

Replies to review 1

We want to thank the anonymous referee for the review of our manuscript. Our replies are marked in blue.

The manuscript by Maier et al. presented measurements of $^{14}\text{CO}_2$ and CO in flasks collected at two sites, and the purpose of these measurements is to assess the ratio and the associated uncertainties of CO and fossil-fuel sourced CO₂ (ΔffCO_2). The latter, proposed by the authors, can be further used to estimate ΔffCO_2 based on CO measurements which is easy doing. The idea behind this study appears to be that since C-14 analysis is difficult and there is a need of alternatives to estimate ΔffCO_2 , while CO that is produced mainly from the same fossil fuel combustion source can serve as a tracer to estimate ΔffCO_2 as long as the ratio of CO to ΔffCO_2 can be constrained.

I would say this is a fair theory, however, the manuscript is more like a measurement report rather than a research article. This is my first impression of reading this manuscript. The second, as the authors indicated in the manuscript, there are many issues regarding the ratio based on flask measurements, so as the ability of this ratio used to predict ΔffCO_2 from CO measurements. This whole idea has a few confusions or flaws that leads to little confidence for its applications. I list my major concerns as follows:

We regret that we have not succeeded in explaining the relevance of our study to the broader community. As we state in the introduction, the basic idea of using CO as a proxy for ffCO_2 is more than 20 years old. Even older is the realisation that there will be no semi-continuous measurements of the direct ffCO_2 tracer $\Delta^{14}\text{CO}_2$ in atmospheric observing networks for the foreseeable future. As we discuss in the paper, CO is not a perfect ffCO_2 proxy for many reasons. Therefore, we consider it the primary goal of our study to emphasise the shortcomings of the CO-proxy approach clearly. This includes showing that the use of the CO proxy requires calibration by ^{14}C measurements to achieve the necessary precision. Despite all the difficulties and deficits of the CO-proxy-based ffCO_2 estimation, we demonstrate in this paper and in the companion paper by Maier et al. (2023) the great potential of this method. We understand that due to our comprehensive and in-depth analysis of the problems of the CO-proxy, the impression of the measurement report may arise. However, it is precisely this detailed and dedicated investigation of the CO-proxy approach that sets this publication apart from its predecessors and makes future users of the CO-proxy approach, whether for in-situ or remote sensing approaches, aware of its potential and shortcomings.

1). The authors point out the disadvantage of using C-14 measurement to assess ΔffCO_2 , high cost, low coverage, and etc., and thus there is a need of independent tracers that are easy monitoring. The proposed tracer is CO. But in order to use CO to estimate ΔffCO_2 in a site or regions, one has to first measure enough C-14 data to build a robust CO/ ΔffCO_2 ratio? This is sort of a loop, if there is already C-14 measurements, isn't that can be directly used to calculate ΔffCO_2 ? Although CO measurements can be continuous, so as the derived ΔffCO_2 with a known CO/ ΔffCO_2 ratio, would continuous ΔffCO_2 record be offering significantly more valuable information than discrete (e.g., daily or hourly average) ΔffCO_2 measurements?

As mentioned above, using $^{14}\text{CO}_2$ measurements is the most direct way to estimate ΔffCO_2 concentrations. However, the sparse $^{14}\text{CO}_2$ observations lead to a small amount of ΔffCO_2 estimates, which could be used in inverse models to infer ffCO_2 emissions. The question is then: is the amount of ΔffCO_2 data enough for getting robust and data-driven inversion results? This is exactly what we investigated in the companion paper (Maier et al., 2023), which followed up this study. It turned out, that we indeed get no robust ffCO_2 emission estimates for the surroundings of Heidelberg if we use the ^{14}C -based ΔffCO_2 estimates from the Heidelberg flasks. This can mainly be explained by the very heterogenic distribution of the ffCO_2 sources around Heidelberg (including several large point sources) and the shortcomings of the transport model in accurately simulating ffCO_2 concentrations for individual (afternoon) hours. In contrast, the continuous Heidelberg CO-based ΔffCO_2 estimates, which we derived in this study, yield robust and data-driven inversion results that could be used to investigate the effect of the Corona restrictions and to validate the seasonal cycle of the TNO ffCO_2 emission inventory in the main footprint of Heidelberg. Thus, the continuous CO-based ΔffCO_2 record indeed yields more valuable information than the discrete ^{14}C -based ΔffCO_2 estimates from flasks for this urban region around Heidelberg and at the present time when the traffic and heating sectors show here similar CO/ ffCO_2 emission ratios. Of course, if the ^{14}C -based ΔffCO_2 had a similar temporal resolution like the CO-based ΔffCO_2 , the information content of the ^{14}C -based ΔffCO_2 would be higher than that of the CO-based ΔffCO_2 . However, as this is not (yet) the case, we conclude that the usage of CO-based ΔffCO_2 to infer ffCO_2 emissions could be a valuable approach for other (urban) sites.

