Review of Li et al. (2025), "Drivers and implications of declining fossil fuel CO_2 in Chinese cities revealed by radiocarbon measurements"

In this study, the authors present estimates of the fossil fuel CO_2 (C_{ff}) concentration in several Chinese cities, based on $\Delta^{14}CO_2$ flask observations from one summer and one winter month in 2022. Additional $\delta^{13}CO_2$ and CO measurements are used to estimate the contributions from coal, oil and gas in the C_{ff} signals, and to derive $R_{CO/CO2ff}$ ratios that provide information on combustion efficiency. By comparing their results from 2022 with historical estimates, the authors conclude that the trend in fossil fuel CO_2 in Chinese cities is declining.

Overall, this manuscript is well structured and written. The estimation of the C_{ff} concentrations and their uncertainties is carried out carefully and the results are presented in a clear way.

However, I have two major concerns regarding the analysis of the C_{ff} concentration trend.

First, the atmospheric C_{ff} concentration is greatly affected by transport-driven variability, e.g., on diurnal and synoptic time scales. Weekly flask samples with an air integration time of ca. 15-20 min can only capture a snapshot of the variability in the C_{ff} concentration. I therefore miss an analysis that shows how representative the flasks collected in August and December 2022 are for the entire winter and summer of that year. Were August and December 2022 typical summer and winter months, respectively, in terms of atmospheric transport? I think this is important to address when these measurements are used to represent the "winter" and "summer" of 2022 and compared with measurements from previous years. It is also important to make this information available so that future studies can refer to it when using the C_{ff} estimates for 2022 from this study. This concern mainly relates to the trend in the C_{ff} concentrations. The effect of atmospheric transport variability on the trend in fuel type contribution and $R_{CO/CO2ff}$ ratios may be minor or even cancel out when the CO concentration is divided by the C_{ff} concentration.

My second concern relates to the C_{ff} trend analysis in Guangzhou. The authors compare their C_{ff} estimates from 10 sites in Guangzhou in 2022 with C_{ff} estimates from Ding et al. (2013) for 2010-2011. However, the C_{ff} estimates from Ding et al. (2013) are only from one site, which "may be influenced by local signals rather than representing a general urban signal" (Ding et al., 2013). Furthermore, in the present study, the 2022 flasks were collected "between 13:00 and 17:00 local time, coinciding with the deepest planetary boundary layer and well mixed atmospheric conditions" (Li et al., 2025). However, in the study by Ding et al. (2013) the flasks were collected at 20:00, which, according to Ding et al. (2013), is directly after the city's rush-hour. Ding et al. (2013) state that "18:00 to 19:00 is the "rush hour" of the city, and CO_2 emitted from the traffic and domestic activities such as cooking reaches its highest point at that time. Thus, the atmospheric CO_2 concentration is close to its peak in that time period". Therefore, based on the different flask sampling times alone, I would expect higher C_{ff} concentrations in the Ding et al. (2013) study than in the current study, even if there were no declining trend in the fossil fuel CO_2 emissions. Furthermore, sampling during rush-hour in 2010-2011 vs. sampling in the afternoon in 2022 could also impact the fuel type mixture and the $R_{CO/CO2ff}$ ratios. Please note that I have not checked whether there are similar issues in the C_{ff} trend analysis at the other cities.

In my opinion, these points should be addressed, or at least discussed in more detail, to improve the reliability and the robustness of the reported trends in the C_{ff} concentration. Maybe the continuous CO and CO_2 observations (if available) and the FLEXPART simulations could help assess the representativeness of the C_{ff} estimates and the effect of the diurnal cycle on the C_{ff} estimates (in the case of Guangzhou).

Specific comments:

l. 57: Please introduce the 'Δ' in "ΔCO" to avoid confusion with the 'Δ' in "$\Delta^{14}CO_2$".

l. 74-75: You describe that there is prevailing southeast monsoon in summer and northeast monsoon in winter. Hence, during winter the NL background site tends to be upwind of the targeted cities. However, in summer, air masses travel over the targeted cities and become polluted before reaching the NL background site. Could this have an influence on the difference between the winter and summer C_{ff} estimates derived from the $\Delta^{14}CO_2$ gradient between the background site and the target sites? In other words, could the smaller C_{ff} signals in summer at least partly be explained by pollution at the background site? Can you detect such pollution events at the NL site, or is the background site far enough away that the pollution signals from the cities are already diluted?

