Potential of $^{14}$C-based versus $\Delta CO$-based $\Delta ffCO_2$ observations to estimate urban fossil fuel CO$_2$ (ffCO$_2$) emissions

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Abstract. Atmospheric transport inversions are a powerful tool for independently estimating surface CO$_2$ fluxes from atmospheric CO$_2$ concentration measurements. However, additional tracers are needed to separate the fossil fuel CO$_2$ (ffCO$_2$) emissions from natural CO$_2$ fluxes. In this study we focus on radiocarbon ($^{14}$C), the most direct tracer for ffCO$_2$, and the continuously measured surrogate tracer carbon monoxide (CO), which is co-emitted with ffCO$_2$ during incomplete combustion. In the companion paper by Maier et al. (2023a) we determined for the urban Heidelberg observation site in Southwestern Germany discrete $^{14}$C-based and continuous $\Delta CO$-based estimates of the ffCO$_2$ excess concentration ($\Delta ffCO_2$) compared to a clean-air reference. Here, we use the CarboScope inversion framework adapted for the urban domain around Heidelberg to assess the potential of both types of $\Delta ffCO_2$ observations to investigate ffCO$_2$ emissions and their seasonal cycle. We find that discrete $^{14}$C-based $\Delta ffCO_2$ observations from almost 100 afternoon flask samples collected in the two years 2019 and 2020 are not well suited for estimating robust ffCO$_2$ emissions in the main footprint of this urban area with a very heterogeneous distribution of sources including several point sources. The benefit of the continuous $\Delta CO$-based $\Delta ffCO_2$ estimates is that they can be averaged to reduce the impact of individual hours with an inadequate model performance. We show that the weekly averaged $\Delta CO$-based $\Delta ffCO_2$ observations allow for a robust reconstruction of the seasonal cycle of the area source ffCO$_2$ emissions from temporally flat a-priori emissions. In particular, the distinct COVID-19 signal with a steep drop in emissions in spring 2020 is clearly present in these data-driven a-posteriori results. Moreover, our top-down results show a shift in the seasonality of the area source ffCO$_2$ emissions around Heidelberg in 2019 compared to the bottom-up estimates from TNO. This highlights the huge potential of $\Delta CO$-based $\Delta ffCO_2$ to verify bottom-up ffCO$_2$ emissions at urban stations if the $\Delta CO/\Delta ffCO_2$ ratios can be determined without biases.
1 Introduction

The combustion of fossil fuels (ff) like coal, oil and gas is the major reason for the steep increase in the atmospheric CO$_2$ concentration, which causes current global warming. About 70% of the global ffCO$_2$ emissions are released from urban hotspot regions (Duren and Miller, 2012). However, the atmospheric CO$_2$ increase is fortunately strongly weakened, since about half of the human-induced CO$_2$ emissions are currently taken up by the terrestrial biosphere and the oceans in roughly equal shares (Friedlingstein et al., 2022). Indeed, there are large seasonal and inter-annual variations in the natural CO$_2$ sinks and sources that need to be better understood in order to make predictions about future changes in the carbon cycle owing to increased atmospheric CO$_2$ levels.

The “atmospheric transport inversion” (Newsam and Enting, 1988) is a powerful tool for deducing surface CO$_2$ fluxes from atmospheric CO$_2$ observations. Hence, many studies have applied this top-down approach to constrain natural CO$_2$ fluxes (e.g., Rödenbeck et al., 2003; Peylin et al., 2013; Jiang et al., 2016; Rödenbeck et al., 2018; Monteil et al., 2020; Liu et al., 2021). In these calculations, ffCO$_2$ emissions are typically prescribed using bottom-up information from emission inventories. These bottom-up ffCO$_2$ emission estimates are typically based on national annual activity data that describe the fuel consumption and sector-specific emission factors (Janssens-Maenhout et al., 2019). While annual national total ffCO$_2$ emissions are associated with low uncertainties of typically a few percent for developed countries (Andres et al., 2012), their proxy-based distribution on individual spatial grid cells and individual months, days or hours can dramatically increase the uncertainties (Super et al., 2020). Therefore, it is essential to have an independent verification of the bottom-up statistics, especially on the relevant urban scales where emission reduction measures are implemented. This is essential on the path to net zero emissions. Furthermore, the seasonal cycle of bottom-up ffCO$_2$ emissions needs to be validated, if they are used in CO$_2$ inversions to deduce biogenic CO$_2$ fluxes that are dominated by a large seasonal cycle.

Atmospheric transport inversions can be used to validate these bottom-up ffCO$_2$ emissions (e.g., Lauvaux et al., 2016; Basu et al., 2020). However, their success relies on the ability of the used observational tracers to separate fossil fuel from natural CO$_2$ contributions (Ciais et al., 2015; Bergamaschi et al., 2018). The most direct tracer for ffCO$_2$ is radiocarbon ($^{14}$C) in CO$_2$. Radiocarbon has a half-life of 5700 years and is therefore no longer present in fossil fuels (Suess, 1955). Thus, the $^{14}$C depletion in ambient air CO$_2$ compared to a clean-air reference site can directly be used to estimate the recently added ffCO$_2$ excess ($\Delta$ffCO$_2$) at the observation site (Levin et al., 2003; Turnbull et al., 2006). These $\Delta$ffCO$_2$ estimates can then be implemented in regional inversions to evaluate bottom-up ffCO$_2$ emissions in the footprints of the observation sites (Graven et al., 2018; Wang et al., 2018). However, a drawback of $^{14}$C-based $\Delta$ffCO$_2$ estimates is that they have poor temporal and spatial coverage due to the labor-intensive and expensive $^{14}$C sampling and analysis. Therefore, continuously measured atmospheric excess concentrations of trace gases like CO, which is co-emitted with ffCO$_2$, have been used as alternative proxies for $\Delta$ffCO$_2$ (e.g., Gamnitzer et al., 2006; Turnbull et al., 2006; Levin and Karstens, 2007; van der Laan et al., 2010; Vogel et al., 2010). However,
to construct a high-resolution ∆CO-based ΔffCO2 record requires to correctly determine the ∆CO/ΔffCO2 ratio in the footprint of the observation site. This can indeed be a big challenge: As the CO/ffCO2 emission ratio depends on the combustion efficiency and applied end-of-pipe measures, it is very variable for different emission processes and changes with time due to technological progress (Dellaert et al., 2019).

In the companion paper by Maier et al. (2023a) we calculated a ∆CO-based ΔffCO2 record for the urban Heidelberg observation site from the ∆CO/ΔffCO2 ratios of almost 350 14CO2 flask samples collected between 2019 and 2020. By comparing the ∆CO-based ΔffCO2 with the 14C-based ΔffCO2 from the flasks we estimated for the hourly ∆CO-based ΔffCO2 record an uncertainty of about 4 ppm, which is almost 4 times larger than typical 14C-based ΔffCO2 uncertainties. About half of this uncertainty could be attributed to the spatiotemporal variability of the ∆CO/ΔffCO2 ratios.

