EGUsphere, author comment AC1
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Reply on RC1

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., EGUsphere, https://doi.org/10.5194/egusphere-2022-625-AC1, 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)

RC1: Comments by Anonymous Referee #2

RC1R: Reply on behalf of all co-authors

RC1.01

The authors present an upgrade on the analytical technique for the measurement of 14C in carbonaceous aerosols. The manner of isolation of EC is a key aspect for conducting radiocarbon-based source apportionment. A plethora of techniques are in use with most employing an intermediate temperature correction step and/or pre-treatment step, while one in particular not employing either correction. Therefore, there is a need for a far superior method. This study addresses this key research gap well.

Yield correction for EC is one the most daunting aspects and major challenges for how fm(EC) results are to be presented/interpreted. The modeling aspect presented here for yield correction is thus critical and something many published works have failed to address or take into account at all. In this regard, the new method is a new benchmark

14C applications for source fingerprinting in atmospheric aerosols.

RC1.01R

We highly regard the attitude of the Anonymous Referee #2 towards the significance of a comprehensive approach for carbonaceous aerosol analysis. We further thank the reviewer for the appreciation of our efforts to improve the source apportionment of carbonaceous aerosols in general and of EC in particular .

RC1.02

While the analytical aspect as well as the mathematical aspect are well documented and researched, my main concern is the application to field samples directly. What is the yardstick to know if these numbers from this new method are 'real' values ? Are the readers supposed to take these numbers at face value?

RC1.02R

Although we believe that the theoretic concept based on a first-order kinetic coupled with the Arrhenius equation is superior to all existing approaches to correct for EC losses in thermal-optical separation methods, we agree that the validation of this method is crucial. Unfortunately, this task is not straightforward. Typical validation operations in analytic chemistry employ certified reference materials of high quality that are similar to the sample material of interest and provided by metrological institutions such as the US National Institute of Standards and Technology (NIST). For carbonaceous aerosols on filter material, however, such certified reference materials that may represent ambient condition of PM receptor sites have not been made available yet (see our comment RC1.03R). Alternatively, an agreement of measurement results in intercomparisons provided by different laboratories with expertise in the field is also acceptable. As the correction of EC losses and charring artefacts on 14C analyses of EC from PM has not been addressed by other groups to our best knowledge, however, this option is neither available yet. In the work of Zotter et al. (2014), we attempted to fill this gap by investigating, how individual PM filters behave under different conditions of OC removal that lead to varying EC yields, aiming at the development of a correction method that result in identical (within uncertainties) outcomes for the different treatments. Due to the scarcity of the Svalbard filters, however, we could not directly apply the same idea in this work. Nevertheless, we involved the data of Zotter et al. (2014) to establish and optimize the Arrhenius model of this work. This is shown in Figs. 2b as well as S6 and discussed in Chapter 3.1. We consider that this strategy is justified until adequate reference materials are available.

RC1.03

• In the present form the paper is missing an entire section/discussion on reference materials and how well does the present method work for a suite of reference materials. The authors should have addressed this first. In fact, this is a good opportunity to make comparisons with newly established protocols as well (e.g., Huang et al, 2021).

RC1.03R

Reference materials were not measured, as most of which are provided in powder form only. This powder must be dispersed homogeneously on a filter first, which is difficult to achieve and usually leads to inhomogeneities. Furthermore, such reference materials (e.g., NIST SRM 1649a) typically contain a certain fraction of coarse particles of up to 100 µm, which is substantially larger than the PM10 size cut from the field samples. According to our experience, coarse particles differ in the OC/EC separation and charring behaviour from field samples collected with a PM10 size cut or smaller. We assume that different reaction conditions and kinetics of coarse particles (compared to fine particles) cause these observations: on the one hand, deficient oxygen supply to the interior may entail enhanced pyrolysis; on the other hand, short temperature steps may lead to an inhomogeneous and incomplete heating that hampers chemical reactions. The usefulness of reference materials in powder form is therefore limited. Szidat et al. (2013) utilised NIST SRM 8785 (i.e., SRM 1649a dispersed on filter material using a PM2.5 size cut) for an aerosol intercomparison, however, the study revealed that this material suffers from inhomogeneity, which was caused by the size segregation and filtering step.

