Interactive comment on "On the isolation of OC and EC and the optimal strategy of radiocarbon-based source apportionment of carbonaceous aerosols" by Y. L. Zhang et al.

Responses to Reviewers

We would like to thank the anonymous reviewers for their careful reading which helped to improve the manuscript.

Anonymous Referee 1

General comments:

"Throughout the paper, however, I found one aspect odd; often it was implicitly assumed that there is a real and definitive distinction between OC and EC, whereas it is just an operationally defined delineation based on some property that does not abruptly segregate OC and EC, but instead varies continuously."

…

"Thus, I suggest these types of statements made in the introduction need to be qualified based on the idea that TC is a complex mix having a continuum of properties, and OC and EC are subsets based on a method. The point is the authors here work hard on not subjecting the aerosol collected on filters to processes that bias the results based on how they have generally decided to define OC and EC. This idea should guide the discussion throughout the paper where details of how to adhere to this separation with minimal artifacts are presented."

***Reply*:**

The classification of OC and EC is widely acknowledged, but their boundary is still not clear and highly method-dependent. That is one of the reasons we pointed out the distinction between OC and EC at the first part of the introduction section, followed by emphasizing the difficulties in both determination and separation of OC and EC due to the continuum properties in OC and EC. Specifically, we explained why the complete OC and EC separation was crucially important for ^{14}C measurements. Overall, we thought this idea has already met the logic raised by the reviewer and also has been well written throughout the paper. We only modified this section slightly in the revised manuscript; e.g. we included this clarification in the introduction: "The classification of OC and EC is widely acknowledged, but their boundary is still not clear and highly operational-dependent (Schmid et al., 2001; Pöschl, 2005). Among the commonly accepted OC/EC determination methods, the thermal-optical analysis (TOA) method is one of the most well-known techniques (Schmid et al., 2001; Chow et al., 2004; Phuah et al., 2009; Cavalli et al., 2010)."

Specific Comments:

"**Pg 17670**, why does removing WSOC reduce charging on all filters. 1) Is it because the water wash step removes a substantial amount of the overall OC on the filter (ie, what is the WSOC/OC ratios of these filters, or 2) WSOC is must susceptible to charring?"

Reply:

Charring can be much reduced by removing WSOC because WSOC is susceptible to charring. This was underlined by the comparison of the thermograms of a typical aerosol filter and of its WSOC fraction loaded on a blank filter (Fig 4. in ACPD version). In the revised manuscript, this statement has been added: "…Charring is negligible if analysing the water-extracted aerosols (Fig. 4a), most likely due to the fact that WSOC is susceptible to charring..."

Page 17678 line 6-8. Not sure the statement that TC will not provide source information is really necessary, it seems obvious.

Reply:

This statement was removed in the revised manuscript.

Page 17680 line 16 type artefacts

Reply:

Sorry, maybe we did not understand you correctly. But it was "artefacts" already in the ACPD manuscript before.

Anonymous Referee 2

P 16660, line 1: "Consequently, : : :." Does not follow from the previous sentences. The next sentences could be moved to **p 17659, line 6**

Reply:

We changed the sequence of the sentences according to the suggestion.

Section 2.4, p 17666, line 11: How do you determine the OC recovery?

Reply:

OC recovery is estimated by the equation below:

$$\text{OC recovery} = \frac{measured\ OC}{\text{total OC}} = \frac{Carbon\ in\ S1}{\text{TC} - \text{EC}} = \frac{Carbon\ in\ S1}{\text{TC} - \frac{\text{Carbon in S4}}{\text{EC yield}}}$$

TC, carbon in S1and S4 can be calculated by default calculation software in Sunset. The estimation of EC yield has been already written in p 17667, line 8-9 (ACPD version). The key point in this paper was not concentration determination of OC and EC but the separation of them for ^{14}C measurement. So we did not include this detailed calculation explanation in the manuscript.

Section 3.1, p 17670, line 21: Please state exactly how the EC yield is defined. There is a general definition in section 2.5, with ATNt/ATNo. Which time t was used for this purpose?

Reply:

To clarify it, we added "ATNt is the attenuation at the time t, which is usually at the time when S4 (EC step) begins" in the revised manuscript.

Section 3.2.2, p 17671, line 16: To call the EC that is lost in S2 and S3 "non"-refractory is misleading, especially if it evolves at the same temperature as "refractory" OC. Perhaps a better term could be found.