The goal of this study is to investigate which type of ΔffCO2 observations provides the greater benefit in an atmospheric transport inversion to verify bottom-up ffCO2 emission estimates in an urban region: (1) sparse 14C-based ΔffCO2 observations from flasks with a small uncertainty or (2) ΔCO-based ΔffCO2 estimates at high temporal resolution but with an increased uncertainty? For this, we adapt the CarboScope inversion framework (Rödenbeck, 2005) for the highly populated and industrialized Rhine Valley in Southwestern Germany around the Heidelberg observation site. We perform separate inversion runs with the 14C- and ∆CO-based ΔffCO2 observations from Heidelberg. Thereby, we mainly focus on the seasonal cycle in the ffCO2 emissions and investigate which ΔffCO2 information is best suited to verify the seasonal cycle of the bottom-up emissions in the main footprint of Heidelberg.

2 Methods

2.1 Heidelberg observation site

Heidelberg is a medium-sized city with about 160’000 inhabitants, which is part of the Rhine-Neckar metropolitan area with over 2 million people. The Heidelberg observation site is located on the university campus in the northern part of the city. The sampling inlet line is 30 m above ground on the roof of the institute’s building. Local ffCO2 emissions originate mainly from traffic and residential heating but there is also a nearby combined heat and power station as well as a large coal-fired power plant and the giant industrial complex from BASF at 15-20 km to the North-West. Due to its location in the Upper Rhine Valley, Heidelberg is frequently influenced by south-westerly air masses, which carry the signals from heterogeneous sources in the Rhine Valley. A more detailed description of the Heidelberg observation site can be found in Levin et al. (2011). The 14C-based and ∆CO-based ΔffCO2 observations from Heidelberg are presented in Sect. 2.2.3.
2.2 Inversion setup

The CarboScope inversion algorithm was initially introduced by Rödenbeck et al. (2003) to estimate inter-annual and spatial variability in global CO₂ surface-atmosphere fluxes. The algorithm can also be applied to regional inversions (Rödenbeck et al., 2009). In the present study we adapt this inversion modelling framework to estimate ffCO₂ surface fluxes in the regional Rhine Valley domain (see Fig. 1) with ΔffCO₂ observations from the Heidelberg observation site (see Fig. 2). This requires a high-resolution atmospheric transport model and a careful estimation of the lateral ΔffCO₂ boundary conditions.

The CarboScope inversion system uses Bayesian inference to minimize the deviations between observed and modelled ΔffCO₂ concentrations by finding the (global) minimum of the cost function (for technical details see Rödenbeck, 2005). This cost function consists of a data constraint and an a-priori constraint, which are needed to regularize the underdetermined problem and to prevent large and unrealistic spatiotemporal ffCO₂ flux variabilities (Rödenbeck et al., 2018). The data constraint is weighted by the uncertainties of the transport model and the ΔffCO₂ observations. Furthermore, the uncertainty applied for the a-priori ffCO₂ emissions determines the impact of the a-priori constraint. Overall, the ratio between the model-data uncertainty and the a-priori flux uncertainty controls the strength of the a-priori constraint over the observational constraint (Rödenbeck, 2005; Kountouris et al., 2018; Munassar et al., 2022).

2.2.1 Atmospheric transport model

We use the Stochastic Time-Inverted Lagrangian Transport (STILT; Lin et al., 2003; Nehrkorn et al., 2010) model, driven by meteorological fields from the high-resolution Weather Research and Forecasting (WRF) model, to simulate the atmospheric transport in the Rhine Valley domain (see red rectangular in Fig. 1). The WRF meteorological fields have a horizontal resolution of 2 km and are based on hourly 0.25°-resolved European ReAnalysis 5 (ERA5, Hersbach et al., 2020) data from the European Centre for Medium-Range Weather Forecasts (ECMWF). As there are many point source emissions within the Rhine Valley, we apply the STILT volume source influence (VSI) approach introduced by Maier et al. (2022) to model them. This model approach takes into account the effective heights of the point source emissions, which are typically released from elevated chimney stacks. For the area source emissions, we apply the standard approach in STILT, which assumes that all emissions are released from the surface.
Figure 1: (a) Map with the Central European STILT domain (blue) and the high-resolution Rhine Valley STILT domain (red). The observation site Heidelberg (HEI) and the marine background site Mace Head (MHD) are indicated. (b) Zoom into the Rhine Valley domain with the mean prior ffCO$_2$ emissions from the TNO inventory for 2019-2020. The blue surrounded region in the zoom shows the “50%-footprint” range, i.e., the area accounting for 50% of the Heidelberg average footprint within the Rhine Valley.

2.2.2 A-priori information

We use the ffCO$_2$ emissions from TNO (Dellaert et al., 2019; Denier van der Gon et al., 2019) with a horizontal resolution of about 1 km (1/60° lon, 1/120° lat) as a-priori estimates for our Rhine Valley inversion. The TNO emission inventory provides annual total ffCO$_2$ emissions for 15 different source sectors as well as sector-specific temporal profiles. In this study, we treat the ffCO$_2$ emissions from the point source dominated “energy production” and “industry” TNO sectors separately due to the following reasons: (1) While the VSI approach (see above) strongly improves the vertical representation of point source emissions in STILT, it still remains difficult to correctly describe the mixing and transport of narrow point source plumes with meteorological fields that have a resolution of 2 km. (2) Due to the elevated release of point source emissions from high stacks, the Heidelberg observation site with an air intake height of only 30m above ground is rarely influenced by distinct emission plumes from nearby point sources (see Maier et al., 2023a). This makes it difficult to evaluate those point source emissions with ΔffCO$_2$ observations from the Heidelberg observation site alone. (3) We expect that the energy and industry emissions in the Rhine Valley are better known in TNO than the more diffuse area source emissions. We thus focus on how well our observations are able to constrain area source emissions in the footprint of the Heidelberg site.

For these reasons, we prescribe the energy and industry emissions in our inversion setup and adjust only the area source emissions in the Rhine Valley, which mainly originate from the heating and traffic sector. We use the sector-specific monthly profiles provided by TNO to calculate from the annual total emissions monthly ffCO$_2$ emissions for the energy and industry sectors and treat them as fixed fluxes in our inversion system. As we aim to investigate the information of the ΔffCO$_2$
observations regarding the seasonal cycle of the area source ffCO₂ emissions, we apply temporally constant ("flat") a-priori ffCO₂ emissions for the area sources. For this, we use the (spatially highly resolved) 2-year average TNO area source emissions of the years 2019 and 2020.

### 2.2.3 Observations

In separate inversion runs, we use either the discrete ¹⁴C-based ΔffCO₂ estimates from flasks, collected as integrals over one hour, or the hourly ∆CO-based ΔffCO₂ record from the Heidelberg observation site (see Fig. 2). The companion paper (Maier et al., 2023a) describes in detail the construction of this continuous ∆CO-based ΔffCO₂ record and gives an estimation of its uncertainty. In short, the ∆CO-based ΔffCO₂ record has been constructed by dividing the observed hourly ∆CO offsets compared to the marine reference site Mace Head (MHD) by an average ∆CO/ΔffCO₂ ratio, which was determined by the ∆CO and ¹⁴C-based ΔffCO₂ observations of almost 350 day- and night-time flask samples collected in 2019 and 2020. In the inversion, however, we only use the afternoon ¹⁴C-based and ∆CO-based ΔffCO₂ observations between 11 and 16 UTC, as night-time situations are associated with a poorer transport model performance. Note that the hourly-integrated ΔffCO₂ observation e.g. at 11 UTC corresponds to the time period between 11 and 12 UTC.