We have already organized ourselves or participated in intercomparisons between laboratories applying different techniques of EC isolation for 14C analysis (Szidat et al., 2013; Zenker et al., 2017), which revealed that employing or omitting water extraction is crucial for an agreement between the individual labs – besides the selection of differing protocols. Most participants in the aerosol intercomparison study from Szidat et al. (2013) did not employ water extraction, which resulted in a larger scatter compared to Zenker et al. (2017), where all participants used water extraction to reduce charring. As the ECT9 protocol employed by Huang et al. (2021) does not include a water extraction step, thus leading to more charring with the present water-soluble OC on the filter, we are unconvinced to apply this protocol ourselves in order to verify our results. Nevertheless, we'd welcome very much, if another intercomparison were organized on the 14C analysis of EC from particulate matter (on filters).

We thank the reviewer for pointing to the topics of reference materials and intercomparisons and have addressed these in chapter 3.1 in the revised manuscript.

RC1.04

• This relates to my point above, the authors have a good chance to compare with previously published results for 14C -EC analysis for samples collected at Zeppelin observatory (Winiger et al., 2015). While the samples are from 2009 winter and the method used for EC isolation is perhaps the most inferior compared to all out there, the authors could add a discuss section on why a glaring difference in the fm values is there and if this is related to the yield correction aspect.

My argument here is that based on the method used in Winiger et al, the biomass fraction ought to have been overestimated (as no charring correction or filter pretreatment is done). Even so their fm values were on average 52% compared to the 66% reported in this study. Why is there this big a difference? Does it mean a bigger input of biomass BC to the Arctic over these years?

This is precisely my point about which numbers to believe and what could be the 'real' values?

RC1.04R

We think that such a comparison should be taken with caution, as the assumption that the source composition of different winters from the same site are similar may not be correct. For Zeppelin/Svalbard, this has already been proven, as the results from winter 2009 (Winiger et al., 2015) and winters 2012/2013 (Winiger et al., 2019) were substantially different from each other with average fractions of biomass burning (fbb) of EC of 0.60 and 0.37, respectively. Nevertheless, we agree that it still makes sense that the results of these studies should be presented here and compared with our data. For this purpose, our results should be converted from the measured F14C into fbb of EC, as the used conversion factors change from year to year (value used for 2017/2018: 1.082). Average fbb of EC for summer (i.e., April – October) and winter (i.e., November – March) amount 0.59 and 0.62, respectively, for this work. There is a good agreement of our summer results with the summer data of Winiger et al. (2019) as well as for our winter results with the winter data of Winiger et al., 2015), whereas there is a large discrepancy of the winter data of Winiger et al. (2019) with both our winter results and the winter data of Winiger et al. (2015). This was discussed in the revised version in Chapter 3.4.4. this way:

14C measurements of EC were already performed earlier at the Zeppelin Observatory. Winiger et al. (2015) investigated 14 winter samples from January – March 2009 and observed an average fraction of biomass burning (fbb) of 0.60 ± 0.21. Later, Winiger et al. (2019) analysed 11 samples from late 2012 to late 2013, which can be classified into 6 winter samples from November 2012 to March 2013 as well as November to December 2013 and 3 summer samples from April to early November 2013. Whereas the winter samples showed fbb values of 0.37 ± 0.03 indicating a much higher fossil contribution compared to their results from four years before and a small variability between the

samples, the summer samples revealed a larger scatter with fbb values of 0.54 ± 0.11. In order to compare our measurement with these two studies, we converted 14C(EC) results into fbb values using conversion factors of 1.084 and 1.080 for 2017 and 2018, respectively, based on the approach described in Zotter et al. (2014), providing 0.59 ± 0.24 and 0.63 ± 0.06 for winter and summer, respectively. Our values for summer (i.e., April – October) correspond very well with the summer data from 2013 by Winiger et al. (2019). For the winter data, our results from November to March compare well with the measurements for 2009 from Winiger et al. (2015), whereas there is a large discrepancy of the dataset from 2012/2013 from Winiger et al. (2019) with both our outcome and the study of Winiger et al. (2015). This comparison suggests that two substantial changes have occurred from 2009 to 2012/2013 from wood-burning dominated to fossil-fuel-combustion dominated EC sources and from 2012/2013 to 2017- 2018 back to wood-burning dominated emissions. The discussion and interpretation of this result is beyond the scope of this work. We nevertheless emphasize that the EC isolation procedure of Winiger et al. (2015, 2019) neither involved water extraction nor applied oxygen in the OC removal steps so that these datasets should be compared with caution with our results.

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Please also note the supplement to this comment:
https://egusphere.copernicus.org/preprints/2022/egusphere-2022-625/egusphere-2022-625-AC1-supplement.pdf