



EGUsphere, author comment AC2
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Reply on RC2

Martin Rauber et al.

Author comment on "An optimised organic carbon/elemental carbon (OC/EC) fraction separation method for radiocarbon source apportionment applied to low-loaded Arctic aerosol filters" by Martin Rauber et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-625-AC2>, 2022

Review of

Rauber et al., An Optimised OC/EC Fraction Separation Method for Radiocarbon Source Apportionment Applied to Low-Loaded Arctic Aerosol Filters (<https://doi.org/10.5194/egusphere-2022-625>)

RC2: Comments by Anonymous Referee #1

RC2R: Reply on behalf of all co-authors

RC2.01

The paper egusphere-2022-625 by Rauber et al. proposes a new methodology to improve the determination of the fraction of modern carbon for different carbonaceous fractions of atmospheric aerosol.

In the reviewer's opinion the paper is well written, the proposed methodology is extensively discussed, and the topic is of interest for the scientific community. Nevertheless, some weaknesses are present in the manuscript and major revisions are necessary before final publication.

RC2.01R

We thank the Anonymous Referee #1 for acknowledging the relevance of our work for the scientific community. We are further grateful for the efforts of Anonymous Referee #1 to improve our manuscript aiming at a final publication in AMT.

RC2.02a Major issue

The most critical aspect concerns the determination of the EC yield required for F(EC). It is determined by comparison of ATN after WINSOC removal and the initial ATN on washed filters.

First of all, differences between optical and thermal quantification of EC by thermal-optical methods has been evidenced in the literature and it should be evidenced and properly discuss, as it strongly impacts the presented results.

Furthermore, some critical aspects concerning the correction approach in the text are not properly discussed:

RC2.02aR

We understand that Anonymous Referee #1 addresses a series of technical details that ought to be tackled in order to improve our approach of an optimum of measured F14C results of EC. Before we discuss the individual suggestions in detail in the following, we'd like to emphasize that our approach aims at a best possible congruence with existing TOA protocols, especially with EUSAAR_2, as these protocols are widely accepted in the community of atmospheric researchers, although they involve several flaws that may be decreased, but probably never will be solved completely. Besides the aspects that Anonymous Referee #1 is pointing to, these flaws of EUSAAR_2, NIOSH and IMPROVE protocols include for instance a) a strict separation of OC and EC irrespective of the fact that there is rather a smooth transition instead of a separation and b) a limitation for the optical correction of charring and determination of the "split point" between OC and EC based on one wavelength only. We are certainly willing to improve our approach even further, however, we cannot eradicate these general flaws of TOA analyses.

RC2.02b

- pyrolytic carbon (PyC) attenuation coefficient was demonstrated to be different from the EC one (e.g. Yang and Yu, 2002) – and more specifically to be higher than the EC one (e.g. Boparai et al. 2008 and therein cited literature, Subramanian et al., 2006). The authors state that they assume that 50% of the formed PyC evolves in other WINSOC removal steps. Nevertheless, they do not mention the values assumed for the attenuation coefficient of EC and PyC respectively. This information is mandatory to clarify the calculation procedure – and thus the evaluation of EC yield and F(EC) correction. Moreover, as both attenuation coefficients are affected by large uncertainties, an estimate of the impact of these uncertainties on the correction scheme should be evidenced

RC2.02bR

Up to now, we have not considered different attenuation coefficients of EC and pyrolytic carbon (PC). Thanks to the hint in this comment, we implemented this improvement in the revised manuscript (Chapter 2.10, lines 292-298) based on the approach of Winiger et al. (2015) that refers to the work of Chow et al. (2004), which assumes that the actual concentration of PC is only 40% of its apparent value from ATN determination. This approach is also consistent to Boparai et al. (2008). Consequently, a factor of 0.2 (corresponding to 40% of actual PC concentrations related to ATN determination of 50% of the PC that finally may enter the measured EC fraction) is used to correct for both the losses of PC during the thermal treatment and the effect of the different MAC values of PC and EC. All results were recalculated due to this improvement and tables as well as figures were updated accordingly. The implementation of different MAC values for PC and EC changed the absolute values of FEC(final) only marginally by <1% on the average – mainly because the PC contribution was anyway small due to our extraction procedure that was optimized for low PC formation. Estimated uncertainties of FEC(final) and FOC(final) amount $\pm 15\%$ and $\pm 4\%$, respectively, which was mentioned in the revised manuscript in lines 310-311.