For such a CO-based ΔffCO_2 inversion, it is essential to have a reliable quantification of the uncertainties of the CO-based ΔffCO_2 estimates and an investigation of potential seasonal or diurnal cycles in the $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios. Both aspects are treated in detail in our present study, which is why it forms the basis for CO-based ΔffCO_2 inversions.

2) I am not sure if this is the authors' idea: once a robust CO/ ΔffCO_2 ratio was available, then perhaps this ratio is able to apply to other locations or the same location but at a different time? This is my impression of reading the manuscript, and this is perhaps the most (if not only) significance of establishing the ratio. However, as the measurement reports from the two sites indicates, the CO/ ΔffCO_2 ratio are different among these sites, and there are also large temporal variations. This causes doubts on the ability of the ratio to be applied to period or regions without C-14 but only CO observations. In fact, due to spatial and temporal variations in the use of fossil fuel energy, as well as the spatial and temporal variations in other sources/factors that could influence the production and atmospheric removal of CO, there is a doubt that whether the CO/ ΔffCO_2 ratio can stay relatively constant with time and space.

We agree, the $\Delta\text{CO}/\Delta\text{ffCO}_2$ can show large spatial and temporal differences due to the spatiotemporal variability of the CO/ ffCO_2 emission ratios and/or non-fossil CO contributions. This is also what we found in our study: the average $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratio in Heidelberg is lower compared to that at OPE. That's why we do not recommend to apply a single $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratio for different sites or times, if it is not validated by ^{14}C measurements at the respective sites. In our study, we discuss how many ^{14}C measurements should be

performed to get robust $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios, which can then be used to construct a CO-based ΔffCO_2 record with high temporal resolution.

Moreover, our comparison of the observed ratios with inventory-based ratios from TNO clearly reveals that the $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios should be calibrated with ^{14}C measurements to avoid large biases in the CO-based ΔffCO_2 estimates. Ongoing ^{14}C measurements are therefore a prerequisite for monitoring changes in future $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios and continuing to apply the CO proxy approach. This information is also relevant for studies combining satellite-based CO observations and inventory-based CO/ ffCO_2 emission ratios to derive ffCO_2 emissions.

The first concern emphasizes that no matter what one needs to measure C-14, and the second indicates the established ratio is probably not able to fulfil the intended tasks. As such, the scientific significance of these measurements is somewhat weak, and this is why I suggested that this manuscript is more like a measurement report.

Unfortunately, it is not straightforward to calculate ΔffCO_2 concentrations, which then could be used to derive top-down ffCO_2 emission estimates. If there were continuous ^{14}C measurements with high spatiotemporal coverage and low uncertainty, we would hardly need to think about using CO as a tracer for ffCO_2 . However, this is at least not yet the case. Thus, the CO proxy approach is a way to bridge the gap between more reliable but sparse ^{14}C -based ΔffCO_2 estimates with temporal information derived from CO.

With this in mind, we are convinced that our present study is important and has a scientific significance. We want to summarize here the main points, why we do not think that this study is just a measurement report:

1. In addition to quantifying the uncertainties of the CO-based ΔffCO_2 , we conducted a synthetic data experiment to characterize and interpret the cause of these uncertainties. From this study, we were able to draw conclusions about the impact of the spatiotemporal variability of the CO/ ffCO_2 emission ratios on the CO-based ΔffCO_2 uncertainties at an urban and a rural site.
2. We used the STILT model to also simulate $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios for both sites. We carefully compared the simulated ratios with our measurements and demonstrate that there can be substantial biases. Our study suggests that the TNO inventory may underestimate the CO/ ffCO_2 emission ratios in the Rhine Valley. A more detailed investigation (in the revised version of the manuscript) reveals that especially the CO/ ffCO_2 emissions from the TNO heating sector might be too low in the main footprint of Heidelberg. Such studies are important to improve the emission inventories.
3. By performing a bootstrapping approach, we provide a rough estimate on how many ^{14}C flasks should be collected at other sites to obtain robust $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios, which can then be used to derive CO-based ΔffCO_2 concentrations at those sites. This is an essential information if CO-based ΔffCO_2 data is to be used in inverse models to estimate ffCO_2 emissions. In our follow-up study, we show that the CO-based ΔffCO_2 data from Heidelberg lead to robust ffCO_2 emission estimates, which could be used to validate the seasonal cycle of the TNO emission inventory.

