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$_2$ (ΔFFCO$_2$) mixing ratios. We investigate three different ^{14}C calibration schemes to calculate ΔFFCO$_2$: (1) the long-term median ΔCO/ΔFFCO$_2$ ratio of 14.6 ppb ppm^{-1} (mean: 15.5 $\pm$ 5.6 ppb ppm^{-1}), (2) individual (2-)week-long integrated ΔCO/ΔFFCO$_2$ ratios, which take into account the large week-to-week variability of $\pm$5.6 ppb ppm^{-1} (1σ; interquartile range: 5.5 ppb ppm^{-1}), and (3) a calibration which also includes diurnal changes of the ΔCO/ΔFFCO$_2$ ratio. We show that in winter a diurnally changing ΔCO/ΔFFCO$_2$ ratio provides a much better agreement with the direct ^{14}C-based hourly ΔFFCO$_2$ estimates whereas summer values are not significantly improved with a diurnal calibration. Using integrated ^{14}CO$_2$ samples to determine weekly mean ΔCO/ΔFFCO$_2$ ratios introduces a bias in the CO-based ΔFFCO$_2$ estimates which can be corrected for with diurnal grab sample data. Altogether our ^{14}C-calibrated CO-based method allows determining ΔFFCO$_2$ at a semi-polluted site with a precision of approximately $\pm$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 (ΔFFCO$_2$) 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; Turnbull 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 ΔCO/ΔFFCO$_2$ 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 ΔCO/ΔFFCO$_2$ 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$_2$

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 'bottom-up CO-based' approach. The second method uses the measured long-term mean $\Delta CO/\Delta FFCO_2$ ratio determined from week-long or 2-week-long integrated CO mixing ratios and [14]CO$_2$-based $\Delta FFCO_2$ 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 $\Delta CO/\Delta FFCO_2$ ratio, and call this approach the 'diurnal CO-based' approach. Hourly $\Delta CO/\Delta FFCO_2$ 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 $\Delta FFCO_2$ 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 inversion situations, 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 $\Delta CO/\Delta FFCO_2$, 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 Münnich (1992). The typical [14]CO$_2$ measurement precision of individual samples is $\Delta^{14}C = \pm 2$–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 $\pm 3\permil$. 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 $^{14}CO_2$ 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 ± 5–$10\permil$ (Gamnitzer 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 ± 2–$3\permil$.

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

$$\Delta FFCO_2 = \frac{CO_{2bg}\left(\Delta^{14}C_{bg} - \Delta^{14}C_{bio}\right) - CO_{2meas}\left(\Delta^{14}C_{meas} - \Delta^{14}C_{bio}\right)}{\Delta^{14}C_{bio} + 1000}. \quad (1)$$

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-CO2, 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 $^{14}CO_2$ 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 $100\permil$ in 2002 to $\sim 70\permil$ 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 $\Delta^{14}C$ 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 ΔCO data according to

$$\Delta FFCO_2^{hourly} = \Delta CO^{hourly} \left(\frac{\Delta FFCO_2^{14C\text{-based}}}{\langle \Delta CO^{hourly}\rangle}\right)^{mean:2002-2009}. \quad (2)$$

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 ΔCO according to Levin and Karstens (2007b)

$$\Delta FFCO_2^{hourly} = \Delta CO^{hourly} \left(\frac{\Delta FFCO_2^{14C\text{-based}}}{\langle \Delta CO^{hourly}\rangle}\right)^{weekly}_{smoothed}. \quad (3)$$

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 Ratio$_{\text{mean}}^{\text{diurnal}}$/Ratio$_{\text{meas}}^{\text{diurnal}}(t)$. 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 Ratio$_{\text{meas}}^{\text{diurnal}}$ are given in Fig. 3. The hourly $\Delta FFCO_2$ is calculated according to

$$\Delta FFCO_2^{\text{hourly}}(t) =$$
$$\Delta CO^{\text{hourly}}(t) \left(\frac{\Delta FFCO_2^{^{14}\text{C-based}}}{\langle \Delta CO^{\text{hourly}} \rangle} \right)_{\text{smoothed}}^{\text{weekly}} \omega(t). \quad (4)$$