Furthermore, we apply a 2σ-selection criterion to the ΔffCO₂ observations as introduced by Rödenbeck et al. (2018). For this, we take the high-resolution annual total ffCO₂ emissions from TNO and apply the hourly sector-specific temporal profiles. These hourly resolved ffCO₂ emissions are then transported with the WRF-STILT model to simulate hourly ΔffCO₂ concentrations. The mean difference between the simulated and the ∆CO-based ΔffCO₂ observations is only -0.04ppm during moon hours with a standard deviation of 6.76 ppm, which indicates that the model is able to reproduce, on average, the afternoon ∆CO-based ΔffCO₂ observations without a significant mean bias. This directly allows the application of the 2σ-selection criterion, which means that we only use those ΔffCO₂ observations, whose deviation to the modelled ΔffCO₂ is smaller than 2 times the standard deviation between observed and modelled ΔffCO₂, i.e. which is within the 2σ-range. Therewith, we exclude the data outside the 2σ-range, which obviously cannot be represented with our transport model. Examples of such data are observations during very strong air stagnation events in winter, which are often underestimated in the model, or vice versa, situations when the model overestimates the point source influence at the observation site. Since the inversion system assumes a Gaussian distribution for the model-data mismatch, these extreme outlier events would have a strong impact on the inversion results (Rödenbeck et al., 2018). Thus, this 2σ-selection can be seen as an additional regularization for the inversion to avoid using situations with unrealistic model simulations. We apply the 2σ-selection criterion to both the ¹⁴C-based ΔffCO₂ observations from the afternoon flask samples and the afternoon hours of the ∆CO-based ΔffCO₂ record.
Figure 2: Afternoon $\Delta f f CO_2$ observations from the Heidelberg observation site. The grey curve indicates the $\Delta CO$-based $\Delta ffCO_2$ record and the black circles the $^{14}C$-based $\Delta ffCO_2$ estimates from flasks. Both, the $^{14}C$-based and $\Delta CO$-based $\Delta ffCO_2$ observations are 2$\sigma$-selected.

2.2.4 Lateral boundary conditions

We set up the inversion system for the Rhine Valley domain (6.00°E – 10.25°E, 47.75°N – 50.25°N, red rectangular in Fig. 1a) around the Heidelberg observation site and run the inversion for the full two years 2019 and 2020 within this domain. As we calculated the $^{14}C$- and $\Delta CO$-based $\Delta ffCO_2$ excess compared to MHD (see Maier et al., 2023a), however, we need to define a suitable $\Delta ffCO_2$ background representative for the boundary of the Rhine Valley domain. In the following, we call this the “Rhine Valley $\Delta ffCO_2$ background”. By definition, we assume that the $\Delta^{14}CO_2$ observations from MHD correspond to $\Delta ffCO_2 = 0$ ppm, which might be reasonable since the MHD $^{14}CO_2$ samples were only collected during situations with clean westerly air masses from the Atlantic. Therefore, it seems to be suitable to apply the MHD ($\Delta ffCO_2 = 0$ ppm) background to the entire western boundary of the Central European STILT domain (blue rectangular in Fig. 1a). But how representative is this background for the other boundaries of the Central European domain? Maier et al. (2023b) estimated the representativeness bias of the MHD background for the probably most polluted eastern boundary of the Central European domain. They could show that the representativeness bias is on average smaller than 0.1 ppm for an observation site in Central Europe. Therefore, we neglect this bias and assume $\Delta ffCO_2 = 0$ ppm also at the non-western boundaries of the Central European domain. To estimate the Rhine Valley $\Delta ffCO_2$ background we use a nested STILT model approach with a high (2 km) resolution WRF meteorology in the Rhine Valley domain and a coarser (10 km) WRF resolution in the Central European STILT domain outside the Rhine Valley. We use for both domains nearly $ffCO_2$ emissions from TNO (Dellaert et al., 2019; Denier van der Gon et al., 2019). This new approach allows us to separate the $ffCO_2$ contributions from each STILT domain. With this setup we model for the Heidelberg site for each hour during 2019 and 2020 the $\Delta ffCO_2$ contributions from the Central European domain.
outside the Rhine Valley ($\Delta^{ff}CO_2, CE-RV$), which we use as the Rhine Valley background. We then subtract this modelled Rhine Valley $\Delta^{ff}CO_2$ background ($\Delta^{ff}CO_2, CE-RV$) from the estimated $\Delta^{ff}CO_2$ excess compared to MHD ($\Delta^{ff}CO_2, MHD$), to obtain the $\Delta^{ff}CO_2$ excess compared to the Rhine Valley boundary ($\Delta^{ff}CO_2, RV$):

$$\Delta^{ff}CO_2, RV = \Delta^{ff}CO_2, MHD - \Delta^{ff}CO_2, CE-RV$$ (1)

The $\Delta^{ff}CO_2, RV$ excess concentrations compared to the Rhine Valley boundary are then introduced into the inversion system to constrain the $^{ff}CO_2$ emissions within the Rhine Valley.

### 2.2.5 Model-data mismatch

The model-data mismatch is calculated by subtracting the modelled from the observed $\Delta^{ff}CO_2, RV$ concentrations. The uncertainties of the $^{14}C$-based and $^{14}C$-based $\Delta^{ff}CO_2$ observations are estimated to be 3.9 ppm and 1.1 ppm, respectively (see Maier et al., 2023a). The transport model uncertainty of urban, continental sites like Heidelberg with complex local circulations was assumed to be 5ppm. The quadratically added observational and transport model uncertainties yield the total uncertainty of the model-data mismatch. To account for the temporal correlations of observations that are close together in time, we apply a data density weighting as described in Rödenbeck (2005). It artificially increases the uncertainty of the model-data mismatch, that all observations within one week lead to the same constraint as a single observation per week. The weighting interval was set to one week because this is a typical duration of synoptic weather patterns.

### 2.2.6 Degrees of freedom

Since we only use $\Delta^{ff}CO_2$ observations from a single station in the Rhine Valley, we restrict the number of degrees of freedom in our inversion system so that the inverse problem is not too strongly underdetermined. Therefore, we only investigate the area source emissions in the Rhine Valley and prescribe the energy and industry emissions, as mentioned above. Moreover, the inversion system adjusts only one spatial scaling factor, which increases or decreases the area source emissions in the whole Rhine Valley domain. Hence, we expect that the high-resolution TNO inventory is much better at describing the large spatial heterogeneity in the $^{ff}CO_2$ emissions within the Rhine Valley than our top-down approach. As we want to investigate the seasonal cycle of the $^{ff}CO_2$ emissions, additional temporal degrees of freedom are needed. For this, we choose a temporal correlation length of about 4 months (“Filt3T” in CarboScope notation), which should be appropriate to explore seasonal cycles. Finally, since the Heidelberg observations cannot be used to constrain the emissions in the whole Rhine-Valley domain, we only analyze the a-posteriori area source emissions in the (most constrained) nearfield of the observation site. We define the nearfield of Heidelberg as the area which accounts for 50% of the temporally accumulated footprint in the Rhine Valley domain for the two years 2019 and 2020 (blue surrounded region in Fig. 1b).
3 Results

