

## Response to Interactive comment on “Application of the ECT9 protocol for radiocarbon-based source apportionment of carbonaceous aerosols”

By Anonymous **Reviewer #1** (Received and published: 4 September 2020)

Thanks very much for the editor’s effort to coordinate the reviewing and for the reviewer’s constructive feedback and comments. We will answer the questions and address the concerns point by point raised by the reviewer#1 below in the format of “reviewer’s comments/ author’s responses”.

This paper presents an evaluation of the ECT9 separation protocol for the measurement of radiocarbon in OC and EC. Radiocarbon measurements of OC and EC in carbonaceous aerosols provide a powerful tool for understanding the sources of these materials. Overall, the authors do an excellent job of describing the method, conducting the critical tests for validating the radiocarbon measurements, and comparing it to other standard methods currently in use. I recommend accepting the paper for publication with minor revisions noted below. [Appreciated for the general constructive feedback. Thanks for your effort.](#)

Instead of using the term “FM14C”, I recommend using the term “F14C” as recommended by Reimer et al. (2004). Reimer, P. J., Brown, T. A., & Reimer, R. W. (2004). 1299–1304. A better acronym for pyrolyzed organic carbon might be PyOC; the term POC means particulate organic carbon for researchers in the aquatic sciences.

[We thank the reviewer for these suggestions!](#)

[“F<sup>14</sup>C” will replace for “FM<sup>14</sup>C” and PyOC will replace for POC through the entire text.](#)

Line 112. Rewrite “The fraction are separated based on their thermal refractory.”

[The sentence is re-written as “The fractions are separated from each other according to their degree of refractory”.](#)

Section 2.3 There is a lot of detail in this section and some of it could be removed but some of it enhanced. I am not clear as to how you load dissolved material onto a filter without losing some of it. Please explain.

[Only water soluble OC i.e., sucrose were injected onto filters. Please see the description at section 2.3 from L151-152, which will be modified as “OC materials were first dissolved in MQ-water with known volumes to obtain their concentrations, and then a known amount of OC solution \(5-10 µl\) was volumetrically loaded onto a pre-cleaned quartz filter punch \(1.5 cm<sup>2</sup>, Pall Canada Limited\) with a syringe carefully”. The loading of sucrose solution onto filters is a routine procedure of daily standard checks in OC/EC measurements. The liquid volume is so small that it moistens only the surface of the filter.](#)

Lines 210 on. There is a lot of reliance on the Santos et al. 2007 paper for assigning errors to the amount of extraneous carbon added during sample preparation. I’m sure more work has been done since then although perhaps not published. It might be useful to mention this unpublished work. However, an assignment of ±50% is very conservative and hard to argue with.

[Thanks to the reviewer for raising this point. As noted, although Santos et al., 2007 described modifications to the spectrometer, sample processing, mass balance correction approach and validation on how to effectively measure and report the results of small and ultra-small graphite target <sup>14</sup>C, indeed, the results in this work call for an error assignment more than our standard ± 30% of the blank. Santos et al., 2010 \(cited in line 216\) shows the long-term measurements of small to ultra-small blanks of combustible reference materials as well as the blanks related to processing chemicals. In the work by Santos et al.,](#)

2010 and many subsequent ones, reporting blank assessment for specific case studies (e.g., Fernandez et al. 2014, Mouteva et al. 2015, Reyerson et al. 2016), we confirmed that a more conservative assignment to error propagation into individual uncertainties would be suitable for a method evaluation. Basically, long-term evaluations of the blank are essential to determine its variance. Therefore, we prefer to maintain a large assignment of blank error for the ECT9 method for now. A possible reduction of it will be pursued in future works.

Line 219. Please better define what “<sup>14</sup>C analysis” refers to. Is it from graphite prep on or does it start later in the process.

The reviewer raised a good point. The “<sup>14</sup>C analysis” in the manuscript referred to “<sup>14</sup>C sample preparation and analysis”

Line 232. How was the mass determined at the CAIR lab? Is it from the integration of the OC/EC signals or from manometry? If it is from manometry, it is not a great comparison and probably does not warrant a figure.

The mass values in Figure 2- a. by the CAIR lab were determined by gravimetric methods either via weighing on a 6 or 7 digit balance for individual references, including Regal black, C1150, Rice char, Adipic acid or volumetric injection for sucrose solution. Whereas the mass values in Figure 2-b) were determined by the combination of gravimetric methods mentioned with OC/EC ratios in Table 1 (i.e., adipic + Rice char, regal black + sucrose). As the methods used at CAIR lab are different from the manometric method used at KCCAMS lab, the comparison does show the importance of the final mass recovery at KCCAMS for those were originally loaded via gravimetric or volumetric methods through ECT9 protocol.

Line 244 on. The data seem a bit iffy below 10 μg

On average, results for all individual (Table S6) and mixed reference materials (Table S7) are within 2±3% of their corresponding consensus value (Table 2). For samples containing > 10 μg C data are within 1±1% of the consensus, whereas samples containing between > 5 μg C and < 10 μg C are around 6±4% in average. We will make this point clearer in the revised version.

Line 260. I think it is optimistic to state that the technique is good for samples containing as little as 2 μg C. It definitely seems robust for samples containing >10 μg C and appears useful down to 5 μg C.

We agree that we may have overestimated the lower limit of the method here. Initially, we reported the minimal sample size based on the ECT9 blank size only. We have made some changes in response to this comments and are now reporting the minimum sample size for unknown samples based on what we confidently measured so far (i.e., approximately 5 μg C as suggested by the reviewer).

Lines 270-279. I am a little confused about the discussion of the rice char. If 14% of the carbon in the rice char is OC and rice char is modern, it would be expected that you would find modern carbon in the combined OC sample. The question is whether a mass balance indicates that the measured fraction modern is what one would expect.

The assessment of the reviewer is correct. The initially unremoved ~14% OC fraction from the modern rice char was found in the isolated fossil adipic acid (pure OC) after running the ECT9 method.

Consequently, final <sup>14</sup>C results of OC from the sequence UCIAMS#s 159822-159832 (Table S7) are elevated, rather than closer to zero. The results yielded an average F<sup>14</sup>C value of 0.1081 ± 0.0259 (n=6) after blank corrections. Based on this value, a mass balance calculation indicates that 10 ± 3% of OC-Rice char is present. This estimate is close to the lower limit within the validity range to what one would expect. We have expanded our discussion of the effects of the unremoved 14%-OC fraction from the

modern rice char mentioned by the reviewer, and added a couple of statements in this section to clarify this point.

Is it possible to redraw Figure 8 so that it is possible to see the peaks as robust features?

Lines 325 on. I find the comparison of the SRM 8785 analyses using the ECT9 and Swiss\_4S protocols not as compelling as the previous figures. The results for the Swiss\_4S protocol are difficult to interpret and more discussion is warranted. It certainly looks as though it would be very challenging to isolate OC from EC in the final peak in Figure 9C.

Yes, it is possible to re-draw Figure 8 to change the scale to show peak features more clearly (although the extent of change is limited due to a consistency with other figures). The Figure 8 has been revised.