

Inferring high-resolution fossil fuel CO₂ records at continental sites from combined ¹⁴CO₂ and CO observations

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ABSTRACT

An uncertainty estimate of a purely observational approach to derive hourly regional fossil fuel CO₂ offsets ($\Delta\text{CO}_2(\text{foss})$) at continental CO₂ monitoring sites is presented. Weekly mean ¹⁴C-based fossil fuel CO₂ mixing ratios and corresponding regional CO offsets (ΔCO) are proposed to determine weekly mean $\Delta\text{CO}/\Delta\text{CO}_2(\text{foss})$ ratios in order to derive hourly $\Delta\text{CO}_2(\text{foss})$ mixing ratios from hourly ΔCO measurements. Respective regional model estimates of CO and CO₂(foss) are applied to test this approach and obtain root mean square errors of the correspondingly determined regional hourly fossil fuel CO₂ component. The method is further validated with campaign-based observations in Heidelberg. The uncertainty of the proposed method turns out to increase with decreasing fossil fuel CO₂ fraction ranging from about 15% up to 40% for continental Europe. Together with the uncertainty of the $\Delta\text{CO}/\Delta\text{CO}_2(\text{foss})$ ratio, which is determined by the precision of the ¹⁴CO₂ measurement, this method is still more accurate and precise than any model-based approach.

1. Introduction

The greenhouse gases budget over Europe and other highly populated regions is largely influenced by anthropogenic emissions. Even in remote areas of, for example, Europe, about 30%–50% of the continental CO₂ signal is originating from fossil fuel (i.e. coal, oil and natural gas) burning (Levin and Karstens, 2007). Separating the fossil fuel from the natural biogenic signal in the atmosphere is, therefore, a crucial task for quantifying exchange fluxes of the continental biosphere from atmospheric observations and inverse modelling. As the biospheric CO₂ signals in the atmosphere are highly variable with diurnal and seasonal cycles caused by respective changes in the fluxes combined with changing atmospheric transport, also the fossil fuel CO₂ signal needs to be determined with high temporal resolution. ‘Monitoring’ fossil fuel CO₂ in the atmosphere is, in principle, possible via radiocarbon (¹⁴CO₂) measurements. CO₂ from burning of fossil fuels, due to their long storage time of several hundred million years, is essentially free of ¹⁴C. Adding fossil fuel CO₂ to the atmosphere, therefore, leads not only to an increase in the CO₂ mixing ratio but also to a decrease in the ¹⁴C/¹²C ratio in atmospheric CO₂ (Suess, 1955). From a ¹⁴CO₂

measurement at a polluted sampling site, for example, in the boundary layer on the continent, we can directly calculate the regional fossil fuel CO₂ surplus if the undisturbed background ¹⁴CO₂ level is known (Levin et al., 2003). However, determining hourly fossil fuel CO₂ from hourly ¹⁴CO₂ measurements at high precision would be a very expensive undertaking, which so far has only been realized on a campaign basis (e.g. Gamnitzer et al., 2006).

Due to the lack of continuous high-resolution ¹⁴CO₂ observations, other tracers have been discussed in the past which could possibly serve as proxy for fossil fuel CO₂. In particular, the use of CO as a quantitative tracer of fossil fuel CO₂ has been investigated recently in a number of experimental and modelling studies (Gamnitzer et al., 2006; Rivier et al., 2006; Turnbull et al., 2006). In highly populated and industrialised regions, CO emissions are closely linked to those of fossil fuel CO₂: any fossil fuel combustion process with CO₂ as an end product is, to some extent, associated with the production of CO. However, the CO/CO₂ ratio of different fossil fuel combustion processes, such as domestic heating or emissions from traffic, can vary by orders of magnitude (Olivier et al., 2005; UNFCCC, 2005). Moreover, the chemical sink of CO in the atmosphere has strong diurnal and seasonal cycles, and CO also has a strong atmospheric source from oxidation of volatile organic compounds (VOCs) (Granier et al., 2000), thus complicating the use of this tracer for quantitative estimates (Potosnak et al., 1999; Gamnitzer et al.,

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2006). Also, accurately determining the $\text{CO}/\text{CO}_2(\text{foss})$ ratio of emissions from inventories which is necessary to use CO as a quantitative tracer for fossil fuel CO_2 is highly uncertain. Here, we suggest a purely observational approach to determine hourly fossil fuel CO_2 mixing ratios from the combination of $^{14}\text{CO}_2$ and CO observations, and provide an estimate of its uncertainty in polluted and semi-polluted regions over Europe using model simulations of fossil fuel CO_2 and CO. The method is further validated with measurements of hourly CO_2 , CO and $^{14}\text{CO}_2$ observations performed during a number of diurnal sampling campaigns in Heidelberg published by Gamnitzer et al. (2006).