3.1 Potential of flask-based ∆ffCO₂ estimates to investigate the seasonal cycle in ffCO₂ emissions

First, we investigate the potential of flask-based ∆ffCO₂ estimates to explore the seasonal cycle of the area source ffCO₂ emissions around the urban Heidelberg observation site. For this we use the average of the TNO area source ffCO₂ emissions...
of the two years 2019 and 2020 as a temporally constant prior estimate (see Sect. 2.2.2). To analyze the impact of the observational constraint on the a-posteriori results, we apply different prior uncertainties, which effectively lead to different ratios between a-priori and data constraint (see Fig. 3). In a first inversion run (Fig. 3a), we use the $^{14}$C-based δfCO$_2$ observations from the 94 afternoon flasks collected in the two years 2019 and 2020 in Heidelberg. The distribution of the flask samplings over the two years can be seen in Fig. 2. Due to various reasons (e.g. testing of the flask sampler associated with frequent changes of the flask sampling strategy) the flasks were not evenly collected and especially the winter 2019/2020 has only thin flask coverage. The $^{14}$C-based a-posteriori ffCO$_2$ emissions show a clear seasonal cycle for the larger prior uncertainties, which is fully data-driven. However, large and unrealistic a-posteriori flux variabilities emerge for prior uncertainties larger than 50% of the flat a-priori emissions. For example, the low flask coverage during the winter period 2019/2020 leads to a huge maximum in the area source ffCO$_2$ emissions in November 2019 when the inversion algorithm tries to minimize the model-data mismatches of individual flasks. Similarly, the flask samples with vanishing or even negative δfCO$_2$ estimates in summer 2020 (cf. Fig. 2) cause a strong reduction of the a-posteriori emissions. Therefore, this urban inversion setup obviously needs a very strong regularization through low prior uncertainties to prevent the fitting of individual flask observations.

We further investigate whether these overfitting patterns can be attributed to the uneven distribution of the flask samples. For this, we subsample the continuous ΔCO-based ΔffCO$_2$ record. In a first step, we use the ΔCO-based ΔffCO$_2$ observations from those 94 afternoon hours with flask samplings as observational constraint (Fig. 3b). For the most part, the subsampled ΔCO-based ΔffCO$_2$ observations reproduce the a-posteriori results of the $^{14}$C-based ΔffCO$_2$ estimates. However, there are differences like the shifted summer minimum in 2019. These differences can be explained by the variability of the ΔCO/ΔffCO$_2$ ratios that we fully neglected by using a constant mean ratio for constructing the ΔCO-based ΔffCO$_2$ record. Thus, when comparing the results with the TNO seasonality of emissions (grey histogram) it seems obvious that the $^{14}$C-based ΔffCO$_2$ estimates provide the more accurate data than the subsampled ΔCO-based ΔffCO$_2$ record. However, the general similarity between both results means that we can use the continuous ΔCO-based ΔffCO$_2$ record to investigate an even data coverage with hypothetical flask samples collected in Heidelberg. The middle panels in Fig. 3 show the inversion results if the ΔCO-based ΔffCO$_2$ record is subsampled for one flask every week on Tuesday (c) or on Friday afternoon (d), respectively. The increased number of evenly distributed weekly flasks strongly dampens the variability of the a-posteriori results. However, they show large differences depending on which day of the week the hypothetical afternoon flask was collected. Whereas the Tuesday flasks for example lead to a quite unrealistic gradual increase in the ffCO$_2$ emissions between January and November 2019, the Friday flasks show a more realistic seasonal cycle in this year. In contrast, both Tuesday and Friday flasks lead to an unexpected maximum in summer 2020. This implies that the a-posteriori results are still dependent on the selection of the individual hypothetical flasks. Therefore, it seems that even a uniform data coverage with a realistic flask sampling frequency of one flask per week is not sufficient to determine a plausible seasonal cycle of the area source ffCO$_2$ emissions around Heidelberg, as suggested by the TNO inventory. However, the situation should be better in the case of real, hourly-integrated $^{14}$C flasks that are collected
e.g. once per week, as the average $\Delta CO/\Delta ffCO_2$ ratio used to construct the $\Delta CO$-based $\Delta ffCO_2$ record might be inappropriate for individual hours.

Finally, we investigated the benefit of an extremely high flask sampling frequency with one flask per afternoon (see Fig. 3e). Here, the a-posteriori results seem to approach towards the TNO bottom-up emissions in 2019. However, there are still unexpectedly strong deviations between the top-down and bottom-up estimates in the summer half-year 2020 for increased prior uncertainties. These differences might be caused by individual afternoon hours with a negative model-data mismatch in summer 2020. To reduce the impact of such hours, we perform a separate inversion run where we average the modelled and observational data of all 7 hypothetical afternoon flasks within each week (Fig. 3f). This further reduces the spread of a-posteriori results, particularly in summer 2020, further approaching towards the seasonal amplitude of the bottom-up TNO emissions. Thus, several afternoon flasks per week would be needed so that the influence of individual flasks on the inversion results can be averaged out and a plausible seasonal cycle amplitude in the area source $ffCO_2$ emissions around Heidelberg can be obtained.

Overall, these results show that the a-posteriori estimates are very sensitive to individual flask observations in this target region with very heterogeneously distributed $ffCO_2$ sources. Obviously, the transport model fails to appropriately simulate the $\Delta ffCO_2$ concentrations for individual afternoon hours. This can be explained by remaining shortcomings in the transport model but also by the enormous heterogeneity of the $ffCO_2$ emissions in the footprint of the Heidelberg observation site. As already mentioned in Sect. 2, modelling individual plumes from point source emissions is a particular challenge in this urban region, and e.g. the forward model estimates of point source signals, even with the improved VSI approach seem often incorrect, at a temporal resolution of one hour. Therefore, we decided to aggregate our observations over multiple hours, and change the observation operator in the model such that only aggregated model results are compared to aggregated observations. This minimizes the impact of individual hours with poor model performance.

### 3.2 Potential of continuous $\Delta CO$-based $\Delta ffCO_2$ estimates to investigate the seasonal cycle in $ffCO_2$ emissions

![Graphs showing $\Delta CO$-based $\Delta ffCO_2$ estimates](https://doi.org/10.5194/egusphere-2023-1239)
Figure 4: Area source ffCO₂ emissions in the nearfield (blue surrounded area in Fig. 1b) of Heidelberg. In (a) a flat prior (black dashed line) was used for the area source emissions and in (b) the monthly bottom-up estimates from TNO (grey line) were used as a-priori estimate. Shown are the a-posteriori emissions for different prior uncertainties between 20 and 200% (colored solid lines). The inversion was constrained with weekly averages of hourly, 2σ-selected afternoon ΔCO-based ΔffCO₂ observations from Heidelberg.

The big advantage of the continuous ΔCO-based ΔffCO₂ record is that it provides a full temporal coverage of the inversion period and can, thus, also be averaged such that the sensitivity of the a-posteriori results on individual (hourly) model-data mismatches is strongly reduced. In Appendix A1, we investigate if the averaging over the five (11 – 16 UTC) afternoon hours of the ΔCO-based ΔffCO₂ record is enough to sufficiently reduce the impact of the point source emissions on the a-posteriori area source emissions (see magenta curves in Fig. A1). For this, we perform in addition to the standard inversion runs with fixed point source emissions further sensitivity runs with adjustable point source emissions. Ideally, the a-posteriori area source emissions are identical for both inversion runs, meaning that the modelling of the well-known point source emissions has no impact on the area source emissions. However, depending on whether the point source emissions are being adjusted in the inversion framework or not, the a-posteriori area source ffCO₂ emissions can differ by more than 100% for individual seasons. Thus, an averaging interval of one afternoon only seems to be too short.

