Answers to referee 1

Comparison of co–located rBC and EC mass concentration measurements during field campaigns at several European sites

We thank the referee for the timely review of our revised manuscript, which helped in further clarifying potential interferences from different types of brown carbon in EC and rBC mass measurements. Please find below reviewer comments repeated in black text, our responses in blue text, and passages in the revised manuscript in red text.

1) Most of the concerns raised in the first review have now been rectified and the manuscript has improved significantly. However, there remain two issues that are not addressed properly. In the Abstract and Conclusion there is the explicit statement that "Overall, considering the five field campaigns, the median of the observed rBC to EC mass ratios for the whole dataset was 0.92, with a GSD of 1.50." While it is true that mathematically the very high GSD practically means that the two methods are indistinguishable within the limits of inherent uncertainties, given the fact that the mean only refer to the specific combination of individual campaigns of markedly different durations (14, 21, 24, 30, 54 days) without a-priori methodological planning and standardization, to provide a mean value is absolutely meaningless. If, for example, the campaign that provides mean value greater than unity had lasted twice as long whereas the other having mean value less than unity had been significantly reduced in duration, a 'mean value' exceeding unity would have been easily obtained (of course, with a similarly large GSD which conveys basically the same mathematical meaning). So I strongly suggest the authors should refrain from reporting 'mean' numbers in the Abstract and Conclusion, because it explicitly implies that the experimental setup had been well designed, standardized and balanced and are able to provide robust and high-quality data for detailed statistical analyses. This was certainly not the case with the manuscript.

   We have removed any reference “mean” values from abstract and conclusions.

   Abstract:
   […]The observed values of median rBC to EC mass concentration ratios on single campaign level were 0.53, 0.65, 0.97, 1.20 and 1.29, respectively, and the geometric standard deviation (GSD) was 1.5 when considering all data points from all five campaigns. This shows that substantial systematic bias between these two quantities occurred during some campaigns, which also contributes to the large overall GSD.[…]

   Conclusions:
   […]The observed rBC and EC mass concentrations correlated well with each other. However, the median of the observed rBC to EC mass ratios varied from 0.53 to 1.29 from campaign to campaign. Potential reasons for discrepancies are as follows:[…]

2) My second concern is about the way the role of tar brown carbon is addressed in the revision (see Section 2.2.1). The reference and the quoted statement "...its absorbance decreases strongly from the blue–UV region of the electromagnetic spectrum towards the red region (Karanasiou et al., 2015), thereby reducing the potential impact of brown carbon interference” is outdated given the fact the significant red absorption of tar brown carbon has been only recently discovered (see references in my previous comments). The addition of "per unit mass" does not resolve the issue since tar brown carbon is in the form of large tar balls of several hundred nm from biomass burning emission (which is the most significant single source of PM2.5 in Europe according to

several 14C studies), therefore their smaller mass-specific absorption may not necessarily mean that their overall contribution is not significant.

We modified Sect. 2.2.1 in order to put more emphasis on how soluble brown carbon and tar brown carbon can interfere with EC measurements. The modified text reads:

[…]Moreover, soluble brown carbon on filters can affect the laser correction if it was evolving during the OC steps, thereby causing a positive EC artefact. However, soluble brown carbon absorbs much less per unit mass than EC at the red wavelength (λ = 635 nm) of the laser used in the thermal–optical instruments, since its absorbance decreases strongly from the blue–UV region of the electromagnetic spectrum towards the red region (Karanasiou et al., 2015). This reduces the potential interference of soluble brown carbon via the introduction of a bias in the optical charring correction. Recently, Massabò et al. (2019) developed a modified Sunset Lab Inc. EC/OC analyser to measure the brown carbon content in the sample by adding a second laser diode at λ = 405 nm.

Tar brown carbon only evolves in the oxidizing step of TOA due to its refractoriness (Corbin et al., 2019). Therefore, it is assigned to EC independent of its light absorption properties. This is in contrast to LII, where tar brown carbon only gives marginal contribution to observed rBC mass (Sect. 2.3.3).[…]

We also added more discussion in Sect. 3.3.3 to address the hypothesis of tar brown carbon interference:

[…]Furthermore, tar brown carbon has been shown to be assigned to EC mass in TOA (Sect. 2.2.1), while it does not contribute to rBC mass in LII (Sect. 2.3.3). Such tar brown carbon interference would cause a negative relationship of data points as presented in Fig. S4, which was not observed. Hence, the observations do not provide evidence of substantial fraction of tar brown carbon in total EC in daily averaged samples. We conclude that the variation of BC sources and carbonaceous aerosol composition, as implied by AAE variability, may contribute to variations in the discrepancy between m_{EC} and m_{rBC}, while not being the main driver of it.[…]