RC2.02c

- the lack of a standard reference material for atmospheric EC/BC (already evidenced more than a decade ago – Baumgardner et al., 2012) and of a gold instrumentation still impact all the discussion in the paper. This implies that the “true” value for the yield is unknown. Thus, it should be mentioned in the discussion and conclusions that this method is a step towards improvements in F(EC) determination – but there is currently no real way for a validation of the proposed methodology.

- it is unclear how was PyC quantified. Indeed, PyC formation can be masked by concurrent EC evolution

RC2.02cR

We thank the reviewer for highlighting the potential of our work to the broader community. It is still true that the lack of reference material and an artefact-free instrumentation is missing, which makes it also difficult for our method to be validated properly. The lack of reference materials is already addressed in our reply RC1.03R to a comment of Anonymous Referee #2, which we have implemented in Chapter 3.1 and in the Conclusions in the revised manuscript. We further discuss in our reply RC1.02R that the validation of our method is a crucial task that unfortunately is not straightforward, which we discussed in the revised manuscript also in Chapter 3.1 and the Conclusions.

The formation of pyrolytic carbon (PC) was determined using the laser signal/ATN for each step. We typically observed an ATN increase at the moment, when the temperature was increased, whereas to onset of ATN decrease due to EC losses occurred later in each step. This was explained in the revised manuscript in lines 288-290. We cannot exclude, however, that PC formation that may have developed later in the temperature steps was masked by large EC losses. Nevertheless, we regard this as negligible, as the fractions of charring were anyway rather small in the submitted version (see Fig. 4) and became even less relevant by adaptation of comment RC2.02b, which caused a diminution of the weight PC for the determination of FEC(final) in general (see RC2.02bR).

RC2.02d

- evolution of not light-absorbing materials during S1-S3 steps can in principle modify ATN value even if no evolution of light-absorbing components occurs, due to the impact of not light-absorbing materials on transmittance signal related to scattering properties. This effect should be limited by sample washing, but residual effect cannot be excluded. Did the authors evaluate this effect as negligible?

RC2.02dR

Yu et al. (2002) investigated the influence of inorganic compounds on charring and report a certain effect for ammonium bisulfate, which they also assume for similar components such as inorganic nitrate salts. They emphasized the complete water solubility of these compounds and identified water extraction as an efficient removal process. As these inorganic components also constitute the most relevant non- light-absorbing materials, we assume that water extraction also minimizes substantially the effects Anonymous Referee #1 discusses so that we evaluate them as negligible.

RC2.02e

In the reviewer's opinion, these limitations have to be discussed and insights into the role of these topics on the results have to be gained before manuscript publication. More in detail:

- introduction should be revised evidencing these problems;

- more investigation is needed to revise and improve the discussion in paragraph 3.1 and figure 2. The uncertainty related to the role of PyC in the evaluation of the EC yield and F(EC) correction merits to be evidenced and widely discussed in the text, identifying if it is a major or minor source of uncertainty in the proposed F(EC) correction.

- conclusions have to be extended and the impossibility of a validation of the method related to a lack of a reference material should be evidenced.

RC2.02eR

We followed the suggestions for improvement of Anonymous Referee #1 and implemented them in the revised manuscript at these lines:

- *lines 68-70 and 88-91*

- *line 351-365; Fig. 2 was updated*

- *lines 288-290*

- *lines 292-298*

- lines 310-311

Minor comments RC2.03

- Introduction: a deeper discussion on the problems concerning EC quantification and isolation should be carried out. More in detail,

RC2.03R

As we already pointed out in RC2.02R (see above), we implemented this discussion in the revised version of the manuscript in the Introduction and further parts.

RC2.04

- Throughout the paper, "EC measurement", "EC data", ... are often used instead of "F(EC) measurement", "F(EC) data", This makes the reading quite confusing. Please perform thorough check and modify where needed.

RC2.04R

We checked the manuscript accordingly and corrected terms where necessary.

RC2.05

Line 104 vs. line 475. Is F(WINSOC) available or not?

RC2.05R

As we already mentioned in Chapters 3.3.2 and 3.4.3, F(WINSOC) was not measured, however with our method it could be measured as well if sufficiently loaded filters are available. We now added a respective comment also in line 104 (line 109 in the revised manuscript).

RC2.06

Line 128-129: WSOC was not analysed on back filters, whereas TC was because of quantities. Thus, do WINSOC dominate on back filters?

RC2.06R

We only focussed on ^{14}C measurements of TC on the back filters in order to provide an estimate of the ^{14}C value of the particulate TC fraction, which was determined by an isotopically balanced subtraction of the back from the front filter. As this estimation is already quite uncertain, further measurements on sub-fractions of TC would have been meaningless. As only SVOCs are trapped on the back filters, however, we assume that WSOC fraction is larger than the WINSOC fraction.