The averaging interval of one week strongly reduces the impact of the point sources on the a-posteriori area source emissions (see blue curves in Fig. A1). It limits the differences between the a-posteriori area source emissions of the inversion runs with fixed and adjustable point source emissions to below 30% for individual seasons. Averaged over the two years 2019 and 2020, these differences are below 10%. We also tested an extreme averaging interval of one month, which further reduces the difference between the respective a-posteriori area source emissions to below 20% for individual seasons (see pink curves in Fig. A1). However, such a long interval would lead to an averaging of very different meteorological situations, which reduces the temporal information of the observations. Therefore, we decided to apply in the following an averaging interval of one week, which is the typical length scale of synoptic weather patterns. The difference between the a-posteriori area source emissions of the inversion runs with fixed and adjustable point source emissions can be seen as an uncertainty estimate for the area source emissions due to imperfect point source modelling.

In the following, we use the weekly averaged afternoon ΔCO-based ΔffCO₂ observations to investigate the seasonal cycle of the area source ffCO₂ emissions around Heidelberg (see Fig. 4a). If the prior uncertainty is chosen large enough, the seasonal cycle amplitude of the a-posteriori estimates agrees with that of the TNO inventory reasonably well. Moreover, the data-driven inversion results distinctly show the effect of the COVID-19 restrictions with lower emissions in 2020 compared to 2019. In Southwestern Germany, the first COVID-19 lockdown started in mid-March 2020. Indeed, the inversion results show at that time a strong decrease in the area source ffCO₂ emissions. In particular, the decline in the a-posteriori ffCO₂ emissions is much deeper in spring 2020 compared to spring 2019 and the minimum of the seasonal cycle is flatter in 2020 as it extends over several summer months.
The agreement with the phasing of the seasonal cycle of the TNO inventory seems to be better in 2020 than in 2019. In 2020, TNO provides country-specific “COVID-19” seasonal cycles, which take into account the timing and the strength of the respective national restrictions. In Fig. 4 an average over the German and French seasonal cycle is shown, which seems to be confirmed by our observations. The shown TNO seasonal cycle for 2019 is a general European average estimate that is not specific for 2019. It assumes minimum emissions in July, whereas our observations show minimal emissions in August and September. Indeed, this shifted minimum of the seasonal cycle coincides with the summer holidays in Southwestern Germany, which are from August to mid-September.

We want to further investigate the consistency of the seasonal cycles from the bottom-up and the top-down estimates. For this, we explore the effect of using the monthly TNO bottom-up seasonal cycle for the a-priori emissions (see Fig. 4b). As expected, the phase of the a-posteriori seasonal cycle is in agreement with the TNO inventory in 2020. However, in 2019 the a-priori information pulls the summer emission minimum to July. With weakening regularization of the prior the inversion algorithm tries to shift the minimum of the a-posteriori seasonal cycle from July towards August and September. Due to the limited temporal degrees of freedom of the inversion this shifting results in artificially increasing the emissions in May 2019 and lowering them in October. Hence, these results point to some inconsistencies in the seasonality of the TNO emissions in the footprint of the Heidelberg observation site. In fact, a correct phasing of the fossil emissions is essential when prescribed ffCO₂ emissions are used in CO₂ model inversions to separate the fossil from the biogenic contribution in atmospheric CO₂ observations to constrain CO₂ fluxes from the biosphere. Although these biospheric CO₂ signals are typically estimated with observations from sites that are more remote and rural than the urban Heidelberg site, a correct seasonality in the prescribed ffCO₂ emissions still seems to be important when deducing the month-to-month variations in the biospheric CO₂ fluxes.

Overall, the (weekly averaged) ∆CO-based ΔffCO₂ record seems to be well suited to estimate (and verify) the seasonal cycle of bottom-up ffCO₂ emissions in the nearfield of the Heidelberg observation site. This is a very promising result, especially considering how simple the ∆CO-based ΔffCO₂ record was constructed. It is based on the average ∆CO/ΔffCO₂ ratio estimated from ¹⁴C measurements on flask samples where a potential seasonal cycle in the ∆CO/ΔffCO₂ ratios was fully neglected. In the following we investigate, among other possible error influences, the effect of a hypothetical seasonal cycle in the ∆CO/ΔffCO₂ ratios on the inversion results.
3.3 Robustness of the ∆CO-based ∆ffCO₂ inversion results

Figure 5: (a): Area source ffCO₂ emissions in the nearfield (blue surrounded area in Fig. 1b) of Heidelberg for different sensitivity runs. Shown are the a-posteriori results for 20% reduced flat a-priori emissions (solid magenta line), for an alternative Rhine Valley ∆ffCO₂ background modelled with EDGAR emissions (blue) and for an assumed seasonal cycle in the ∆CO/∆ffCO₂ ratios (cyan, see Fig. A2). As a reference, the a-posteriori result of the base inversion from Fig. 4a is shown in black. All a-posteriori results correspond to a 150% prior uncertainty. The dotted lines indicate the flat prior emissions (black) and the by 20% reduced prior emission (magenta). (b): Relative deviations between the different a-posteriori area source emissions of the sensitivity runs and the base inversion in %.

In the following we want to investigate the robustness of the (weekly averaged) ∆CO-based ∆ffCO₂ inversion results. For this, we (1) reduce the flat prior emissions by 20%, (2) assume a seasonal cycle in the ∆CO/∆ffCO₂ ratios, and (3) apply an alternative Rhine Valley ∆ffCO₂ background. Figure 5 shows the respective a-posteriori results for a 150% prior uncertainty, which constitutes enough weighting on the (weekly averaged) ∆CO-based ∆ffCO₂ observations to reconstruct the seasonal cycle from the flat a-priori area source ffCO₂ emissions (see Fig. 4a).

First, if the a-priori area source ffCO₂ emissions in the Rhine Valley domain are equally reduced by 20% (see dotted magenta curve in Fig. 5a), the ∆CO-based ∆ffCO₂ inversion manages to compensate for almost all of this bias (compare the magenta curves with the black curves in Fig. 5). The deviations between the a-posteriori emissions of the inversion runs with perturbed
and unperturbed flat prior emissions is typically below 5% for all seasons. Accordingly, the a-posteriori seasonal cycle of the ffCO₂ emissions is hardly affected by a potential bias in the flat prior emissions. The deviations between the annual totals of the a-posteriori estimates of the perturbed and unperturbed prior inversion runs is only 2% for both years. This means that on an annual scale about 90% of this 20%-bias in the perturbed flat prior could be corrected for.

With the second sensitivity test, we want to investigate the effect of the ΔCO/ΔffCO₂ ratios used to construct the ΔCO-based ΔffCO₂ record. For our base inversion, the ΔCO-based ΔffCO₂ record was constructed by using the average ΔCO/ΔffCO₂ ratio of 8.44 ppb/ppm, which was calculated from all flask samples collected in 2019 and 2020. However, as discussed in Maier et al. (2023a), the ratio during summer with lower signals is hard to determine and thus less constrained. The question is thus: How would our inversion results change if the ΔCO/ΔffCO₂ ratios would have a (small) seasonal cycle? For this, we assume a seasonal cycle in the ratios for the two years with 5% lower ratios in summer and correspondingly 5% larger ratios in winter, so that the two-year mean is still 8.44 ppb/ppm (see Fig. A2). Notice, that we use the ratios to calculate the ΔffCO₂,MHD excess compared to the MHD background site and then subtract the modelled Rhine Valley ΔffCO₂,CE-RV background to get the ΔffCO₂,RV observations for our Rhine Valley inversion (see Eq. 1). This effectively results in summer and winter ΔffCO₂ concentrations being more than 5% larger and lower, respectively, than the ΔffCO₂ concentrations based on the average ratio. Obviously, this leads to larger a-posteriori emissions (cyan curve in Fig. 5) during summer and lower emissions in winter compared to the base inversion results. The largest seasonal deviations to the base inversion a-posteriori emissions are 10%. Since by construction the mean of the seasonally varying ratios corresponds to the average ratio used for the base inversion, the effect on the annual totals of the a-posteriori ffCO₂ emissions is neglectable.

