Replies to review 1

We want to thank Maarten Krol for the review of our manuscript and his helpful suggestions. We directly replied to the comments in the .pdf document. Where not stated otherwise we adapted the suggestions.

Replies to review 2

We would like to thank the anonymous referee for the thoughtful review of our manuscript. Our replies are marked in blue and embedded below.

The manuscript entitled "Using NO_x as quantitative fossil fuel CO2 proxy in urban areas: challenges and benefits" describes the use of NO_x and $^{14}CO_2$ measurements in Heidelberg (Germany) to estimate the seasonally averaged ratios of local excess NO_x (ΔNO_x) to local excess fossil fuel (ff) CO_2 ($\Delta ffCO_2$) concentrations and to derive $\Delta ffCO_2$ concentrations from the NO_x measurements. The analysis presented in the manuscript is overall sound and sufficiently detailed. However, I believe the scope of this study is too narrow, and I doubt that the presented results are sufficiently significant to warrant publication of the manuscript in ACP. My specific concerns and some suggestions are outlined below.

Major points

1. The title of the manuscript is not quite appropriate, since the study addresses only one possible way to use NO_x observations as a $ffCO_2$ proxy, that is by using $^{14}CO_2$ measurements. A more common way does not require the availability of rather scarce $^{14}CO_2$ measurements but instead involves emission ratios from inventories. Hence, I suggest narrowing the title, for example as follows: "Using NO_x as quantitative fossil fuel CO_2 proxy *based on $^{14}CO_2$ measurements* in urban areas: challenges and benefits".

   We agree that including radiocarbon in the title helps to clearly outline the purpose and scope of our study. We therefore changed the title to "Challenges and benefits of using NO_x as a quantitative proxy for fossil fuel CO_2 in an urban area based on radiocarbon measurements".

2. It is quite obvious that variations of NO_x (linearly scaled or not) should correlate with variation $^{14}CO_2$ in vicinity of relatively strong local emission sources. It is also clear that this correlation can never be perfect due to atmospheric chemistry and the fact that the NO_x-to-CO_2 emission ratios differ for different source types. Furthermore, since the relationships between the NO_x- and ^{14}C-based $ffCO_2$ are likely to differ (quantitatively) for various sites across the Europe and the world, the quantitative findings of this study are not necessarily relevant to any other sites. Thus the results of the study seem relatively trivial and the scientific message is unclear.

   We appreciate the reviewer's insightful comment and fully agree that the co-emission of NO_x and CO_2 from combustion processes is a well-known and conceptually straightforward relationship. In fact, we consider this apparent simplicity to be a key strength of our approach: the underlying physical connection between NO_x and $ffCO_2$ emissions is robust and directly linked to combustion processes.

However, the central scientific question of our study is not whether such a correlation exists, but whether this seemingly trivial process-level relationship can be exploited quantitatively for the retrieval of $\Delta ffCO_2$, and what uncertainties arise from doing so. This aspect is far from trivial, as it involves assessing how differences in atmospheric lifetimes, chemical transformations, and emission heterogeneity affect the usability of NO_x as a proxy under real-world urban conditions.

We agree with the reviewer that the specific quantitative results obtained in this study are only directly applicable to the investigated city and, within it, to the specific measurement site. At no point do we suggest that our numerical values can be transferred to other locations. The scientific relevance of this work lies instead in demonstrating the feasibility of the approach — a proof of concept — and in quantifying the associated uncertainties. Moreover, our detailed discussion of the conceptual challenges arising from the differing atmospheric behaviours of NO_x and $ffCO_2$ provides valuable insights for future applications.

We remain convinced that continuous $ffCO_2$ estimates based on site-specific, $^{14}CO_2$-calibrated $NO_x/ffCO_2$ ratios can provide crucial information for urban-scale inverse modelling efforts. We have clarified this perspective in the revised introduction and conclusion sections (L 45-47, 447-448).

Unfortunately, the authors did not show how the performance of the NO_x-based $ffCO_2$ record depends on the configuration of the local domain, even though they noted in the Introduction that “the choice of a suitable and common background for all species is of paramount importance”. A more detailed examination of this point (with dedicated test cases) could perhaps help justifying the study and generalizing its results.

The importance of the choice of background mainly relates to the “common” part of the statement, in that the background needs to have the same spatial representation for NO_x and $ffCO_2$. The simplified approach seen in previous studies was using a European background for $ffCO_2$ and no background correction for NOx, i.e. using the (variable) boundary of the local area that contributes to the measured NO_x signal due to atmospheric chemistry. Using this approach leads to a ~1 ppm increase in the uncertainty of the ΔNO_x -based $\Delta ffCO_2$ estimates. The exact choice of the background per se is not as crucial, as stated in sections 2.3 and 4.1. We changed the corresponding wording in the introduction (L 47) and the discussion (L 361) and included the above comparison to using a European background (L 373).