Reply:

The EC fraction in S2 and S3 is indeed comparably less refractory than EC combusted in S4. Both terms of "refractory OC" and "non-refractory EC" only refers to and comparable in OC and EC, respectively. Throughout the manuscript, we did not compare the refractoriness property in these two fractions ("refractory OC" and "non-refractory EC"), so we keep these terms in the manuscript.

Section 3.2.4 Please provide additional detail what was done in this comparison. Since OC and EC in the swiss protocol are only collected with around 80% recovery, I am surprised at the 1:1 correlations. Or were the OC and EC amounts corrected to 100% recovery (and if so how was this done)?

Reply:

Yes, the OC and EC amounts shown here were corrected to 100% recovery. As we explained in above comment concerning OC recovery, the corrected OC and EC is the ratio of the measured OC and OC recovery (carbon in S1/OC recovery), and the measured EC and EC yield (carbon in S4/EC yield). We added a sentence: "The EC amount measured by Swiss_4S was corrected to 100% recovery applying: EC=carbon in S4/EC yield; and OC was calculated as OC=TC-EC."

Section 3.3 Again please provide a more detailed description of what was done in this comparison. What were the oven temperatures in THEODORE and S2 temperatures? How was the EC recovery determined for the THEODORE method?

Reply:

The oven temperatures in THEODORE and S2 temperatures were updated in the Fig. 9 in the revised manuscript. For the THEODORE method, offline optical measurement by the white-light Aethalometer was used to determine the EC yield (p17667, Eq 2 in ACPD), and this information has already been added in section 2.5. In general, we call for caution when relying on temperatures as displayed by the oven as actual temperatures on the filter, especially when comparing results from different instruments. This discrepancy can be overcome by referring to the EC yield instead of temperatures alone. Therefore, we stated more precisely in chapter 3.4.1 p 17670, line 23 following the sentence "……, the recovered EC may not fully represent the total EC." read as "This procedure also avoids possible discrepancies between temperatures as displayed by the oven from actual temperatures on the filter."

Section 3.3 Please provide some extra discussion of the results.

a) Since the THEODORE method does not use a He step, can one conclude that the He step for this filter was not very important in removing OC, or is it rather that the THEODORE method is equally successful in removing OC than step 2 and 3 of the new method combined?

***Reply*:**

The helium step indeed is very import to assure OC is completely removed as other thermal-optical protocols do. Although Fig. 9 may imply that the THEODORE method can be regarded as sufficient to remove OC due to a longer duration (4 hours) under the similar conditions (i.e. 375℃ in pure O_2), we are convinced that only the Swiss_4S protocol with on-line optical monitoring guarantees optimum OC/EC separation for ^{14}C analysis, as the number of samples for inter-comparison of both method is scarce.

b) I am also not completely convinced about the extrapolation of fm(EC) to 100% EC yield. If the complete removal of OC is not guaranteed (which seems difficult in the THEODORE protocol), then the increase of fm(EC) with EC recovery could also stem from small amounts of residual OC. How do you make sure this is not the case? Could this have anything to do with the different slopes between mass yield and optical yield, see supplement?

***Reply*:**

As we stated in section 3.2.3 in ACPD, the factor biases fM(EC) most is rather the premature EC removal, as the maximum OC contamination was only 5%, corresponding an accepted uncertainty (<5 %) in fM(EC) with our method. As far as we know, no method can guarantee OC is completely removed before EC step as OC and EC have continuum of properties. Compared to commonly accepted OC/EC separation or determination techniques, our Swiss_4S method is a new 'state of the art', since not only the positive EC artifact (i.e. OC slipping into EC step) and also negative EC artifact have been evaluated and reduced. Moreover, as both methods led to a consistent fM(tEC) (Fig 9, in ACPD), we believe the extrapolation of fM(EC) to 100% EC yield was convincing in both, Theodore and Swiss_4S method. Varying slopes between mass yield and optical yield was most likely due to the different absorption cross section for non-refractory and refractory EC, which we have pointed out in the supplement. It was very unlikely that this difference stem from the small amounts of residual OC in the Theodore method as both methods resulted in the consistent fM(tEC) values.

Section 3.4.1: How exactly do you calculate the amount of non-rEC and tEC. How do you calculate tEC and the mass yield without using optical measurements?