From that we argue that our study has enough scientific significance to be published as a research article.

In addition, I have some technical suggestions that the authors can consider to use or not:

1) in the method part, please state more clearly how other sources especially the biomass burning source of CO is treated to get ΔCO ; This includes the modeling of inventory based ratio.

The TNO inventory includes CO emissions from agricultural waste burning, i.e. the burning of crop residues based on a 10 year climatology. However, CO emissions from forest fires are not included. These emissions are erratic and can be obtained from e.g. the Copernicus Global Fire assimilation system (GFAS). For the central European region, forest fires are not a dominant source of CO. We clarified this in the manuscript. (p. 7, l. 205-207)

2) In 2.2.1., the defined Rflask is in fact not used but instead $\Delta\text{CO}/\Delta\text{ffCO}_2$ in follow-up results and discussion. I suggest to keep constant throughout the manuscript.

Thank you for this hint. We replaced Rflask by $\Delta\text{CO}/\Delta\text{ffCO}_2$ in our manuscript.

3) Figure 3b, could not understand how real flask measurements can be plotted in the figure, the X-axis is measurements, while the Y-axis is synthetic data which is not scaled to real measurements.

The real and synthetic data share the same X-axis and Y-axis. We labelled the X-axis with “ ^{14}C -based ΔffCO_2 ” because it refers to the ^{14}C -based ΔffCO_2 observations (in case of the real observations, i.e. the black and grey dots) and to the error-prone synthetic ΔffCO_2 data (in case of the synthetic data, i.e. the red and orange dots), which should mimic the variability of the ^{14}C -based ΔffCO_2 observations. Similarly, the Y-axis with label “ ΔCO -based ΔffCO_2 ” refers to the ΔCO -based ΔffCO_2 observations as well as to the synthetic ΔCO -based ΔffCO_2 data, which were constructed by dividing the synthetic ΔCO data by a constant $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratio of 8.44 ppb/ppm. We tried to make this clearer in the caption of Fig. 3.

References:

Maier, F. M., Rödenbeck, C., Levin, I., Gerbig, C., Gachkivskyi, M., and Hammer, S.: Potential of ^{14}C -based versus ΔCO -based ΔffCO_2 observations to estimate urban fossil fuel CO_2 (ffCO_2) emissions, EGU sphere [preprint], <https://doi.org/10.5194/egusphere-2023-1239>, 2023.

Replies to review 2

We want to thank John Miller for the review of our manuscript and his helpful suggestions for improving this study. Our replies are marked in blue.

Review of Maier et al, "Uncertainty of continuous ΔCO -based ΔffCO_2 estimates derived from ^{14}C flask and bottom-up $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios" by John Miller

General comments

Overall, this is a very good study focused on developing high frequency proxies (here CO) for the estimation for the recently added fossil content of atmospheric CO_2 measurements. The writing is generally very good and the figures are excellent, reflecting the analysis itself. The pdf has numerous comments but I will highlight two here:

1. Although this is clear in the title, use of "Delta(CO)-based DffCO2 estimates", when used without explanation, has the potential to be highly misleading because these estimates (the atmospheric data-based ones the paper shows to be trustworthy) are still based on D^{14}C I'm not exactly sure of the solution, but perhaps you can employ nomenclature/notation that identifies such values as 'calibrated' by ^{14}C .

We agree, that this can lead to confusion. We tried to make this clearer in our manuscript, e.g. by using "proxy-based ΔffCO_2 " in the abstract, as you suggested. However, in the main text we would like to use " ΔCO -based ΔffCO_2 " because this is also what we used in the companion paper (Maier et al., 2023). We also added some text in the introduction, to make it clear, that the " ΔCO -based ΔffCO_2 " is calibrated with ^{14}C . (e.g., p. 3, l. 71-72; p. 3, l. 90; p. 5, l. 137)

2. I have a few questions about the TNO inventory that could benefit by a bit more investigation and explanation. First, it appears that TNO includes biofuels such as wood. But what about ethanol and biodiesel? Generally, can the fossil components of the TNO inventory be isolated for a more direct comparison with ^{14}C -based observations? Second, in investigation of the point source impacts for Heidelberg, can you transport the non-point-source sectors to see how much the match to data is improved – i.e., is the mismatch mainly due to the ratio of (dilute) point to area sources in TNO or mainly due to incorrect emission ratios for the area sources?