Finally, we investigate the impact of the lateral ΔffCO₂ boundaries on the area source ffCO₂ emissions estimates. For our base inversion, we used the high-resolution TNO emission inventory and WRF-STILT to model for the Heidelberg observation site the ΔffCO₂ contributions from the European STILT domain outside the Rhine Valley (see Sect. 2.2.4). For the following sensitivity run (blue curve in Fig. 5), we model the Rhine Valley ΔffCO₂ background with ffCO₂ emissions based on the Emissions Database for Global Atmospheric Research (EDGAR, Janssens-Maenhout et al., 2019) and use the coarser ECMWF meteorology in STILT. The application of this alternative Rhine Valley ΔffCO₂ background leads to more than 10% lower emissions in the autumn of both years, which can be explained by strong deviations between the weekly averages of the two modelled background concentrations during these periods (see Fig. A3). Thus, the Rhine Valley background affects the seasonal cycle of the area source ffCO₂ emissions. During summer, the deviations to the base inversion results are below 5%. The annual totals of the area source ffCO₂ emissions around Heidelberg are 3% and 7% lower in the years 2019 and 2020, respectively, if the alternative Rhine Valley ΔffCO₂ background is used.
4 Discussion

In the present study we investigate the potential of $^{14}$C-based and $\Delta CO$-based $\Delta ffCO_2$ observations to evaluate the ffCO$_2$ emissions and their seasonal cycle in an urban region around the Heidelberg observation site. This urban area is characterized by a complex topography and a large spatial heterogeneity in the ffCO$_2$ sources, including several nearby point sources. Thus, deficiencies in the transport model and inaccuracies in the driving meteorology strongly impact the model-data mismatch at the observation site, which will be minimized by the inversion algorithm. We focus on the estimation of the ffCO$_2$ emissions from area sources, since the observations from the Heidelberg site with an air intake height of 30 m above the ground are not suitable to constrain the emissions of nearby point sources with elevated stack heights. Indeed, the analysis of the $\Delta CO/\Delta ffCO_2$ ratios in Maier et al. (2023a) showed that the Heidelberg observation site is hardly influenced by pure point source emission plumes. Moreover, we expect that point source emissions can be better quantified a-priori from bottom up compared to area source emissions. Therefore, we prescribe the well-known point source ffCO$_2$ emissions in the inversion setup and only adjust the area source emissions in the Rhine Valley domain.

4.1 Can flask-based $\Delta ffCO_2$ observations be used to predict the seasonal cycle of ffCO$_2$ emissions at an urban site?

To investigate the potential of $\Delta ffCO_2$ observations to predict the seasonal cycle of the area source ffCO$_2$ emissions around Heidelberg, we applied temporally constant (flat) a-priori ffCO$_2$ emissions in our inversion system, such that all seasonal information comes from the atmospheric data. We could show that $^{14}$C-based $\Delta ffCO_2$ observations from almost 100 hourly flask samples collected in the two years 2019 and 2020 are not sufficient to reconstruct a robust seasonal cycle from the flat a-priori estimate. As the Bayesian inversion setup assumes a Gaussian distribution for the model-data mismatch, the inversion algorithm tries to primarily reduce the largest model-data differences. Therefore, we applied a 2σ selection to exclude the flask events with the largest model-data mismatches and thus worse model performances. However, the a-posteriori ffCO$_2$ emissions are still very sensitive to individual flask observations. Therefore, a strong regularization through small a-priori uncertainties (i.e., $\leq$ 50% prior uncertainty, Fig. 3a) is needed to avoid large overfitting patterns in the inversion results.

By subsampling the $\Delta CO$-based $\Delta ffCO_2$ record, we further investigate the potential of a uniform data coverage with one hypothetical afternoon flask per week to reliably estimate the seasonal cycle in the area source emissions. Indeed, several afternoon flask samples per week are needed, as well as an averaging of the flask observations within one week so that the overfitting of individual flask data is reduced. However, the situation should be better for real, e.g. sub-weekly, $^{14}$C flasks compared to the subsampled $\Delta CO$-based $\Delta ffCO_2$ record; as the applied average $\Delta CO/\Delta ffCO_2$ ratio may be inappropriate for individual hours, this could amplify the sensitivity to the individual hypothetical flasks. For the Heidelberg observation site where the flask sampling during our study period was rather irregularly, we used the $\Delta CO/\Delta ffCO_2$ flask ratios to construct a continuous $\Delta CO$-based $\Delta ffCO_2$ record (see Maier et al., 2023a) that, due to its high frequency could then be averaged in the inversion framework to explore the seasonal cycle of the ffCO$_2$ emissions.
4.2 What is an appropriate averaging interval for urban observations?

The main advantage of the ∆CO-based ∆ffCO₂ record is its continuous data coverage that allows an averaging so that the influence of individual hours with poor model performance on the inversion results is strongly reduced. In this urban region, this is especially necessary because of the shortcomings in the STILT model and its driving meteorology to describe the transport and mixing of nearby point source emissions. Imagine that the plume of a point source arrives a few hours earlier or later at the observation site than simulated by STILT. In such cases, averaging is inevitable to prevent a wrong adjustment of the ffCO₂ emissions. Moreover, the STILT-VSI approach itself has its deficits as it assumes mean effective emission height profiles for all meteorological situations and ignores the stack heights of individual power plants. Furthermore, the VSI approach still relies on a correct vertical mixing in STILT. Whereas in Maier et al. (2022) we could show that the VSI approach strongly improves the agreement between modelled and observed ∆ffCO₂ concentrations from two-week integrated samples, it thus still may overestimate the point source contributions for individual hours. 

Therefore, an averaging of the observations is very helpful when a transport model like STILT is used to describe the transport and mixing of nearby point source emissions.

In Appendix A1, we investigate how to appropriately average the observational data. Ideally, the a-posteriori area source ffCO₂ emissions are independent of a wrong modelling of the point source emissions. Thus, they should not be affected by whether the a-priori point source emissions are fixed or adjustable in the inversion framework. We showed that an averaging interval of one week limits the differences between the a-posteriori area source ffCO₂ emissions of the inversion runs with fixed and adjustable point source emissions, respectively, to below 30% for all seasons. This deviation can be used as a measure for the uncertainty of the a-posteriori area source ffCO₂ emissions that is induced by an inadequate modelling of the point source emissions. A longer, e.g. monthly, averaging interval further reduces this difference, but comes along with an averaging over very different meteorological situations and thus reduces the spatiotemporal information comprised in the observations. This might be especially important if there are several observation sites, and the inversion system optimizes the ∆ffCO₂ gradients between these different stations. The averaging interval of a week corresponds to the typical length scale of synoptic weather patterns. Therefore, a certain correlation between the model-data-mismatch uncertainty within one week has anyhow to be considered in the inversion and the weekly averaging should, thus, not destroy too much information. In this study, we thus applied an averaging interval of one week as a compromise between reducing the impact of hours with an inadequate model performance and using as much observational information as possible.

