modelling study. But in our case where also a large number of grab sample data are available, these could even be used to correct for part of the bias shown in Fig. 4. Altogether the standard deviation of the mean difference between the diurnal CO-based ΔFFCO₂ and the ¹⁴C-based ΔFFCO₂ is 25%. This is much better than any model-based estimates of ΔFFCO₂ using emission inventories. Experimentally derived diurnal CO-based ΔFFCO₂ estimates, if corrected for the integration bias discussed above, could, therefore, be a valuable tool to evaluate or even calibrate modelled ΔFFCO₂ (Geels et al., 2006; Peylin et al., 2009).

3.5. Implications of the diurnal calibration for the diurnal cycle of ΔFFCO₂

Besides the improved accuracy of the diurnal CO-based approach compared to the advanced approach, applying the diurnal correction has further implications for the ΔFFCO₂ record, especially the mean diurnal hourly ΔFFCO₂ values obtained from grab samples.

4. Conclusions and Outlook

Our results imply that ΔCO is a good proxy to estimate regional FFCO₂ offsets at hourly resolution in an urban environment. Although there is a large temporal variability of anthropogenic emissions of CO and FFCO₂ which is different for both gases, this can be accounted for by using weekly ¹⁴CO₂ calibrations of the ΔCO/ΔFFCO₂ ratio. Analysing grab samples for ¹⁴CO₂, we...
found systematic variations of the $\Delta$CO/$\Delta$FFCO$_2$ ratio on the diurnal time-scale of up to 30%. These diurnal variations can be accounted for in an extended algorithm to calculate hourly $\Delta$FFCO$_2$ with two season-specific diurnal correction functions, one for summer and one for winter. The observed diurnal variations are in-line with traffic and energy use emission statistics, and also seem to show an influence from biospheric heterotrophic respiration of CO$_2$ enriched in $^{14}$C and CO from photo-oxidation of VOCs. Applying the diurnal CO-based approach significantly alters amplitude and phasing of the mean diurnal cycle of $\Delta$FFCO$_2$ in winter, which is important if CO$_2$ exchange processes on the diurnal timescale shall be evaluated. We could show that using individually weekly mean $\Delta$CO/$\Delta$FFCO$_2$ ratios instead of one constant value largely improves the CO-based $\Delta$FFCO$_2$ estimates (by $\sim$30%). However, these ratios of week-long integrated $\Delta$CO and week-long integrated $^{14}$C-based $\Delta$FFCO$_2$ seem to be biased towards high values resulting in 15% too low CO-based $\Delta$FFCO$_2$ offsets. If sufficient individual diurnally collected grab samples (from all seasons) are available, which are required to determine the diurnal cycle of the $\Delta$CO/$\Delta$FFCO$_2$ ratio, these can also be used to correct for part of this bias.

For urban and suburban sites with relatively large fossil fuel CO$_2$ signals our results are promising as they will, if combined with air mass trajectory data, allow to assess emission inventories. This concerns not only emission factors but also the hourly profiles of emissions. We, therefore, suggest to set up a dense observational network of combined integrated and occasional diurnal $^{14}$CO$_2$ and continuous CO measurements to provide the necessary input data for determining the fossil CO$_2$ component at high temporal resolution, an important pre-requisite to better quantifying the non-fossil carbon fluxes. The advantage of a combined approach of using grab and integrated samples over a purely grab samples based approach is twofold: (1) the integrated $^{14}$C samples allow measuring the true mean value of $\Delta$FFCO$_2$ at a station and (2) they provide calibration of the $\Delta$CO/$\Delta$FFCO$_2$ ratio at a much better precision than, for example daily flasks could do. The big advantage is, thus, that this approach needs a much smaller number of $^{14}$C analyses, therewith reducing the costs of monitoring.

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