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 Gam-

nitzer 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 Gamnitzer 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 ΔCO 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)
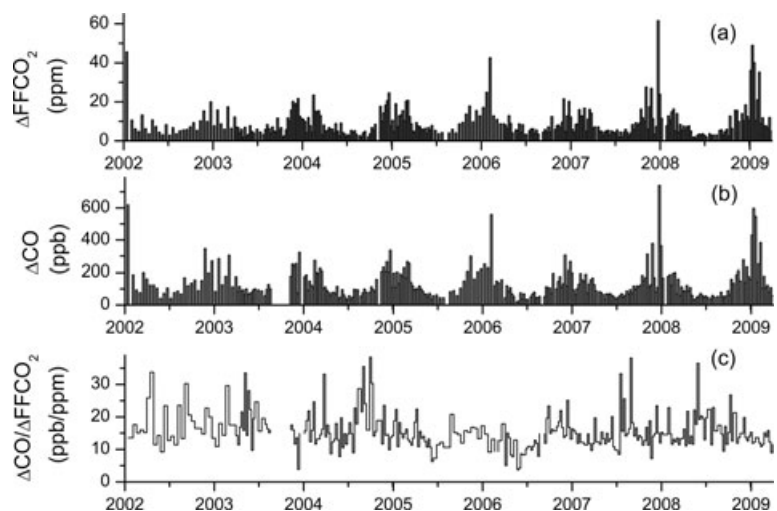

Fig. 1. Integrated ^{14}C-based fossil fuel CO$_2$ offset (a), the CO offset (b) as well as the respective ratio of both (c). There is a striking covariance of $\Delta FFCO_2$ and ΔCO, however, the ratio still shows a large variability (see text).
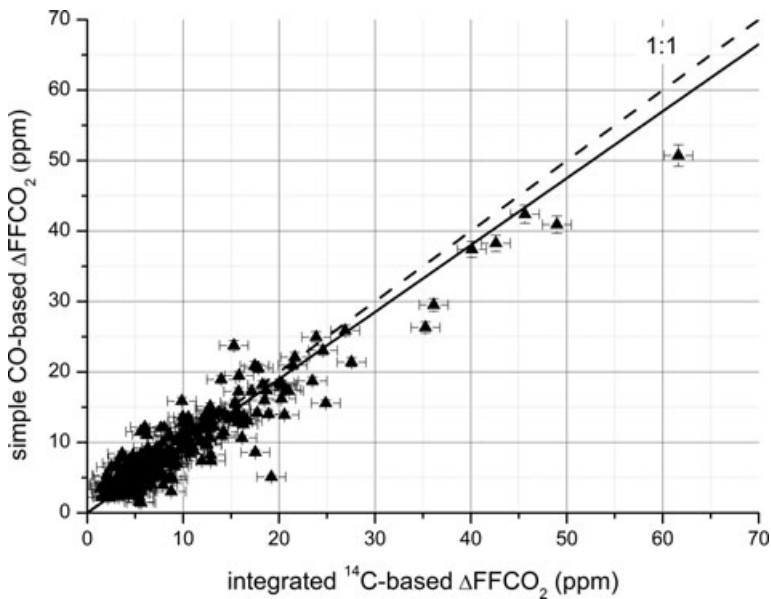
Fig. 2. Comparison of simple CO-based $\Delta FFCO_2$ estimates for the integrated samples using a constant ratio of $\Delta CO/\Delta FFCO_2 = 14.6$ ppb/ppm (i.e. the median of all measured values in Fig. 1c) with respective individual ^{14}C-based $\Delta FFCO_2$ offsets. Using weekly integrated ratios for the calibration thus reduces the uncertainty of the CO-based $\Delta FFCO_2$ estimates by $\sim$30% (i.e. the interquartile range of the $\Delta CO/\Delta FFCO_2$ ratios in Fig 1c) compared to the simple CO-based estimate.

