Reply to Anonymous Referee #1

We would like to thank Referee #1 for reviewing this manuscript and providing positive feedback. We found the comments and suggestions very helpful to improve this paper. Our responses to each comment are provided below in black font, and the Referee's comments are indicated in blue. Unless stated otherwise, all page and line numbers refer to the originally submitted manuscript.

Page 2 line 36. I agree that EC is the only method to directly measure fluxes. Given the discussion in the previous paragraph of inventory methods, it would be worthwhile to mention that there are multiple other atmospheric methods available besides EC. This is particularly relevant to this paper because while this paper presents the first time 14C has been used in REA, 14C measurements are widely used in other urban atmospheric methods, such as tracer ratios.

We agree that the paper, describing the novel application of REA to ^{14}C measurements, benefits from a more comprehensive introduction that mentions other atmospheric methods using ^{14}C to infer fluxes. We have therefore added a few sentences referring to three studies (Levin et al., 2003; Maier et al., 2024; Wu et al., 2022) that determined $ffCO_2$ fluxes using ^{14}C measurements. As the state-of-the-art laser-based ^{14}C measurements and the lack of high-precision in situ measurements are closely linked, we combined the text with the changes done on page 2 lines 49-51 (see below).

Page 2 line 44. Human respiration is more typically ~5% of the total annual CO2 flux, and it depends not only on population density, but on emissions density.

We adopted the comment and adjusted the reference accordingly, as our previous references (Moriwaki and Kanda, 2004; Kellet et al., 2013) referred to individual examples where the contribution of human respiration to annual emissions was estimated to be more than 17 % and 8 %, respectively.

Page 2 lines 49-51. Suggest rephrasing this sentence, as it implies that in situ 14CO2 measurements are available, just not at fast-response. In fact, 14CO2 measurements can not yet be made in situ at all, except a few novel laser-based measurements that have not yet acheived the precision or method development to allow them to be used for atmospheric applications such as this.

We reformulated the sentence or section as suggested. In addition, we incorporated the changes from the above comment on page 2 line 36 here.

Page 13. Line 286. Suggest renumbering the 3 points as 5.1, 5.2, 5.3 to match the following section labels.

Done.

Page 14. Line 308. Here it says that the difference between two buffer fillings is 0 ± 52 ppm. In the next sentence, the additional uncertainty is estimated at 0.15 ppm. I don't quite follow how this is calculated, and wonder whether the ± 52 ppm is a typo?

The numbers (± 52 ppm) are correct and the calculations are explained in Appendix B2. To avoid confusion, we omitted the number in the main text and refer the interested reader to Appendix B2.

Page 21. Line 470. Consider adding Turnbull et al 2015, Miller et al 2020 as additional references.

Turnbull JC, Sweeney C, Karion A, Newberger T, Lehman SJ, Tans PP, Davis KJ, Lauvaux T, Miles NL, Richardson SJ et al. 2015. Toward quantification and source sector identification of fossil fuel CO2 emissions from an urban area: Results from the INFLUX experiment. Journal of Geophysical Research: Atmospheres. 120.

Miller JB, Lehman SJ, Verhulst KR, Miller CE, Duren RM, Yadav V, Newman S, Sloop CD. 2020. Large and seasonally varying biospheric CO2 fluxes in the Los Angeles megacity revealed by atmospheric radiocarbon. Proceedings of the National Academy of Sciences of the United States of America.

Done.

Page 21-22 section 6. ΔCO2 partitioning. The authors note that the Δ14C differences between up and downdrafts are small relative to the measurement uncertainty, resulting in many of the differences being indistinguishable from zero. There is some discussion in this section and also in appendix D about this, but the paper would benefit from expanding this discussion.

First, the actual Δ14C measurement precision acheived for these samples is not given, instead the uncertainty in calculated ΔffCO2 is reported. It would be helpful to indicate what the Δ14C uncertainties are for these measurements. My estimate from the reported ΔffCO2 uncertainties is that the Δ14C measurement uncertainties are around 2‰. Reducing these uncertainties would go a long way to improving the utility of the method. Several other labs are now reporting around 1.5‰ uncertainty on 14C measurements, and this modest improvement would make a significant difference to the fraction of usable measurements.

