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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Estimation of continuous anthropogenic $CO_2$ using $CO_2$, CO, $\delta^{13}C(CO_2)$ and $\triangle^{14}C(CO_2)$" *by* S. N. Vardag et al.

**J. Turnbull (Referee)**

j.turnbull@gns.cri.nz

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This paper describes a modelling study that tests how well different tracers (CO2 mole fraction, CO mole fraction, $\delta$13C of CO2 and $\triangle$14C of CO2 and combinations thereof) can be used to determine recently added fuel CO2 mole fractions in the atmosphere. The study is well designed and comprehensive, and the results are both topical and very useful. The results show that in Europe, CO may not be as useful a tracer for fuel CO2 as in other regions, owing to the low CO:CO2 emission ratio from European traffic – a result that is frustrating from a detection point of view, but satisfying from a clean air perspective. The study shows that $\delta$13C of CO2 can be quite useful for quantifying fuel CO2, as long as the isotopic content of the various sources and the relative source mix



is well-known. An extremely helpful outcome (especially for ICOS) is the test of how best to utilise 14C measurements to "calibrate" the CO and $\delta$13C methods, including both how many and what type of 14C samples are realistically needed to provide robust calibration of the other methods.

The paper is quite long, and this is understandable since there is a lot of information to be drawn from the model study. The decision to include all of it in one paper seems sensible since there's no obvious place to split it into a second paper. However, the discussion and conclusions sections are somewhat repetitive of one another and of the results section, so they could be condensed to reduce the overall length. Overall, this paper is well worthy for publication in ACP, with some minor revisions.

Specific comments: The title could be improved to better reflect the subject. Something like - Continuous estimation of anthropogenic CO2: model-based evaluation of CO2, CO, $\delta$13C (CO2) and $\triangle$14C(CO2) methods.

Pg 20183 line 17-19. Is there a particular basis for reducing fuel CO2 uncertainties by half (vs reducing uncertainties even further)? For example, what anthropogenic CO2 uncertainty is needed in global modelling studies so that this uncertainty becomes inconsequential relative to other uncertainties and biases in the models? What about for urban studies?

Intro first paragraph. Here the concept of "fuel CO2" is introduced, and the majority of the paper talks about how to constrain the total fuel CO2 (fossil + biofuel). Only very late in the paper is it mentioned that it may also be useful to determine the fossil fuel CO2 component separately. If the objective of these measurements is to constrain fossil fuel emissions – which is critical to ensuring that emission regulations are working - then total fuel CO2 is not terribly useful. It would be helpful to bring this up early in the introduction, and explain why the focus here is on total fuel CO2 (presumably because in large scale models one objective is to solve for the biospheric flux, requiring the total fuel flux to be known).

Page 20184 line 7-8. Miller 2012 does not attempt to monitor fossil fuel CO2 emissions, rather they assume that these emissions are known and use them to examine emissions of other species. There are many more appropriate references that could be used here.

Page 20184 line 10. Accelerator mass spectrometry!

Page 20184 line 9-12. The main issue with 14C measurement is the need to collect discrete samples, limiting the frequency. The 14C measurement cost is not prohibitive compared to the expensive instrumentation used for the other species.

Page 20184 lines 12-19. The GC-AMS system referred to here (McIntyre et al 2013) does not appear to suitable for continuous measurement of 14C in atmospheric CO2. It is a lab-based method that is not field deployable, so there is no obvious way that it could be used for continuous atmospheric 14CO2 measurement, nor is it designed to separate CO2 from air. The 6‰ uncertainty on modern samples determined in that paper requires 0.67 mgC, somewhat larger amounts than are currently used for flask/graphite/AMS measurement of 14CO2 (cf Graven et al 2007; Turnbull et al 2007), and it requires multiple injections to achieve this uncertainty which likely takes as long or longer than measurement of a single graphite sample. It is likely that laser-based 14CO2 measurement systems will become possible in the next few years, and at some point these may be field deployable for continuous measurement. Even once the significant technical challenges of these methods are overcome, it appears that precision will initially be much poorer than AMS or gas counting, on the order of a few percent precision, even with time averaging. Thus for this modelling study, it would be more reasonable to consider the possibilities of (a) high resolution flask 14CO2 measurements at $\sim$2‰ precision, (b) hypothetical laser-based 14CO2 measurement with $\sim$3% precision, (c) use of flask or gas counting 14CO2 to "calibrate" the other methods, as is already discussed in the paper.

Pg 20185 lines 10-15. The authors may also want to refer to the following paper, which



uses the combined 14C/CO method proposed by Levin and Karstens 2007. Turnbull, J.C., Karion, A., Fischer, M.L., Faloona, I., Guilderson, T., Lehman, S.J., Miller, B.R., Miller, J.B., Montzka, S., Sherwood, T., Saripalli, S., Sweeney, C., Tans, P.P., 2011. Assessment of fossil fuel carbon dioxide and other anthropogenic trace gas emissions from airborne measurements over Sacramento, California in spring 2009. Atmospheric Chemistry and Physics 11, 705-721.