3. The NO_x-based $\Delta ffCO_2$ concentrations are representative of an area of about 30x80 km (according to Fig. 2). Hence, given that $^{14}CO_2$ data are available in Europe from just a dozen or so operational sites, the proposed method can hardly help

constrain the European carbon budget (unlike the original $^{14}CO_2$ observations; see, e.g., https://doi.org/10.5194/acp-25-397-2025).

The study does not intend to help constrain the European carbon budget, but rather city-wide emissions. As stated in the title, the goal is to use NO_x measurements to retrieve $\Delta ffCO_2$ concentrations in an urban context. We have adapted the introduction to more clearly state this (L 40-41).

However, the study's significance in this context could be increased if the authors used their $^{14}CO_2$ measurements to evaluate the inventory-based $\Delta NOx/\Delta ffCO_2$ ratios. A similar analysis (but in the case of the $\Delta CO/\Delta ffCO_2$ ratios) was conducted in a recent study authored by several co-authors of the given manuscript (https://doi.org/10.5194/acp-24-8183-2024).

We fully understand the reviewer's very natural request to use our $^{14}CO_2$ observations to evaluate the inventory-based $\Delta NO_x/\Delta ffCO_2$ ratios, similar to what has been done for CO in our previous work. Unfortunately, such an analysis is not feasible within the framework of the present study.

Even more so than for CO, the relationship between NO_x and $ffCO_2$ is heavily affected by short atmospheric lifetimes and complex chemical reactions of reactive nitrogen species. A meaningful comparison between measured and inventory-based ratios would therefore require not only accurate atmospheric transport modelling down to the specific hour when the sample was collected, which, to our knowledge, does not yet exist, but also the use of a comprehensive atmospheric chemistry model capable of capturing the temporal variability of NO_x and its reaction products.

Therefore, a meaningful comparison of atmospheric $\Delta NO_x/\Delta ffCO_2$ ratios with emission ratios is beyond the capabilities of our group and remains the domain of chemistry and transport modelling experts, to whom we are happy to provide our data. For now, we see no alternative but to experimentally determine the relevant atmospheric $\Delta NO_x/\Delta ffCO_2$ ratios at each specific measuring station using $^{14}CO_2$.

Other points

L 41-42. I suggest clarifying here that the NO_x concentration excesses (ΔNO_x) are derived from in situ observations of *both* NO_x and $^{14}CO2$ concentrations. Otherwise, this statement looks misleading.

The NO_x excess concentrations are only derived from the in-situ NO_x observations (and the modelled background). The ^{14}C measurements are not involved in calculating ΔNO_x. However, we now mention the use of radiocarbon measurements for the derivation of $\Delta ffCO_2$ (L 49).

L 82-83. Were the samples taken evenly throughout the day or mainly during certain hours?
The samples were taken mainly during the morning and evening rush hours, as well as the afternoon and night. A sentence about this was added (L 90-91).

L 104: “This would lead to a higher uncertainty of the derived ΔNO_x-based $\Delta ffCO_2$ estimates (see Sect. 2.3)”. This statement is actually not proven in Sect. 2.3.
This statement was left over from a previous version of the manuscript, and we agree that this is no longer accurate in the current context. The sentence was removed, and we added a remark about the higher variability of ΔNO_x to $\Delta ffCO_2$ ratios (L 111).

Fig. 2(b): Values of the travel time are missing in the plot.
The image was updated.

L 123-124. The sentence is hard to understand. I suggest rephrasing.
The sentence was rephrased to “Thus, in the context of this method only the contribution of the European domain needs to be determined to calculate local excess concentrations.” (L 131-132).

L 209: “40%”: Is this uncertainty for individual grid cells? If so, should not the uncertainty in the simulated NO_x concentrations be much smaller than that (because random errors of emissions in different grid cells tend to compensate each other when these emissions mix in the atmosphere)?
The uncertainty is for individual grid cells. We would agree that the uncertainty of the simulated concentrations should probably be smaller due to random errors compensating each other. As we want to do a conservative estimation of the uncertainty, we choose to use the greater value as an upper boundary. This was clarified (L 219-222).

Fig. 4. In Sect. 3.1, the authors discuss the seasonally averaged concentration ratios, but Fig. 4 shows scatter plots for all valid flask measurements. Could the authors provide similar scatter plots for summer and winter separately?
We included scatter plots for summer and winter in the appendix plot A1 and added a reference to that in Sect. 3.1 (L 277).

L 395: “concentrations show a strong correlation with R^2 values over 0.8”. This statement appears to contradict the results reported on line 274 (for all summer samples … an R^2 value of 0.55 is found), especially since the next sentence refers to the seasonal ratios.
We have clarified the statement, stating the R^2 values for winter and summer (L 415-416).