2. Methods

We propose to estimate regional hourly atmospheric fossil fuel CO_2 mixing ratios ($\Delta\text{CO}_2(\text{foss})_{\text{hourly}}$) from, for example, weekly integrated $^{14}\text{CO}_2$ observations at a continuous CO_2 measurement site [providing the (weekly) mean regional fossil fuel CO_2 contribution ($\Delta\text{CO}_2(\text{foss})_{\text{weekly}}^{14\text{C-based}}$), combined with quasi-continuous, that is, hourly CO observations ($\Delta\text{CO}_{\text{hourly}}^{\text{meas}}$) according to eq. (1) [ΔCO and $\Delta\text{CO}_2(\text{foss})$ are the regional concentration offsets compared to free-tropospheric background air]:

$$\Delta\text{CO}_2(\text{foss})_{\text{hourly}} = \Delta\text{CO}_{\text{hourly}}^{\text{meas}} \frac{\Delta\text{CO}_2(\text{foss})_{\text{weekly}}^{14\text{C-based}}}{\langle \Delta\text{CO}_{\text{hourly}}^{\text{meas}} \rangle_{\text{weekly}}} \quad (1)$$

$\langle \Delta\text{CO}_{\text{hourly}}^{\text{meas}} \rangle_{\text{weekly}}$ denotes the weekly mean ΔCO offset. To estimate the uncertainty of this approach, we have used model-simulated $\Delta\text{CO}_2(\text{foss})$ and ΔCO records. Atmospheric mixing ratios of CO_2 and CO over Europe were calculated at hourly resolution for 2002 using the regional atmospheric transport model REMO (Chevallard et al., 2002). In this set up of REMO, the horizontal grid resolution is $55 \text{ km} \times 55 \text{ km}$ and the model domain covers the area north of 30°N . The same set-up of natural and anthropogenic CO_2 and CO sources and sinks as well as meteorological fields as in Gamnitzer et al. (2006) has been used here. For the fossil fuel CO_2 and CO emissions, this includes data from two independent inventories: (1) the Emission Database for Global Atmospheric Research (EDGAR), which provides *annual mean* emissions for the base years 1990, 1995 and 2000 on a global $1^\circ \times 1^\circ$ grid (Olivier et al., 2005); the emissions for the base year 2000 were used here for 2002 model calculations and (2) a new high-resolution emission inventory on a $50 \text{ km} \times 50 \text{ km}$ grid for the year 2000 with *hourly* emissions, and taking into account different emission characteristics on workdays compared to holidays, which is based on United Nations Framework Convention on Climatic Change (UNFCCC) statistics (Institute of Energy Economics and Rational Use of Energy (IER), University of Stuttgart, Germany; personal communication, 2004). The temporal disaggregation of this IER inventory was adjusted to the year 2002 concerning the changed weekdays compared to the year 2000.

In our study, we assume that the REMO-modelled CO_2 and CO mixing ratios represent the correct hourly mixing ratios of both gases over Europe. From these (simulated) hourly values, regional $\Delta\text{CO}_2(\text{foss})$ and ΔCO offsets were calculated as well as weekly means and subsequently weekly mean $\Delta\text{CO}/\Delta\text{CO}_2(\text{foss})$ ratios. As free tropospheric background $\text{CO}_2(\text{foss})$ and CO mixing ratios model simulations for the High Alpine station Jungfraujoch in the Swiss Alps (3450 m above sea level) were used. In a second step, we applied these mean ratios to the originally simulated high-resolution ΔCO record to recalculate a high-resolution $\Delta\text{CO}_2(\text{foss})$ record (which we then call ' $\Delta\text{CO}_2(\text{foss})$ recalculated') according to

$$\Delta\text{CO}_2(\text{foss})_{\text{hourly}}^{\text{recalculated}} = \Delta\text{CO}_{\text{hourly}}^{\text{model}} \frac{\langle \Delta\text{CO}_2(\text{foss})_{\text{hourly}}^{\text{model}} \rangle_{\text{weekly}}}{\langle \Delta\text{CO}_{\text{hourly}}^{\text{model}} \rangle_{\text{weekly}}} \quad (2)$$