Thank you for your suggestions. The TNO inventory distinguishes between fossil fuel and biofuel CO_2 and CO emissions. Thus, TNO includes emissions from wood-fired heating as well as biofuel emissions from the traffic sector. For the traffic sector this is based on national reporting of shares of ethanol in gasoline and/or biodiesel in diesel. Moreover, there is also data on the amount of biomass co-fired in coal-fired powerplants. This is also in the inventory as CO_2 from biofuel.

We carried out both of the simulations you suggested (see Fig. 1 below). The magenta dots in Figure 1a show the contributions from the non-point-source sector only. They

lead to an average ratio of about 6 ppb/ppm, which is well below the observed ratio (grey crosses). From that we conclude that TNO might underestimate the ratio of the area source emissions in the Rhine Valley. Furthermore, a potential wrong dilution ratio between point sources and area sources (both with correct emission ratios) can't explain the differences between observed and modelled $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratios, because both, the average modelled ratio from only-area sources (6.0 ppb/ppm) and the ratio from only-point sources (1.2 ppb/ppm) are below the observed ratio of 8.44 ppb/ppm.

Fig. 1b shows the simulated contributions from the traffic (orange) and heating (cyan) sectors. The traffic (biofuel plus fossil fuel) sector leads to an average $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratio of 7.72 ± 0.08 ppb/ppm ($R^2=0.93$), which is less than 10% lower compared to the observed average ratio of 8.44 ppb/ppm. However, the heating (wood plus fossil) sector leads to a much lower average $\Delta\text{CO}/\Delta\text{ffCO}_2$ ratio of 3.36 ± 0.09 ppb/ppm ($R^2=0.65$). This might indicate that the CO/ffCO_2 emission ratios from the TNO heating sector are too low in the main footprint of Heidelberg. This could be explained, for example, by an incorrect distribution of the use of fossil and bio fuels in the heating sector.

We included these plots and a discussion in our manuscript. (Fig. 3b and A3 in the manuscript; p. 12, l. 313-314; p. 18-19, l. 474-499)

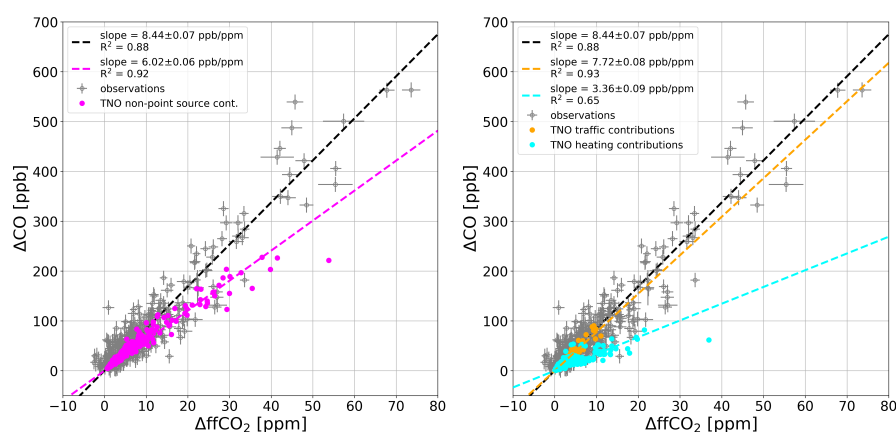


Figure 1: ΔCO and ^{14}C -based ΔffCO_2 observations from the Heidelberg flasks (in grey) and (a) simulated non-point-source ΔCO and ΔffCO_2 contributions for the flask events (magenta), and (b) simulated ΔCO and ΔffCO_2 contributions from the traffic (orange) and heating (cyan) sectors for the flask events.

Specific comments

Suggested edits and comments are embedded in the manuscript .pdf. Blue highlights indicate those that are language oriented and yellow for science/conceptual issues.

Thank you for your comments. We directly replied to them in the .pdf document.

References:

Maier, F. M., Rödenbeck, C., Levin, I., Gerbig, C., Gachkivskyi, M., and Hammer, S.: Potential of ^{14}C -based versus ΔCO -based ΔffCO_2 observations to estimate urban fossil fuel CO_2 (ffCO_2) emissions, EGUsphere [preprint], <https://doi.org/10.5194/egusphere-2023-1239>, 2023.