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 $\Delta FFCO_2$ for offsets larger than 15 ppm is due to the effect that the mean weekly $\Delta CO/\Delta FFCO_2$ ratio and the mean weekly $\Delta FFCO_2$ mixing ratio are not completely independent. We find a mean $\Delta CO/\Delta FFCO_2$ 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 $\Delta CO/\Delta FFCO_2$ ratios than the long-term mean emission ratio in Heidelberg (Section 2.1), this causes a covariance of the $\Delta CO/\Delta FFCO_2$ ratio and total $\Delta FFCO_2$, 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 $\Delta CO/\Delta FFCO_2$ ratio of 15.5 ppb ppm^{-1} for the simple CO-based $\Delta FFCO_2$ determination would cause an underestimation of about 6% here.

3.3. The mean diurnal cycle of $\Delta CO/\Delta FFCO_2$

Besides the variations of the weekly $\Delta CO/\Delta FFCO_2$ 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 $\Delta CO/\Delta FFCO_2$ 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 ω_i (eq. 4) and correct the continuous $\Delta FFCO_2$ record for diurnal variations of the $\Delta CO/\Delta FFCO_2$ ratio.

The slightly smaller mean excess ratio of the winter time of 13.6 ± 2.7 ppb CO ppm^{-1} FFCO$_2$ compared to the summer value of 15.1 ± 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 $\Delta CO/\Delta FFCO_2$ 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 $\Delta CO/\Delta FFCO_2$ ratio rises
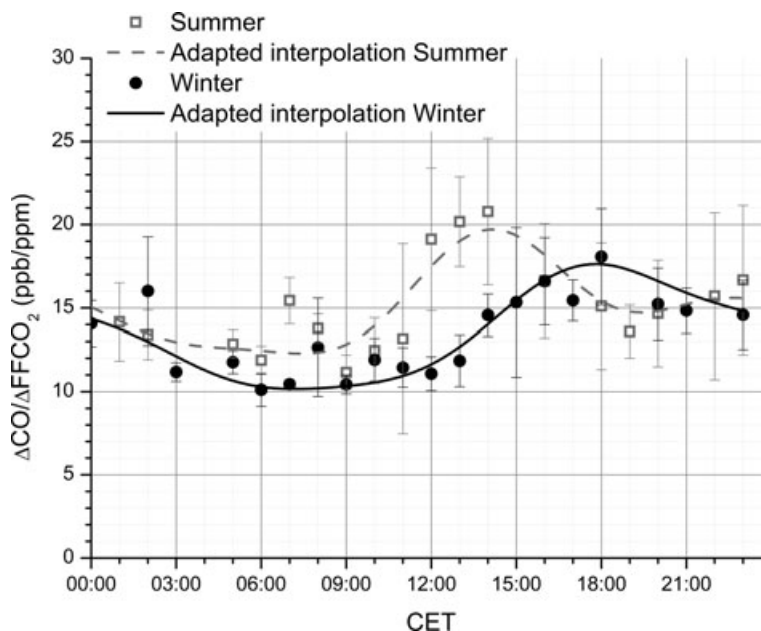
Fig. 3. Mean diurnal cycle of the $\Delta CO/\Delta FFCO_2$ obtained from grab samples collected during pollution events during 2002–2009.

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 $CO/FFCO_2$ 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 $\Delta CO/\Delta FFCO_2$ ratios in the early afternoon. Also assuming a large share from sources with high $CO/FFCO_2$ emission ratios can hardly explain values above 20 ppb ppm^{-1} as there still should be a significant share of $FFCO_2$ emissions from industrial sources with low emission ratios. One reason for this surprisingly elevated ratio may be a possible contribution of ^{14}C-enriched CO_2 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 CO_2 has been corrected for in the weekly fossil fuel concentrations and also when calculating hourly fossil fuel CO_2 mixing ratios (eq. 1), diurnal variations of the isotope flux (i.e. compensating CO_2 fluxes from photosynthesis and respiration which may cancel each other but still may cause a net ^{14}C signal in the atmosphere) are not accounted for. As $\Delta FFCO_2$ is calculated from the depletion of Δ^{14}C between Heidelberg and a reference site (in our case Jungfraujoch), this additional $^{14}CO_2$ from the biosphere will 'artificially' reduce the offset, hence reducing the calculated local $FFCO_2$ excess and thus increasing the $\Delta CO/\Delta FFCO_2$ 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 ^{14}C-based $\Delta FFCO_2$ estimates from grab sample data