The differences between the originally modelled hourly $\Delta\text{CO}_2(\text{foss})$ record and the $\Delta\text{CO}_2(\text{foss})$ record recalculated using eq. (2), provide an estimate of the minimum uncertainty of the method defined by eq. (1). We applied this test to all REMO results and evaluated it for three stations: (1) Heidelberg, which is located in the highly populated upper Rhine valley and which shows actually observed monthly mean fossil fuel CO_2 offsets relative to background air of about 5–20 ppm (Levin et al., 2003); (2) Lutjewad, a coastal site in the Netherlands with fossil fuel CO_2 offsets of about 3–10 ppm (Neubert, private communication, 2005); and (3) Schauinsland, a semi-remote mountain station in the Black Forest (1205 m above sea level), which experiences monthly mean fossil fuel CO_2 contributions of about 1–5 ppm (Levin et al., 2003).

3. Results from REMO simulations

Figures 1a and 1b show the results for Heidelberg with REMO simulations based on hourly IER and those based on annual mean EDGAR emissions, for February and July 2002. The $\Delta\text{CO}_2(\text{foss})$ REMO records named 'orig.' are the originally calculated values assumed to represent the true situation, the $\Delta\text{CO}_2(\text{foss})$ re-calc. values are recalculated according to eq. (2). The differences between original and recalculated hourly $\Delta\text{CO}_2(\text{foss})$ are caused by those parts of the variability in non fossil CO sources, in processes influencing the chemistry of CO and in the fossil fuel CO and CO_2 emissions which are taken care of in the REMO simulations but not in our simplified approach. The root mean square (rms) errors of the hourly deviations from the true values when using the weekly mean ratios and eq. (2) are about 18% in the case of IER emission inventories and about 14% in the case of EDGAR emissions. Deviations for EDGAR are smaller because, in addition to the CO-specific processes, they are caused only by differences in the $\text{CO}/\text{CO}_2(\text{foss})$ emission ratios in the different parts of the catchment area (which the original REMO calculations can take care of), whereas the