***Reply*:**

tEC is calculated by division of rEC by the EC optical yield (tEC=rEC/EC yield). Non-rEC is deduced from subtraction of tEC and rEC. The mass yield is assessed by division of the amounts of rEC by total EC as measured by EUSAAR_2 (mass yield=rEC/EC measured by EUSAAR_2).

Supplement: If you extrapolate the optical yield or the mass yield, you can get quite different results for the final fm(EC). Please comment. Which yield should be used and why. Does the

final uncertainty justify the extrapolation (esp. in the THEODORE method) also considering the additional uncertainty about complete OC removal (see comment b section 3.3)?

***Reply*:**

With the limited samples which we have analyzed for both the mass yield and optical yield, the difference between two calculations based these two yields was quite small and was often within the uncertainty of f_M(tEC) (see Fig 1. below). Our mass yield was calculated based on the OC/EC mass determination by EUSAAR_2 protocol. So the f_M(tEC) may change if we use EC mass yield but measured by different protocols (e.g. NIOSH), as the mass measurement is very method-dependent. Therefore, we recommend using optical yield for this estimation as optical yield is less method-dependent. Above explanation together with Fig. 1 was added in the revised supplementary material.

Concerning the uncertainty estimation, the final uncertainty of f_M(tEC) was calculated by the propagation of the combined uncertainties including the measurement of f_M(rEC) (~5%), EC yield (15%) and extrapolation slop (15%). Indeed, the additional uncertainty about complete OC removal has already been taken into account when we estimated the uncertainty of the EC yield, since the overall 15% uncertainty of EC yield already included the uncertainty due to the un-evolved OC in EC step, leading to a higher EC yield by ~5%. So the uncertainty of complete OC removal was not taken into account to estimate f_M(tEC) separately.

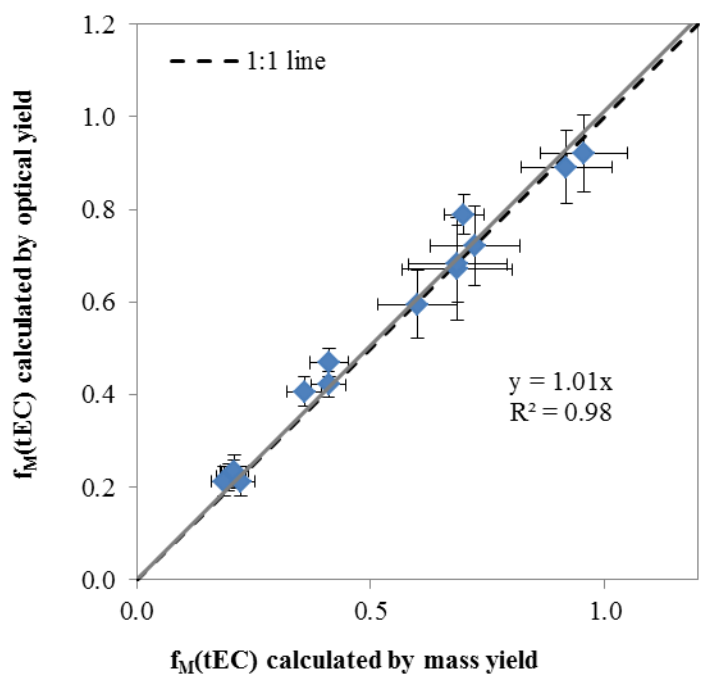

Fig 1. The comparison of the f_M(tEC) calculated by mass yield and optical yield.

Conclusions, page 17681, line 15ff: That " : : :non-fossil EC tends to co-evolve together with refractory OC" is maybe a bit strong statement. From figure 10 it can be seen that the EC that is lost during step 2+3 is still mostly fossil. From Figure 10 I estimate that 20% of the biomass

burning EC prematurely evolves during step 2+3, compared to 16% of the fossil EC. This would mean that BB OC is only slightly (but measurably) less refractory than fossil EC.

***Reply*:** The sentence was changed as “““ : : :non-fossil EC **partially** co-evolve together with refractory OC” according to the suggestion.

Minor comments:

P 17659 line 16: “radiocarbon measurements

***Reply*:** The word was changed.

P 17659 line 28 f: Better “overestimate of fossil sources”

***Reply*:** The sentence was changed.