4.3 What is the potential of ∆CO-based ∆ffCO₂ to estimate the seasonal cycle in urban ffCO₂ emissions?

The potential of weekly averaged ∆CO-based ∆ffCO₂ observations to explore the seasonal cycle of the ffCO₂ emissions in an urban region is very promising. In Heidelberg, we could reliably reconstruct the seasonal cycle from flat a-priori area source ffCO₂ emissions with the ∆CO-based ∆ffCO₂ observations for increased prior uncertainties. We further could detect the
COVID-19 signal in 2020, which is characterized by lower emissions compared to 2019 and a very steep decline in the emissions in spring 2020. In this latter year, the a-posteriori seasonal cycle agrees very well with the bottom-up seasonal cycle from TNO, where the timing of the COVID-19 restrictions has explicitly been considered. For 2019, TNO only provides a non-year-specific European average seasonal cycle, which has its annual minimum in July. In contrast, our ΔCO-based ΔffCO₂ observations suggest the 2019 minimum of the (restricted) Rhine Valley area source ffCO₂ emissions to be in August and September, when local summer holidays take place in that part of Germany. Even when we apply the bottom-up seasonal cycles from TNO to the flat a-priori ffCO₂ emissions the inversion system still tries to shift the minimum in 2019 from July into September. However, due to the limited temporal degrees of freedom in our inversion system, this comes along with artificially increased or decreased emissions in May and October 2019, respectively. Thus, this result of the Heidelberg inversion points to some inconsistencies in the seasonality of TNO emissions in the footprint of the station. A correct phasing of the fossil emissions is essential when prescribed ffCO₂ emissions and associated forward modelling results are used in atmospheric transport inversions to constrain the CO₂ fluxes from the biosphere.

In contrast to the inversion with flask-¹⁴C-based ΔffCO₂ observations, the ΔCO-based ΔffCO₂ inversion allows a weakening of the regularization strength without generating unrealistic variabilities in the seasonal cycle of the ffCO₂ emissions. This implies that the a-posteriori results are less dependent on a potential bias in the a-priori emissions. Indeed, a sensitivity run with a 20% reduced flat prior estimate for the area source ffCO₂ emissions leads for sufficiently large prior uncertainties to similar results as the base inversion run with unperturbed prior estimate. Thus, the ΔCO-based ΔffCO₂ inversion is able to simultaneously reconstruct the seasonal cycle from a flat prior and correct a potential bias in the a-priori emissions.

However, the ΔCO-based ΔffCO₂ inversion results strongly depend on a potential bias in the ΔCO/ΔffCO₂ ratios that are applied to calculate the ΔffCO₂ estimates. Since there is no evidence for a strong seasonal cycle in the ΔCO/ΔffCO₂ ratios at the Heidelberg observation site, we used a constant average ΔCO/ΔffCO₂ ratio to calculate the ΔCO-based ΔffCO₂ record for the two years 2019 and 2020 (see Maier et al., 2023a). But due to the low signals and the weak correlation between ΔCO and ΔffCO₂ during summer, it is hard to determine separate summer ratios. Nevertheless, our results indicate that there might be a small seasonal cycle on the order of 5% in the ratio. In this study, we could show that a hypothetical seasonal cycle with 5% lower and 5% larger ratios in summer and winter, respectively, would lead to changes in the area source ffCO₂ emissions of up to 10% for individual seasons. This emphasizes the importance of a thorough determination of the ΔCO/ΔffCO₂ ratios to prevent biases in estimates of total fluxes and the seasonal cycle of the ffCO₂ emissions.

Indeed, we are currently in a kind of a fortunate situation in Heidelberg, since the emission ratios of the traffic and heating sectors seem to be quite similar in the main footprint of the station (see Maier et al., 2023a). Hence, despite the varying share of traffic and heating over the course of a year, this simply allowed the usage of a constant average flask-based ΔCO/ΔffCO₂
ratio for constructing the \(\Delta CO\)-based \(\Delta ffCO_2\) record. Of course, it is much more challenging to determine continuous \(\Delta CO\)-based \(\Delta ffCO_2\) estimates for stations where the \(\Delta CO/\Delta ffCO_2\) ratios show large seasonal or even diurnal variabilities.

A common challenge in regional inversions is the determination of the lateral boundary conditions (Munassar et al., 2023). In this study, we used two different emission inventories and meteorological fields to estimate the \(\Delta ffCO_2\) background for the Rhine Valley domain by modelling the contributions from the Central European \(ffCO_2\) emissions outside the Rhine Valley. For individual seasons the a-posteriori area source \(ffCO_2\) emissions around Heidelberg can differ by more than 10%. This highlights the strong need for appropriate boundary conditions. In Europe, the Integrated Carbon Observation System (ICOS, Heiskanen et al., 2022) provides high-quality atmospheric in-situ data from a network of tall-tower stations that cover a large part of the European continent. These observations may help to verify the \(ffCO_2\) emissions in Europe. Then, the optimized European \(ffCO_2\) emissions could be used to estimate more reliably the \(\Delta ffCO_2\) background for the Rhine Valley domain.

Overall, our results demonstrate that the weekly averaged \(\Delta CO\)-based \(\Delta ffCO_2\) observations are currently well suited to investigate the amplitude and the phasing of the seasonal cycle of the area source \(ffCO_2\) emissions in the main footprint of the Heidelberg observation site. The different sensitivity runs suggest that \(\Delta CO\)-based \(\Delta ffCO_2\) allows a reconstruction of this seasonal cycle from temporally constant a-priori estimates with an uncertainty of below ca. 30% for all seasons. Thus, one recommend applying this \(\Delta CO\)-based \(\Delta ffCO_2\) inversion at further urban sites with a strong heterogeneity in the local \(ffCO_2\) sources if the \(\Delta CO/\Delta ffCO_2\) ratios can be determined accurately.

Finally, the \(\Delta CO\)-based \(\Delta ffCO_2\) inversion can be seen as a simplification of a multi-species inversion, which is based on collocated \(CO_2\) and CO observations. Such a multi-species inversion exploits the fact that the collocated \(CO_2\) and CO observations are affected by the same atmospheric transport and that these two species have partially overlapping emission patterns (Boschetti et al., 2018). Boschetti et al. (2018) show that the consideration of these inter-species correlations leads to a reduction in the respective a-posteriori uncertainties of the \(ffCO_2\) (and CO) emissions. While our \(\Delta CO\)-based \(\Delta ffCO_2\) inversion assumes a constant but observation-based \(\Delta CO/\Delta ffCO_2\) ratio, the multi-species inversion intrinsically considers the spatiotemporal variability of the ratios. However, this requires reliable a-priori estimates of the CO/\(ffCO_2\) emission ratios and their uncertainties, as well as neglectable non-fossil CO sources and sinks.