The diurnal CO-based hourly $\Delta FFCO_2$ estimates calculated taking into account the diurnal cycle of the ratio [according to eq. (4)] and the advanced CO-based hourly $\Delta FFCO_2$ estimates, calculated according to eq. (3) without diurnal cycle, are compared in Fig. 4 with the results of the $\Delta FFCO_2$ mixing ratios calculated from direct $^{14}CO_2$ measurements of grab samples. The advanced CO-based estimates are generally in good agreement with the ^{14}C-based grab sample results, although systematically lower. Including the diurnal variations of $\Delta CO/\Delta FFCO_2$ the slope increases from 0.80 to 0.85. Also the correlation coefficient R^2 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 $\Delta FFCO_2$. Both x and y errors were accounted for in calculating the slope and R^2 using a weighted total least-squares algorithm from Krystek and Anton (2007). That both estimates are significantly lower by up to 20% than $\Delta FFCO_2$ directly calculated from ^{14}C 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
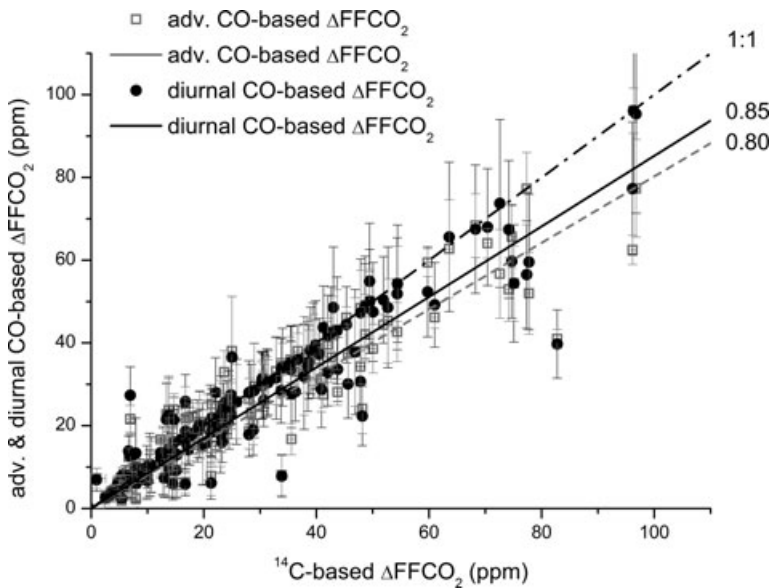
Fig. 4. Comparison of advanced and diurnal CO-based hourly $\Delta FFCO_2$ with direct ^{14}C-based hourly $\Delta FFCO_2$ values obtained from grab samples.

to a substantial bias in the $\Delta CO/\Delta FFCO_2$ ratio. As the ratios are weighted by the total $\Delta FFCO_2$ the weekly mean will be biased towards times with high $\Delta FFCO_2$. 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 $10 \pm 6\%$. This overestimation of the $\Delta CO/\Delta FFCO_2$ ratio from the integrated sampling compared to the flasks translates to a systematical underestimation of the derived $\Delta FFCO_2$ (eq. 3) by $10 \pm 6\%$. The general problem of the representativeness of any integrated approach and possible biases of the ratio of weekly mean ΔCO and $\Delta FFCO_2$ from the true value, that is the weekly mean of hourly $\Delta CO/\Delta FFCO_2$ 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 $\Delta FFCO_2$ and the ^{14}C-based $\Delta FFCO_2$ is 25%. This is much better than any model-based estimates of $\Delta FFCO_2$ using emission inventories. Experimentally derived diurnal CO-based $\Delta FFCO_2$ estimates, if corrected for the integration bias discussed above, could, therefore, be a valuable tool to evaluate or even calibrate modelled $\Delta FFCO_2$ (Geels et al., 2006; Peylin et al., 2009).