RC2.07

Lines 147-148: was possible adsorption of VOCs on the filter during sample removal and storage quantified?

RC2.07R

VOC adsorption was investigated neither during sample removal nor during storage, as such volatile constituents would anyway have been removed again in the following thermal process.

RC2.08

Lines 169-171: how was cross contamination quantified? Did the authors test cycles of heating and cooling of zeolites to verify complete CO_2 release?

RC2.08R

We are thankful for this comment, which indicates that our description was not comprehensive. The cross contamination was determined in an earlier study (Agrios et al., 2015): After analysing fossil and modern samples alternately, 0.5% of the carbon of the previous sample was found to mix and cross contaminate the next injection. We adapted this passage at the end of Chapter 2.5 in the revised manuscript accordingly.

RC2.09

Line 262: using ATN to determine EC yield can further complicate the estimate compared to the considerations

RC2.09R

This particular point was already addressed above in RC2.02.R.

RC2.10

Line 346: TC on back filters look very similar to the values on the front filters. Please check (and, if confirmed, please comment on this).

RC2.10R

*This was a mistake. We thank the referee for thorough reading. The correct values are 22 ng C * m⁻³ (range: 12–49), which was put right in the revised manuscript.*

RC2.11

Line 360: why the paragraph on the development of preparation methods is not in section 2?

RC2.11R

It is one of the special features of the journal AMT that both the development and the verification of methods may be part of the outcome that is presented in the Results and Discussion section.

RC2.12

Line 384-385: this sentence is obscure.

RC2.12R

The sentence was improved as such: The three water-extracted punches from each filter were cut into 12 and 24 quadrants for each individual and pooled sample, respectively.

RC2.13

Line 409: please change "Al" with "All"

RC2.13R

Corrected in the revised manuscript.

RC2.14

Line 479-480: how can fossil contribution be dominant if $F(TC)=0.85$?

RC2.14R

The sentence was improved as such:

Radiocarbon measurements of TC show a larger input from fossil carbon in winter months relative to the summer months with an average F_{14C} of 0.85 ± 0.17 (Table 5).

RC2.15

Line 489: are you saying that some fossil sources emit more WSOC than EC compared to non-fossil sources? Any reference for this? If this is not the correct interpretation, what does your result imply?

RC2.15R

We are grateful for this comment, as it uncovered invalid data. Re-evaluating the raw data, we found out that the 14C measurements of WSOC from two samples should not have been considered in this study due to a too an insufficient measurement uncertainty that was caused by a too low WSOC amount, one of which concerning the sample from 31 May to 26 Jun discussed in line 489 in the submitted manuscript. In the revised manuscript, the whole passage was removed from Chapter 3.4.4 and Table 5 was updated accordingly.

References

Baumgardner D. et al. (2012), Atmos. Meas. Tech. 5, 1869-1887

Boparai P. et al., (2008), Aerosol Sci Technol, 42, 930–948

Subramanian et al. (2006), Aerosol Sci Technol, 40:763–780

Yang, H. and Yu J.Z. (2002). Environ. Sci. Technol., 36, 5199-5204

References

Agrios, K., Salazar, G., Zhang, Y.-L., Uglietti, C., Battaglia, M., Luginbuhl, M., Ciobanu, V. G., Vonwiller, M., and Szidat, S.: Online coupling of pure O₂ thermo-optical methods – ¹⁴C AMS for source apportionment of carbonaceous aerosols, *Nucl. instruments methods Phys. Res. Sect. B beam Interact. with Mater. atoms*, 361, 288–293, <https://doi.org/10.1016/j.nimb.2015.06.008>, 2015.

Boparai, P., Lee, J., and Bond, T. C.: Revisiting thermal-optical analyses of carbonaceous aerosol using a physical model, *Aerosol Sc. Technol.*, 42, 930–948, <https://doi.org/10.1080/02786820802360690>, 2008.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, *Environ. Sci. Technol.*, 38, 4414–4422, <https://doi.org/10.1021/es034936u>, 2004.

Winiger, P., Andersson, A., Yttri, K. E., Tunved, P., and Gustafsson, Ö.: Isotope-Based Source Apportionment of EC Aerosol Particles during Winter High-Pollution Events at the Zeppelin Observatory, Svalbard, *Environ. Sci. Technol.*, 49, 11959–11966, <https://doi.org/10.1021/acs.est.5b02644>, 2015.

Please also note the supplement to this comment:

<https://egusphere.copernicus.org/preprints/2022/egusphere-2022-625/egusphere-2022-625-AC2-supplement.pdf>