Response to Reviewer #2' Comments

General comments

This manuscript presents a solvent-extraction-based mass balance framework to constrain protocol-dependent uncertainties in elemental carbon (EC) quantification by thermal–optical analysis and proposes an optimized OC4 temperature ("KRISS temperature") for EC determination. The topic is relevant to the scope of Atmospheric Measurement Techniques (AMT), as uncertainties associated with thermal–optical EC measurements remain an important methodological issue.

The proposed backup-filter correction and solvent-extraction framework are potentially innovative and may provide a useful perspective for improving EC quantification. However, the central conclusions of the manuscript rely heavily on the assumption that solvent-extracted EC represents an independent and more accurate reference for atmospheric EC. In its current form, this assumption has not been sufficiently validated, which weakens the scientific basis for defining the proposed "KRISS temperature". In addition, the experimental dataset is limited to a small number of ambient samples collected at a single site, making it difficult to assess the broader applicability of the proposed framework.

Overall, although the manuscript presents a potentially valuable methodological approach, several critical issues remain unresolved, including the insufficient validation of the key underlying assumption, the limited dataset, the lack of independent method comparison, and the absence of direct experimental validation. I therefore recommend Major Revision. The manuscript requires substantial additional evidence and clarification before it can be considered suitable for publication.

Authors' Response:

We agree with this central concern. The original manuscript placed too much emphasis on solvent-extracted EC as a reference quantity. In the revised manuscript, we no longer describe solvent-extracted, capture-filter-corrected EC as an independent or more accurate reference for atmospheric EC. Instead, we define it as **SE-EC**, an artifact-reduced operational comparator within the thermal–optical framework.

This change affects the interpretation of the entire manuscript. The revised study no longer claims to establish a true EC reference or a universally optimal OC4 temperature. Instead, it evaluates how EC assigned by thermal–optical analysis changes with OC4 temperature when compared with SE-EC. The regression-derived 615 °C value is now interpreted as a dataset-specific crossover point, not as a universally valid "KRISS temperature".

The limited scope of the dataset and the need for independent validation are now discussed explicitly in Section 3.6 and summarized in the Conclusion.

Comment 1

The study is based on only 14 PM2.5 samples collected at a single site over a relatively short sampling period. Given that the thermal behavior of EC is strongly influenced by aerosol sources and chemical composition, the current dataset is insufficient to demonstrate the broader applicability and robustness of the proposed framework across different atmospheric environments.

Authors' Response:

We agree. The revised manuscript explicitly states that the main analysis is based on 14 daily $PM_{2.5}$ samples from a single suburban site and season. We have removed statements suggesting that the results demonstrate broader robustness across atmospheric environments.

The revised interpretation is that the study provides a dataset-specific assessment of OC4-temperature sensitivity. Section 3.6 now discusses why broader validation is necessary: EC thermal evolution and OC/EC partitioning may depend on source type, atmospheric aging, chemical composition, biomass-burning influence, secondary organic aerosol composition, inorganic matrix effects, filter loading, and analyzer configuration.

Thus, the revised manuscript treats the 615 °C setpoint as an operational result for the present dataset, not as a general recommendation for other aerosol types or measurement networks.

Comment 2

The entire framework relies on the assumption that the solvent-extracted and redistribution-corrected EC represents a more accurate reference EC. However, the manuscript does not provide independent evidence demonstrating that the residual carbon after extraction truly corresponds to atmospheric EC rather than an operationally modified carbon fraction. Therefore, the validity of the proposed reference EC requires further verification.

Authors' Response:

We agree. The revised manuscript no longer treats solvent-extracted, capture-filter-corrected EC as a more accurate or independently validated EC reference. We define this quantity as **SE-EC** and use it only as an artifact-reduced operational comparator.

SE-EC is obtained after reducing extractable OC and potential charring precursors through solvent extraction and after accounting for EC-like carbonaceous material recovered on the extraction-stage capture filter. This definition is useful for evaluating protocol-dependent EC variability, but it does not establish that SE-EC is chemically pure EC or physically equivalent to refractory black carbon.

Sections 3.1 and 3.6 now state this explicitly. We also clarify that agreement between bulk EC and SE-EC at the regression-derived 615 °C OC4 setpoint should be interpreted as agreement with an operational comparator, not as evidence of improved absolute EC accuracy.

Comment 3

The proposed reference EC is evaluated solely within the thermal–optical framework. Comparison with independent black carbon (BC) measurement techniques, such as SP2, MAAP, or Aethalometer, would

substantially strengthen the validity of the proposed reference EC and help determine whether the solvent-extracted EC represents a physically meaningful carbon fraction rather than simply another operationally defined EC metric.