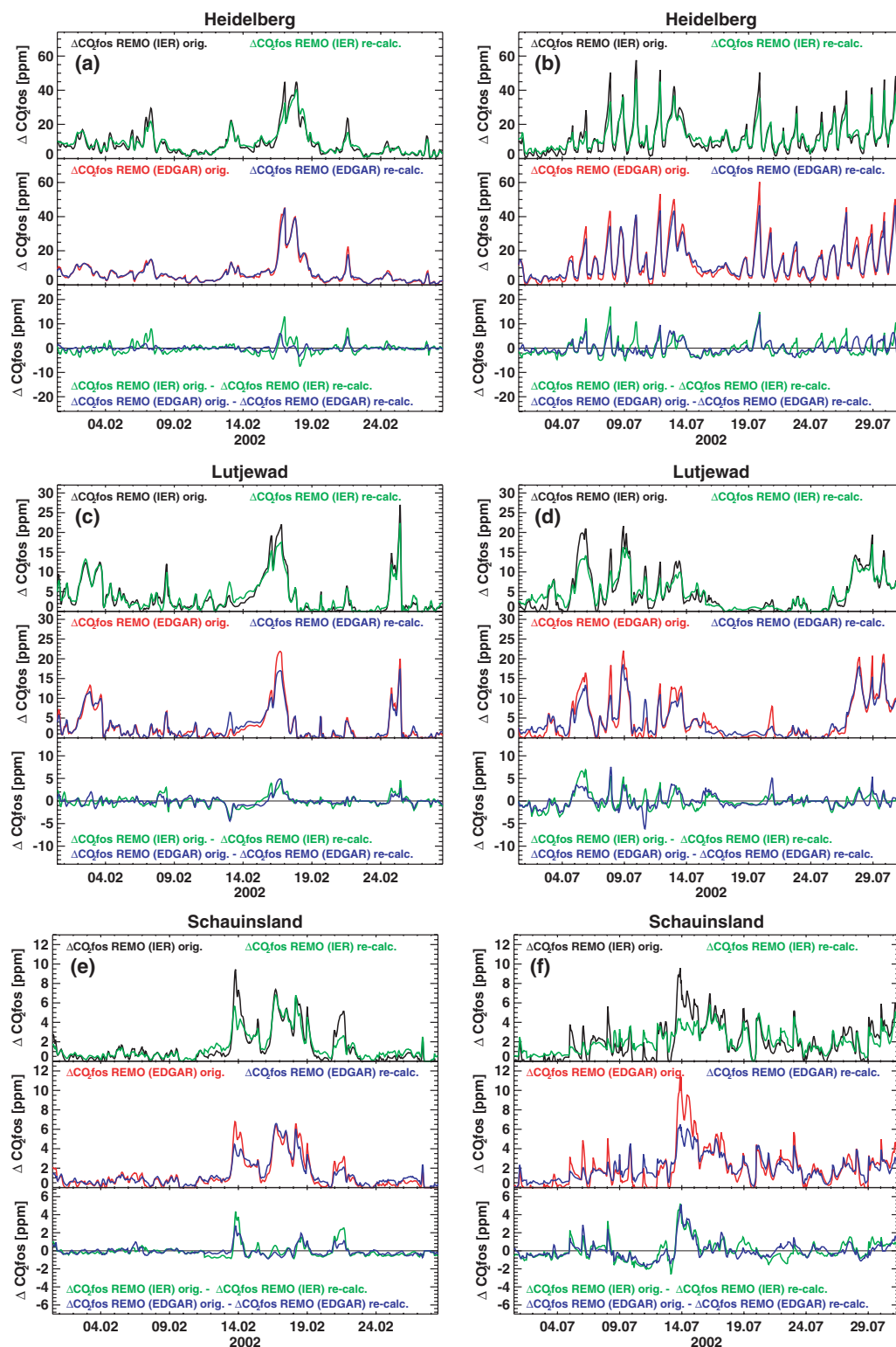


Fig. 1. Panels (a) and (b): comparison of $\Delta\text{CO}_2(\text{foss})$ estimates for Heidelberg during February (left-hand panels, panel a) and July (right-hand panels, panel b) 2002: $\Delta\text{CO}_2(\text{foss})$ recalculated from hourly ΔCO records and weekly mean $\Delta\text{CO}/\Delta\text{CO}_2(\text{foss})$ ratios according to eq. (2) in comparison to the original hourly $\Delta\text{CO}_2(\text{foss})$ records using IER (upper panels) and EDGAR (middle panels) emission inventories, respectively. Lower panels: respective differences between the original $\Delta\text{CO}_2(\text{foss})$ and the recalculated $\Delta\text{CO}_2(\text{foss})$ values. Panels (c) and (d): the same as panels (a) and (b), but for Lutjewad; panels (e) and (f): the same as panels (a) and (b), but for Schauinsland.

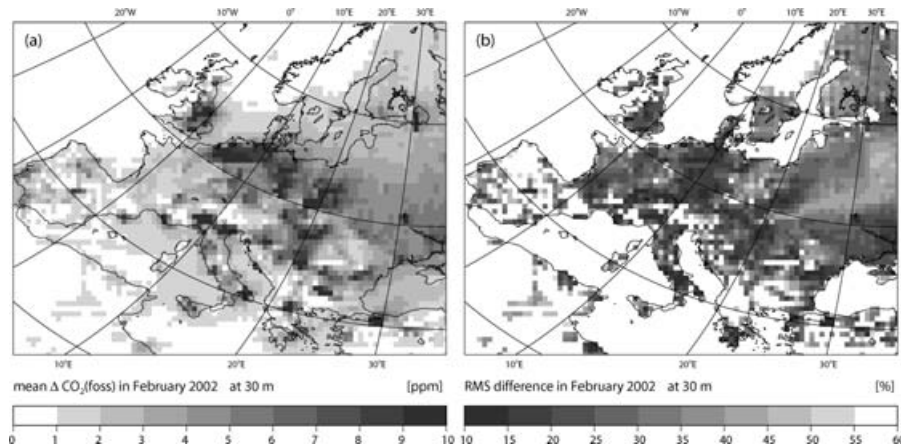


Fig. 2. Panel (a): monthly mean fossil fuel CO_2 mixing ratio as simulated by REMO (EDGAR) for February 2002 for the lowest model level at 30 m above ground. Panel (b): rms difference of CO-based fossil fuel CO_2 estimates (according to eq. 2) and the original estimates displayed in panel (a).

larger deviations in the IER results are caused by both spatial and temporal (i.e. diurnal) variations in the $\text{CO}/\text{CO}_2(\text{fossil})$ ratio of emissions (these vary by about 10% in winter and up to 20% in summer).