Fig. 1: The upper two panels are not labelled with a letter. It would also be helpful to indicate the locations of Beijing, Xi'an as well as the background sites NL and Waliguan in the overview map at the top.

l. 150: Due to the proximity of some sites to the coast, is there also a CO_2 contribution from the ocean?

l. 168-169: This is not clear to me. Which BB and Rh corrections did you apply to the $\Delta^{14}CO_2$ data in the end? Did you use your simulations with the maximum assumptions (100% perennial biomass and α_{BB}=100%)? What do you mean by "literature-based corrections"? Please could you clarify?

l. 186-188: Have you calculated the coal, oil, and gas fractions of C_{ff} separately for the winter and the summer period, given that they may change throughout the seasons?

l. 190: Do you apply an uncertainty to the $\delta^{13}C_{coal}$ end-member signature as well?

l. 205-209: Which grid cells did you use to average the E_{CO} and E_{CO2ff} emissions in the inventory? Are the E_{CO} and E_{CO2ff} estimates for the whole city, or did you use the FLEXPART footprints to define the catchment regions of the observations and to weight the emissions of the respective grid cells within the footprint? Please also mention the inventory that you used.

l. 219-220: Did you only use the observations from the two-month sampling campaign to calculate the "annual" average at the NL site, or were there additional observations throughout the year? Which observations did you use to calculate the average for the Jungfraujoch data (only the 2 months or the full year)? Please specify.

l. 226: In Tab. A1, you report summer values of 5.1±1.3 ‰ and winter values of -2.0±0.8 ‰ for the NL site. These values differ from those stated here. Please could you clarify this?

Fig. 2: In order to compare the $\Delta^{14}CO_2$ data of the city sites with the respective NL background, it would be helpful to include the summer and winter NL background values in Fig. 2, perhaps by indicating the NL summer and winter averages with open and filled circles.

l. 242-244: Do you find different C_{ff} fractions in the summer month of your campaign?

l. 253-254: I wonder if the C_{ff} estimates from the other cities around the world are also based on flask samples collected in the afternoon, as you did. Or are integrated samples also used, containing air from a whole week, for example? I ask because, when nighttime observations are sampled, the C_{ff} could potentially be larger when fossil emissions accumulate in a shallow nocturnal boundary layer.

L. 260-261: Please explain which ODIAC grid cells you used to calculate the correlation with the C_{ff} measurements.

l. 264-266: This is a bit difficult to follow. Could you perhaps indicate the industrial areas in SZs and the port areas in ZJw and ZJs in Fig. 1, to which you are referring?

l. 287-288: I could not find any blue squares "shown as enlarged maps in the right figures" in Fig. 3.

l. 293-295: The C_{ff} estimate from Ding et al. (2013) for 2010-2011 is derived from flask observations from a single measurement site, which "may be influenced by local signals rather than representing a general urban signal" (Ding et al., 2010). In contrast, the C_{ff} estimate for Guangzhou in your study is based on measurements from 10 sites. Moreover, Ding et al. (2013) uses another $\Delta^{14}CO_2$ background from "plant corn leaves in 2010 from Qinghai, Gansu Province, and Tibet, where the human activity can be neglected" (Ding et al., 2013). How does this affect the trend in the C_{ff} concentration? Please see my related comment above.

l. 299-303: I find this site-specific comparison much better suited for analysing trends in the C_{ff} data. However, the issue remains that Ding et al. (2013) sampled rush-hour signals, whereas you sampled well-mixed afternoon situations. Do you have continuous CO and CO_2 observations at this measurement site that could be used to estimate the C_{ff} signal expected after rush-hour at 20:00 in 2022?

l. 305-309: Are the C_{ff} estimates for Beijing (and Xi'an) in different years based on the same measurement sites? For example, you report the following for Beijing: (39.7 ± 36.1) ppm for 2014 and (27.0 ± 0.3) ppm for 2014-2016. Why is the standard deviation of the 2014 estimate almost 100%, whereas the standard deviation of the 2014-2016 estimate is only 1%? Is this due to a different number of observations being averaged? It would also be useful to state the number of observations used to calculate the averages, to give an idea of how representative the values are.