5 Conclusions

This study illustrates the strong potential of continuous \(\Delta CO\)-based \(\Delta ffCO_2\) observations to determine the seasonal cycle of \(ffCO_2\) emissions in an urban region with highly heterogeneous \(ffCO_2\) sources in its vicinity. The ability of averaging and thus reducing the influence of individual hours with an inadequate model performance makes \(\Delta CO\)-based \(\Delta ffCO_2\), despite its larger
uncertainty, currently a better tracer than discrete $^{14}$C-based $\Delta$ffCO$_2$ from weekly flasks for estimating the seasonal cycle of the area source ffCO$_2$ emissions in the Upper Rhine Valley around the urban Heidelberg observation site.

For our study, we set up the CarboScope inversion system in the Rhine Valley. It is based on the high-resolution WRF-STILT model and uses the STILT volume source influence (VSI) approach developed in Maier et al. (2022) to represent the emission heights of point sources. However, despite the high-resolution WRF meteorology and the improved STILT-VSI approach, almost 100 $^{14}$C-based $\Delta$ffCO$_2$ estimates from flasks collected in Heidelberg during the two years 2019 and 2020 are insufficient to robustly estimate month-to-month variations of the area source ffCO$_2$ emissions in the main footprint of the site. Indeed, it seems that several flasks per week would be needed, so that the flask observations within one week could be averaged and overfitting of individual flask observations be prevented.

Due to the fortunate circumstance of currently having similar heating and traffic emission ratios in the main footprint of Heidelberg, we could use the average $^{14}$C-based $\Delta$CO/ffCO$_2$ ratio from the flasks to construct a continuous $\Delta$CO-based $\Delta$ffCO$_2$ record (see Maier et al., 2023a). The weekly averaging of this $\Delta$CO-based $\Delta$ffCO$_2$ record strongly reduces the impact of hours with an inadequate modelling on the a-posteriori ffCO$_2$ emissions. In fact, the weekly averaged $\Delta$CO-based $\Delta$ffCO$_2$ observations can robustly reconstruct the amplitude and the phasing of the seasonal cycle of the ffCO$_2$ area source emissions even from temporally constant a-priori emissions. In particular, the observational data clearly contain the distinct COVID-19 signal in 2020, which is characterized by overall lower emissions compared to 2019 and a steep drop in emissions in spring 2020 with the onset of the restrictions. Moreover, the comparison with the bottom-up emissions from TNO points to some inconsistencies in the TNO seasonality of the area source ffCO$_2$ emissions in the footprint of Heidelberg in 2019.

Overall, our sensitivity runs suggest that we can reconstruct the seasonal cycle of the ffCO$_2$ area source emissions around Heidelberg with an uncertainty of below ca. 30%. Therefore, one may recommend applying the $\Delta$CO-based $\Delta$ffCO$_2$ inversion at further urban sites with heterogeneous ffCO$_2$ sources, if the $\Delta$CO/ffCO$_2$ ratios can be estimated accurately. If ratios from bottom-up inventories are not trusted or the urban region is influenced by CO emissions from the biosphere, the ratios are most reliably calculated from $^{14}$C flasks. Then, at least some of the summer $^{14}$C flasks should be collected during situations with significant CO and ffCO$_2$ signals, so that a possible seasonal cycle in the $\Delta$CO/ffCO$_2$ ratios could be identified. At remote sites, such as at several ICOS atmosphere stations, with low ffCO$_2$ signals and predominant biosphere influence, the calculation of $\Delta$CO/ffCO$_2$ ratios and the construction of a bias-free $\Delta$CO-based $\Delta$ffCO$_2$ record might be more challenging than at an urban site. However, the model performance is expected to be better at remote sites with a typically higher air intake above the ground and a much lower heterogeneity in the surrounding ffCO$_2$ sources with minor influences from nearby point sources. Consequently, the outcome of our urban study cannot directly be transferred to remote sites; further studies are needed to investigate the potential of $^{14}$C-based versus $\Delta$CO-based $\Delta$ffCO$_2$ to estimate ffCO$_2$ emissions at such sites.
Appendix

A1. Impact of point sources on the a-posteriori area source ffCO$_2$ emissions

To investigate the influence of inadequate point source modelling on the a-posteriori area source ffCO$_2$ emissions, we use two different $\Delta$CO-based $\Delta$ffCO$_2$ inversion setups: (1) an inversion with fixed point source emissions (“INV_fix”) and (2) an inversion with adjustable point source emissions (“INV_adj”). The first inversion setup corresponds to the inversion described in Sect. 2. It optimizes the flat a-priori area source emissions by using fixed monthly point source emissions. The second inversion setup optimizes both, the flat a-priori area source emissions, and the monthly a-priori point source emissions. Thereby, the point source emissions from the energy production and the industry sector, respectively, get the same temporal (i.e. “Filt3T” in CarboScope notation, see Sect. 2.2.6) and spatial (i.e. one spatial scaling factor) degrees of freedom like the area source emissions. Ideally, both inversion setups should lead to the same a-posteriori area source emissions, meaning that the modelling of the well-known point source emissions has no influence on the area source emission estimates. Obviously,
this is not the case. If the model-data mismatches of the individual afternoon hours of the $\Delta$CO-based $\Delta$ffCO2 record are not averaged, the INV_fix inversion leads to much lower area source emissions estimates than the INV_adj inversion (see cyan curves in Fig. A1). For individual seasons, e.g. in summer 2020, the differences are larger than 150%. Thus, the INV_fix inversion tends to decrease the area source emissions to compensate for an inadequate modelling of the (fixed) point source emissions. This shows that even with the VSI approach the model seems to overestimate the contributions from point sources at the Heidelberg observation site for individual hours.

The averaging over one afternoon (magenta curve in Fig. A1) leads only to minor improvements; there are still deviations larger than 100% in summer 2020. In contrast, the averaging interval of one week (blue curve) limits the largest deviations in summer 2020 to below 30%. Averaged over the two years 2019 and 2020, these deviations between the INV_fix and INV_adj a-posteriori area source emissions are even less than 10%. A monthly averaging interval (pink curve) further reduces the deviations to below 20% in summer 2020.

**A2. Hypothetical seasonal cycle in the $\Delta$CO/$\Delta$ffCO2 ratios**

![Graph showing hypothetical seasonal cycle in the $\Delta$CO/$\Delta$ffCO2 ratios](image)

*Figure A2: Average $\Delta$CO/$\Delta$ffCO2 ratio (black) and hypothetical seasonal varying ratio (cyan) used to construct the $\Delta$CO-based $\Delta$ffCO2 record for the base inversion (Fig. 4) and the sensitivity inversion run (cyan curve in Fig. 5), respectively.*
A3. Comparison between two modelled Rhine Valley ∆ffCO₂ backgrounds

Figure A3: Difference between the Rhine Valley background modelled with TNO emissions (ΔffCO₂,CE,RV,TNO) and the Rhine Valley background modelled with EDGAR emissions (ΔffCO₂,CE,RV,EDGAR). Shown are weekly averages for afternoon situations.
Data availability

We used the $^{14}$C- and $\Delta$CO-based $\Delta$ffCO$_2$ data published with Maier et al. (2023a).

Author contribution

FM designed the study together with all co-authors. FM performed the inverse modelling and processed the inversion results. CR helped with applying the CarboScope inversion framework for the Rhine Valley domain. CG modelled the alternative Rhine Valley $\Delta$ffCO$_2$ background with emissions based on EDGAR. The various inversion results were discussed by all authors. FM wrote the manuscript with help of all co-authors.

Competing interests

Some authors are members of the editorial board of ACP. The peer-review process was guided by an independent editor, and the authors have also no other competing interests to declare.

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