Authors' Response:

We agree. Independent BC measurements were not available for the $PM_{2.5}$ samples analyzed in this study. Therefore, the revised manuscript does not claim that SE-EC represents a physically validated refractory BC fraction.

We now state that SE-EC was evaluated only within the thermal–optical analytical framework. As a result, the comparison between bulk EC and SE-EC can diagnose protocol-dependent differences within that framework, but cannot determine whether either quantity corresponds to true atmospheric refractory BC.

Section 3.6 and the Conclusion now identify comparison with independent BC techniques, such as SP2, MAAP, Aethalometer, or equivalent optical/single-particle methods, as a necessary step for future validation.

Comment 4

The observation that approximately 37% of EC is redistributed to the backup filter is one of the most important findings of this study. However, the physical and chemical characteristics of the redistributed carbon remain unclear, and no additional characterization is provided. Further evidence is needed to determine whether this material is truly EC or other carbonaceous species affected by the extraction process.

Authors' Response:

We agree. We have revised the terminology from "backup filter" to **"extraction-stage capture filter"** throughout the manuscript. This change is important because the filter was not installed downstream during atmospheric sampling and was not used to correct gas-phase organic adsorption artifacts. It was used only during static solvent immersion to retain material physically detached from the particle-loaded side of the sample punch.

The material recovered on this capture filter is now described as **operational EC-like carbonaceous material** assigned as EC by thermal–optical analysis. We do not claim that it is true atmospheric EC or refractory soot. Because no independent physical or chemical characterization was performed, the material may include weakly bound soot aggregates, refractory EC-like carbon, charred OC, brown carbon, light-absorbing organic carbon, or other extraction-affected carbonaceous species.

The revised manuscript also clarifies that the capture-filter EC is included as an extraction-stage mass-balance term. It is not used as evidence that the redistributed material is chemically pure EC. This limitation is discussed in Sections 3.1 and 3.6.

Comment 5

The proposed KRISS temperature (615 °C) is derived solely from regression analysis rather than direct experimental measurements. Given that this temperature constitutes one of the main conclusions of the study, direct validation at or near 615 °C is necessary to demonstrate its practical applicability and robustness.

Authors' Response:

We agree that the original manuscript relied too strongly on the regression-derived 615 °C value. The revised manuscript now makes clear that 615 °C was obtained from regression and should be interpreted as an OC4 crossover setpoint, not as a directly validated universal optimum.

To provide a practical check, we added Section 3.5 using a separate field dataset collected in Daejeon from 22 December 2015 to 10 January 2016. These samples were analyzed directly using the modified 615 °C OC4 protocol and compared with IMPROVEA/TOT and default NIOSH. The modified 615 °C protocol produced EC concentrations intermediate between IMPROVEA/TOT and NIOSH, consistent with the temperature-dependence observed in the main dataset.

However, we also agree that this field application does not constitute full validation. It did not include SE-EC analysis or independent BC measurements, and the samples were collected in the same regional setting. Therefore, the revised manuscript presents this result as a practical implementability test and consistency check, not as proof of physical accuracy or universal robustness. This interpretation is stated in Sections 3.5 and 3.6.

Comment 6

The proposed optimal temperature (615 °C) is relatively close to the OC4 temperature employed in the EUSAAR2 protocol (~650 °C). The manuscript does not adequately demonstrate whether this difference is analytically significant or whether it provides a meaningful improvement over existing protocols. A more comprehensive comparison with EUSAAR2 and previous protocol optimization studies is therefore recommended.

Authors' Response:

We agree. The revised manuscript no longer claims that 615 °C is analytically superior to 650 °C or to EUSAAR2. We now state that 650 °C was the closest directly tested OC4 condition in the main dataset, whereas 615 °C was obtained by regression. Therefore, the difference between 615 and 650 °C should be interpreted cautiously.

We also clarify that this difference may be affected by analyzer-specific temperature calibration, residence time, carrier-gas conditions, and optical correction implementation. Because the full EUSAAR2 protocol was not applied, including its complete temperature program and implementation details, the present study cannot demonstrate equivalence to or improvement over EUSAAR2.

The revised conclusion is therefore more limited: lowering the default NIOSH OC4 temperature from 870 °C toward the 600–650 °C range strongly affects operational EC assignment for the present samples.

Direct comparison with the full EUSAAR2 protocol and other optimized thermal–optical protocols is now identified as necessary future work in Sections 3.4 and 3.6.