l. 382-388: If you would like you could also mention that lower C_{ff} signals in summer lead to higher uncertainty in the regression slope and, consequently, increased uncertainty in the summer ratio compared to the winter ratio (see e.g., Maier et al., 2024). I think this can also be seen in Fig. H2 of your study, where the summer ratios tend to show a higher uncertainty than the winter ratios.

l. 397-399: What is the uncertainty of the ratios, i.e., of the regression slopes shown in Fig. H2?

l. 403-404: Could you please explain and justify the 20% correction used to derive $R_{CO/CO2ff}$ from $R_{CO/CO2}$ in a bit more detail. Where does the assumption that 20% of the CO_2 enhancement is from non-fossil sources come from? This could be done in the Methods section.

l. 445-447: Could the higher $R_{CO/CO2ff}$ ratio from the study by Silva et al. (2013) compared to the ratio from the study by Mai et al. (2017) and the ratio from your study be explained by the fact that the study by Silva et al. (2013) includes summer ratios in the average $R_{CO/CO2ff}$, whereas the study by Mai et al. (2017) and you calculate the winter mean $R_{CO/CO2ff}$ (according to Tab. H1)? You show that summer ratios are also higher in your study.

Tab. A1: It would be helpful to also have the number of observations per site used to calculate the "summer" and "winter" averages.

l. 544: Please label the "$\Delta^{14}C$" for multi-year biomass in Eq. B1 differently than the atmospheric "$\Delta^{14}C$".

l. 568-579: Although the PWR type has the lowest emission factor for $^{14}CO_2$ release, PWR reactors can also have substantial $^{14}CO_2$ emissions depending on their electricity supply. For example, Zazzeri et al. (2018) estimate substantial $^{14}CO_2$ emissions of roughly 100-200 GBq/yr for each of the three NPPs Daya Bay, Ling'ao and Yangjiang for the year 2016 (see their supplement material S1). Depending on the distance between the NPPs and the measurement sites, this could have an impact on the $\Delta^{14}CO_2$ measurements. The distance between the NPPs and the observation sites should be mentioned here to enable a more rigorous assessment of the potential impact on the $\Delta^{14}CO_2$ observations (e.g., compare with Kuderer et al., 2018).

l. 619: In Eq. C1 (and throughout Sect. C2.2) you use C_{bio} to refer to biofuel/biomass emissions from the EDGAR inventory. In the main text, however, C_{bio} refers to the total CO_2 contributions from the biosphere (e.g., in Eq. 1). It would be better to use two different expressions.

Tab. H1: Why are the uncertainties for the 2022 winter $R_{CO/CO2ff}$ ratios from your study so low (~0.00002 ppb/ppm)? Such low uncertainties seem unrealistic, given the spatio-temporal variability of the $R_{CO/CO2ff}$ ratios. Is this just a typo or an incorrect unit?

Technical corrections:

l. 447: Please insert space "from 72.3".

References:

Kuderer, M., Hammer, S., and Levin, I.: The influence of $^{14}CO_2$ releases from regional nuclear facilities at the Heidelberg $^{14}CO_2$ sampling site (1986–2014), Atmos. Chem. Phys., 18, 7951–7959, https://doi.org/10.5194/acp-18-7951-2018, 2018.

Maier, F., Levin, I., Conil, S., Gachkivskyi, M., Denier van der Gon, H., and Hammer, S.: Uncertainty in continuous ΔCO-based $\Delta ffCO_2$ estimates derived from ^{14}C flask and bottom-up ΔCO / $\Delta ffCO_2$ ratios, Atmos. Chem. Phys., 24, 8205–8223, https://doi.org/10.5194/acp-24-8205-2024, 2024.

Zazzeri, G., Acuña Yeomans, E. and Graven, H. D.: Global and Regional Emissions of Radiocarbon from Nuclear Power Plants from 1972 to 2016, Radiocarbon, 60(4), 1067–1081. https://doi.org/10.1017/RDC.2018.42, 2018.