In Figs. 1c–1f, we present respective comparisons for Lutjewad and Schauinsland stations. The relative rms errors for Lutjewad (IER: 29%, EDGAR: 24%) and Schauinsland (IER: 39%, EDGAR: 35%) are larger, as the absolute fossil fuel CO_2 and CO components are smaller than those in Heidelberg. This is because the importance of non fossil fuel CO sources and sinks is increasing with decreasing fossil fuel influences, and the correlation between CO and fossil fuel CO_2 is decreasing accordingly. This general behaviour of rms errors over Europe can also be seen in Fig. 2, comparing the REMO-estimated fossil fuel CO_2 offset in the boundary layer at 30 m over Europe in February 2002 (Fig. 2a) with the recalculated fossil fuel CO_2 according to eq. (2). In areas with mean fossil fuel CO_2 offsets larger than 5 ppm, the rms deviation (Fig. 2b) is generally lower than 30%.

4. Validation with campaign data from Heidelberg

The reliability of our CO-based method to calculate hourly fossil fuel CO_2 offsets can be validated with a number of high temporal resolution measurements of CO_2 , CO and $^{14}\text{CO}_2$, so-called Event sampling campaigns, performed in Heidelberg from autumn 2001 to spring 2003, and which were recently published by Gammnitzer et al. (2006). Four examples of such Events collected in April, August and October 2002 as well as in February 2003 are shown in Fig. 3. In parallel to continuous half-hourly CO_2 and CO measurements in Heidelberg frequent flask samples have been collected over the course of one or two days during situations of high CO_2 and CO mixing ratios (Events). Besides for CO_2 and CO, the flask air was analysed for $^{14}\text{CO}_2$ by Ac-

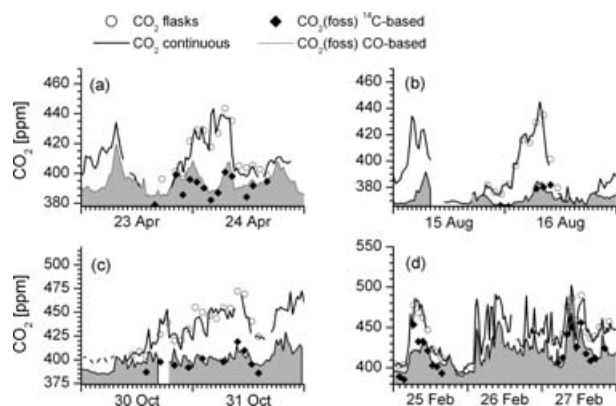


Fig. 3. Panel (a): continuous CO_2 measurements in Heidelberg during Event sampling in April 2002 (solid line) compared to CO_2 in the Event flasks (open circles) and the CO-based hourly fossil fuel CO_2 mixing ratios according to eq. (1) (grey shaded area). The background CO_2 mixing ratio for this period was estimated to 377.8 ppm (zero-point of the mixing ratio axis) so that the grey area corresponds to the fossil fuel CO_2 offset. Also plotted are the ^{14}C -based fossil fuel CO_2 estimates derived from the $^{14}\text{CO}_2$ AMS measurements on the individual flasks (black diamonds). The rms deviation between CO-based and ^{14}C -based fossil fuel CO_2 for this event is 34%. Panel (b): the same as panel (a) but for the Event of August 2002. The CO_2 background is 365.6 ppm, and the rms deviation is 32%. Panel (c): the same as panel (a) but for October 2002. The CO_2 background is 374 ppm, and the rms deviation is 23%. Panel (d): the same as panel (a) but for February 2003. The CO_2 background is 379.4 ppm, and the rms deviation is 20%.