### 3.5. *Implications of the diurnal calibration for the diurnal cycle of $\Delta FFCO_2$*

Besides the improved accuracy of the diurnal CO-based approach compared to the advanced approach, applying the diurnal correction has further implications for the $\Delta FFCO_2$ record,

especially the mean diurnal cycle is altered (Fig. 5). To be able to assess daily recurring processes such as anthropogenic emissions or biological activity, a proper knowledge of the diurnal cycle of $\Delta FFCO_2$ which largely contributes to the diurnal CO_2 signal in continental areas, is indispensible. Comparing the diurnal course of $\Delta FFCO_2$ using a constant $\Delta CO/\Delta FFCO_2$ ratio (eq. 3) compared to a variable ratio (eq. 4), we find a distinct change of the mean amplitude and phasing of the diurnal cycle during winter time (Fig. 5), while the differences in summer are less pronounced, but still recognizable in the amplitude. Here, again, the flask sampling data is used as the basis for evaluating the advanced CO-based and the diurnal CO-based approach. The general course and the variability of the diurnal CO-based $\Delta FFCO_2$ in winter agree better with the ^{14}C-based data than the advanced CO-based $\Delta FFCO_2$ estimate. However, the diurnal calibration seems not to significantly improve the deviation of $\Delta FFCO_2$ from the true ^{14}C-based values during summer. But one has to be aware, that even the ^{14}C-based $\Delta FFCO_2$ estimations of $\Delta FFCO_2$ may be slightly influenced by biospheric [14]CO_2. Still both the advanced and the diurnal CO-based $\Delta FFCO_2$ capture the diurnal variation of the $\Delta FFCO_2$ found in Heidelberg, which is dominated by vertical mixing processes, but also shows pronounced rush hour emissions. Especially for the winter-time the improvement by including the diurnally varying ratio is visible.

4. Conclusions and Outlook

Our results imply that ΔCO is a good proxy to estimate regional $FFCO_2$ offsets at hourly resolution in an urban environment. Although there is a large temporal variability of anthropogenic emissions of CO and $FFCO_2$ which is different for both gases, this can be accounted for by using weekly [14]CO_2 calibrations of the $\Delta CO/\Delta FFCO_2$ ratio. Analysing grab samples for [14]CO_2, we

Fig. 5. Normalized diurnal variation of fossil fuel CO_2 offsets for Heidelberg in (a) summer and (b) winter, calculated from CO offsets with and without taking into account the diurnal variation of the $\Delta CO/\Delta FFCO_2$ ratio. Individual data points are mean ^{14}C-based values with standard errors of the mean.
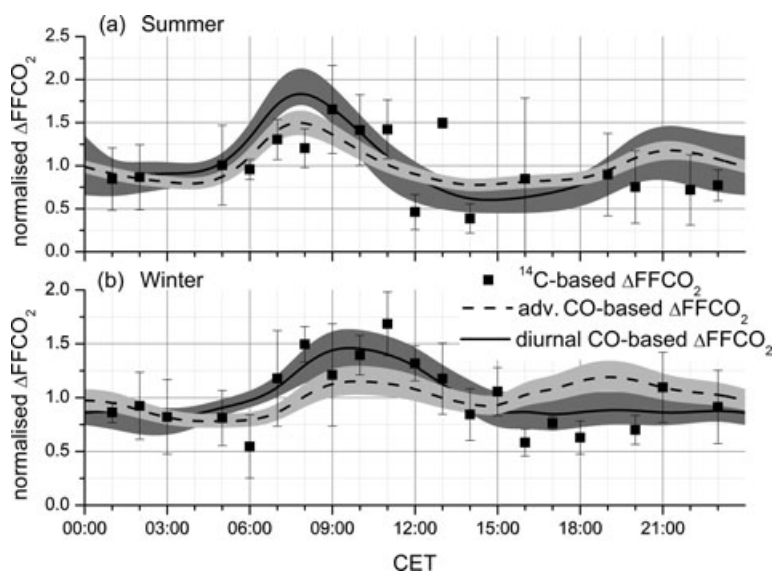
found systematic variations of the $\Delta CO/\Delta FFCO_2$ ratio on the diurnal time-scale of up to 30%. These diurnal variations can be accounted for in an extended algorithm to calculate hourly $\Delta FFCO_2$ with two season-specific diurnal correction functions, one for summer and one for winter. 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 ~30%). However, these ratios of week-long integrated ΔCO and week-long integrated ^{14}C-based $\Delta FFCO_2$ seem to be biased towards high values resulting in 15% too low CO-based 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 Δ^{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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