Pg 20185 line 14. Why not use $\Delta$CO2 and $\Delta$CO rather than $\Delta$x and $\Delta$y?

Pg 20185 lines 19-20. Please reference the production of CO from VOCs.

Pg 20185 lines 23-27. This is an awkward sentence.

Pg 20187 line 10. Please reference how the biodiesel/biogasoline content is known.

Pg 20187 line 11-12. Why is the vehicle biofuel emission ratio higher than for vehicle fossil fuel emissions? This is counterintuitive, since vehicle CO emissions have largely been reduced by the use of catalytic convertors, which one would expect to be similarly effective no matter the source of the fuel. It would be worth clarifying in this discussion what exactly is meant by biofuel. Does it refer only to biodiesel/biogasoline used in vehicles, or to open fires (e.g. for home heating), or other sources? The CO emission ratio can be expected to vary wildly across these different combustion types.

Pg 20188 line 9 and throughout. It is common practice to use ppm and ppb rather than $\mu$mol/mol-1, etc. This could be explained at the first use if the journal prefers SI units.

Pg 20190, lines 1-2. Excluding NMHC oxidation to CO seems problematic. This is discussed to some degree later in the paper, but the potential problems with excluding this CO source should also be mentioned here.

Pg 20190 line 16 to end of section. This whole section is very heavy on equations, and it is difficult to follow. The equations that are given in the main text explain how each individual parameter is determined, but the equations that are used in the 6 different tracer combinations used in the analysis are found only in the appendix and table.

There's no explanation of what these 6 different tracers are or why they were chosen in the main text. Table 2 helps a little, but requires the reader to recall what all the variables mean to interpret it. A paragraph that explains why these tracer combinations were chosen and what the assumptions and prior information required for each are would be helpful.

Pg 20191 line 7-8. Please explain why CH4 minimum values were chosen as background.

Pg 20193 lines 8-9. Are these overestimates at the different sites results from the model study done here, or from previous work?

Pg 20193 lines 18-20. Shouldn't this be the first paragraph of the following section?

Pg 20194 line 12. "Until now"? Does this refer to the initial part of this study described above, or to previous research?

Pg 20195 lines 10-19. Indeed, the model shows that the $\delta$13C method works quite well, but how reliable are the $\delta$13C values of the sources (which are of course critical to the success of the method)? This is discussed in a later section, and that section should be referred to here.

Section 3.3.1. It is also worth noting that the CO2-only method bias varies seasonally.

Section 3.3.3. Have the authors considered the impact of C3 vs C4 plants in the biospheric $\delta$13C signal? In urban areas, lawn grass may be C4, which would have a large impact on the biospheric $\delta$13C, and could introduce quite large biases to the $\delta$13C method.

Section 3.3.4. This section should reference the previous papers that have discussed the importance of $\Delta$14C precision. Also, only a handful of 14C labs (AMS or gas counting) routinely achieve 2‰ precision, and most 14C labs report significantly poorer precisions. Finally, $\pm$2‰ in $\Delta$14C is closer to $\pm$1 ppm than $\pm$1.5 ppm in fuel CO2. Please clarify what is meant by the last sentence of this paragraph.



Pg 20200 line 2-4. Since production of CO from VOCs is not included, this will be a systematic bias in one direction, not random.

Pg 20200 line 8-12. As mentioned earlier, the 14C measurement method described in the McIntyre paper doesn't appear to be applicable to continuous atmospheric 14CO2, so there's no obvious reason for this uncertainty of 5‰ to be chosen.

Pg 20203 lines 6-8. Please reference the use of afternoon-hour-only data in models.

Pg 20203 lines 15-17. Earlier in the paper much larger fuel CO2 values were given for the urban areas. Here I think the 1-2 ppm value indicates mid-afternoon values only, whereas earlier the values included nighttime? Please clarify here and in the earlier discussion.

Pg 20204 lines 7-12. Please reference the ICOS program.

Pg 20204 lines 13-16. The authors may also want to refer to the Turnbull 2011 paper (reference given above) that uses aircraft grab samples.

Pg 20204 line 27. Please just state the number of samples used, rather than using n/24, etc. When only 1 monthly sample is used to determine RF, what is the uncertainty in this value, and how does this influence the results?

Pg 20206 lines 3-10. When only a single background is used, all values could be biased if that background value is biased.

Sections 5 and 6. The discussion and conclusions are thoughtful and interesting, but somewhat repetitive of each other and of the results section. They could be combined and/or substantially shortened.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 20181, 2015.