cellerator Mass Spectrometry (AMS) which then allowed ^{14}C -based estimates of the fossil fuel CO_2 component for these samples. For details of the respective measurement and data evaluation techniques, see Gammnitzer et al. (2006). In parallel to the Event samples, two-weekly integrated high-precision $^{14}\text{CO}_2$ measurements have been performed in Heidelberg and from these measurements and concurrent hourly CO observations we

could determine mean CO/CO₂(foss) ratios for the times of the Events (compare Gamnitzer et al. (2006), fig. 8d). These mean ratios have now been applied to the hourly CO observations during the Events to calculate fossil fuel CO₂ mixing ratios according to eq. (1) (grey shaded areas in Figs. 3a–3d). The CO-based $\Delta\text{CO}_2(\text{foss})$ was then compared to the ¹⁴C-based $\Delta\text{CO}_2(\text{foss})$ estimated for the Event samples (black diamonds in Figs. 3a–3d) (note that contrary to Gamnitzer et al. we use here the same ¹⁴CO₂ background for the Event samples as for the integrated samples, namely measurements from Jungfraujoch).

There is a very good agreement obtained between the CO-based and the ¹⁴C-based fossil fuel CO₂ estimates with rms deviations for the individual events between 20% and 34%. In contrast to our model-based uncertainty estimates (compare Fig. 2), which give only a *lower* limit of the total uncertainty, these rms errors include all errors of the method and rather give an *upper* limit of the uncertainty. This is due to the fact that in the validation presented here the errors of the ¹⁴C AMS measurements also contribute to the total uncertainty. The measurement error of the $\Delta^{14}\text{C}$ AMS analysis was between 5‰ and 10‰ corresponding to an uncertainty of the fossil fuel CO₂ component of 2–4 ppm (the uncertainty of the two-weekly integrated ¹⁴CO₂ samples was only $\Delta^{14}\text{C} = 2\text{‰}$). This error contributes up to 30% to the overall uncertainty of the validation but it will not contribute when the method (eq. 1) is actually applied. The mean rms error of all seven events published by Gamnitzer et al (2006) was 27% with a mean fossil fuel CO₂ offset of 28 ppm. For these events, two-weekly mean CO/CO₂(foss) ratios between 10 and 15 ppb CO per ppm CO₂(foss) have been applied. This clearly shows that there is considerable variation in the ‘calibration factor’ of eq. (1) and confirms that using a constant CO/CO₂(foss) ratio would lead to a large additional uncertainty of any CO-based fossil fuel CO₂ estimate.

5. Discussion and conclusions

Our assessment clearly shows that, if hourly CO measurements are available at a CO₂ monitoring site as well as precise, for example, weekly or two-weekly integrated ¹⁴CO₂ observations to obtain a good estimate of the respective mean regional CO₂(foss), it is possible to estimate regional hourly fossil fuel CO₂ according to eq. (1) with uncertainties between 20% and 40%. It should be noted, however, that the error estimates derived from REMO simulations most probably give a lower limit of the uncertainties. For example, the inventories used in the REMO simulations might inherently assume a too strong spatial correlation of CO and CO₂ emissions from fossil fuel burning and the real independent variability in the regional atmospheric CO and CO₂ offsets might be underestimated in the model. For the sites discussed here, simulated and observed CO time-series have, however, comparable monthly mean standard deviations and show good agreement of the seasonality of this standard deviation. Therefore, we conclude

that testing our method with REMO results yields realistic uncertainties. This could be confirmed for the Heidelberg site. However, generally the uncertainty of the ¹⁴C-based determination of the weekly mean fossil fuel CO₂ offset must be added to the REMO-derived rms errors. With high-precision ¹⁴CO₂ measurements, these will yield random weekly biases of about ± 1 ppm. (The uncertainty of the continuous CO observations, which is of the order of a few ppb, contributes only little to the total error.) Still our approach would provide a fair compromise of affordable observational effort for a continuous monitoring network of fossil fuel CO₂ in a polluted region, such as Europe. Increasing the integration period of ¹⁴CO₂ measurements from one to two weeks increases the absolute rms error by about 10% while reducing it to 3 d would decrease the error by about 20%.

What is very important to emphasize here is that the proposed and validated method would be purely based on observations and would not be biased by uncertainties of emission inventories or in model transport. The uncertainties of model-estimated regional fossil fuel CO₂ offsets are currently of the order of a factor of 2 or even larger (Geels et al., 2006). Therefore, for a reliable network of hourly atmospheric fossil fuel CO₂ observations we recommend high-precision weekly or two-weekly integrated ¹⁴CO₂ observations combined with precise quasi-continuous CO measurements at all those continental CO₂ measurement sites which are envisaged to serve for inversions of biogenic CO₂ sources and sinks from continuous atmospheric observations.

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