You are correct: the mean $\Delta^{14}C$ uncertainty of all Zurich samples was 1.8 ‰, resulting in a mean $\Delta ffCO_2$ uncertainty of 1.2 ppm. However, the uncertainty has already been reduced

over the course of the campaign from 2.1 ± 0.3 ‰ to 1.6 ± 0.2 ‰, as the graphite targets have been measured on a new accelerator mass spectrometer (AMS) since January 2023. Currently, 1.6 ‰ is also the long-term reproducibility of the quality control targets at the AMS, and thus the minimum uncertainty of individual $\Delta^{14}C$ measurements. For the REA measurements, however, even smaller uncertainties can be achieved by measuring updraft and downdraft graphite targets in the same AMS magazine. Thus, we are currently at a mean $\Delta^{14}C$ uncertainty of 1.1 ± 0.1 ‰ and a $\Delta ffCO_2$ uncertainty of 0.7 ± 0.1 ppm. We could indeed significantly increase the fraction of usable measurements, as will be shown in a follow-up paper.

For the present paper we added the mean $\Delta^{14}C$ uncertainties of the Zurich samples and refer to the improvements due to a new accelerator mass spectrometer on page 21 lines 481 - 484, in the conclusions on page 23 line 531, and in Appendix D page 34 lines 677-678 where the uncertainties are discussed in more detail.

Since the REA method doesn't appear to be sample size limited, one could also consider measuring multiple graphite targets to reduce the overall uncertainties. This would of course come at considerable cost in money and instrument time, but might be worth considering in the future.

In principle, this is an interesting idea. However, to effectively exchange the air in the flask with the sample air, the volume should be flushed 10 times (Levin et al., 2020). In addition, at least 6 l of air is required for laboratory analysis, and not all of the air in the buffers can be used because the pumps cannot evacuate the buffers in a reasonable time. Therefore, with the current setup, it is not possible to fill multiple flasks, i.e., obtain multiple graphite targets, from one REA sample. One could consider flushing two flasks in series with the same air, but in addition to a major reconstruction of the automated flask sampler, this would, as already mentioned, be associated with considerable costs in terms of money and instrument time. To share this knowledge, we added a comment on this on page 23, line 518.

Another option would be to make these REA measurements at EC sites that are closer to the surface and/or to sources, so that the Δ14C differences are larger. This would certainly be useful in demonstrating the technique, and could be a necessary constraint for the foreseeable future if Δ14C uncertainties cannot be beaten down further.

I don't suggest that the authors try to implement these things in this paper, but some discussion of these points would be helpful.

For a given surface flux and beta coefficient (e.g., given deadband width), the concentration difference between the updraft and downdraft samples depends mainly on the standard deviation of the vertical wind speed σ_w. Indeed, the latter is often smaller at lower heights, which would lead to an increased concentration difference (half $\sigma_w \rightarrow$ double Δc). However, at a lower measurement height, the flux footprint is much smaller, closer to the tower, and hence more heterogeneous in terms of sources. Consequently, the concentration differences are only larger if the sources are within this smaller footprint, and the measurements are only representative for this local area. Depending on the aim of a study, this may be fine, but for our purpose of urban measurements at the neighborhood to city scale, the EC and REA

measurements should be made in the inertial sublayer (Feigenwinter et al., 2012). There, σ_w, and consequently Δc, are approximately constant with height. Therefore, we did not consider this to be a good solution for our purpose. We added a note to this effect on page 23, line 518.

Page 23. Lines 508-518. The same comments as above apply – indeed the signal-to-noise seems to be the main challenge.

We have expanded the discussion as explained above.

Page 23 line 522. Including CO and/or other species in these analyses would be very interesting. I wonder if incorporating CO measurements could also help resolve the signal-to-noise issues?

We agree that the analysis of CO/ffCO_2 ratios will be interesting, since CO is often used as a tracer for ffCO_2 emissions (see discussion above on other atmospheric measurement techniques). For individual REA measurements, however, this will not improve the signal-to-noise ratio. As for CO_2, the signal-to-noise ratio will be largely dominated by the ^{14}C-driven uncertainty of the ffCO_2 estimate. We will examine and discuss the use of co-emitted species in detail in a follow-up paper.

References:

Feigenwinter, C., Vogt, R., and Christen, A.: Eddy Covariance Measurements Over Urban Areas, in: Eddy Covariance, edited by Aubinet, M., Vesala, T., and Papale, D., pp. 377–398, Springer, Dordrecht, https://doi.org/10.1007/978-94-007-2351-116, 2012.

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