Response to Reviewer #1' Comments

General comments

The manuscript presents a solvent extraction method to constrain protocol-dependent uncertainties in EC measurements by thermal–optical analysis and to derive an operational "KRISS temperature" for OC4 in NIOSH-like protocols. The topic is suitable for AMT, since differences between OC/EC protocols remain a major source of uncertainty. The approach is interesting, but the current version of the manuscript has several serious weaknesses in methodology, documentation, and interpretation. In its present form, it does not yet support the strength of the claimed conclusions.

The dataset is small and narrow in scope. Fourteen PM2.5 samples collected at a single suburban site over a two-week period are used to derive an "optimized" OC4 temperature. With such limited temporal and spatial coverage, a relatively uniform aerosol composition is likely. This strongly restricts the applicability of the proposed KRISS temperature and the method to other environments. At the same time, key information on the instrument type, optical correction mode, temperature protocol (including durations), filter homogeneity, and uncertainty treatment is missing or is inconsistent. These are major issues that need to be addressed.

Overall, the work has potential, but substantial revision is required. In particular, the instrumentation and protocol description must be clarified, the uncertainty analysis strengthened, and the claims on universality and inter-protocol comparability significantly toned down and aligned with the actual evidence.

Authors' Response:

We agree with the reviewer's overall assessment. The original manuscript did not sufficiently distinguish between a dataset-specific operational result and a generally transferable protocol recommendation. We have therefore revised the manuscript throughout to avoid implying universal applicability of the proposed OC4 adjustment.

Specifically, the Abstract, Introduction, Results, Discussion, and Conclusion now describe the work as an operational assessment of OC4-temperature sensitivity using 14 $PM_{2.5}$ samples from one suburban site and season. We no longer state that the approach establishes a universal EC reference or improves inter-protocol comparability in a general sense. Instead, we state that the solvent-extraction-based mass balance helps diagnose protocol-dependent EC variability under the specific analytical conditions examined here.

We also revised the Methods to clarify the instrument configuration, optical correction mode, temperature programs, OC/EC step durations, QA/QC procedures, and filter homogeneity test. Finally, Section 3.6 was added to explicitly discuss the limited scope of the dataset and the need for further validation using broader aerosol types, seasons, sites, instruments, and independent black-carbon measurement techniques.

Comment 1 — Representativity and scope of conclusions

The study uses PM2.5 samples from one suburban site in Daejeon, Korea, collected over two weeks (31 March–13 April 2014). With such limited coverage, a rather homogeneous aerosol composition can be expected. This limitation is not discussed adequately. The current text suggests a broad relevance of the derived OC4 temperature and the KRISS temperature. This is not justified.

The authors should clearly state that the proposed temperatures are operational and specific to the aerosol type and conditions covered here. Claims that the framework provides a "robust basis" or "enhances inter-protocol comparability" must be softened and strictly linked to this dataset only. Without additional evidence from other environments and laboratories, the manuscript cannot argue for a universal or widely applicable OC4 setting.

Authors' Response:

We agree. The revised manuscript now explicitly states that the main dataset consists of 14 daily $PM_{2.5}$ samples collected at a single suburban site during a short spring period. We have removed or qualified statements that implied broad representativity, robustness, or general inter-protocol comparability.

The 615 °C value is now interpreted as a dataset-specific OC4 crossover setpoint derived from the relationship between bulk EC and SE-EC for the present samples. We also clarify that aerosol source type, atmospheric aging, chemical composition, filter loading, and instrument configuration can affect EC thermal evolution and OC/EC partitioning. These limitations are now stated in the Abstract, Introduction, Section 3.6, and Conclusion.

Thus, the revised manuscript does not claim that the 615 °C condition is generally applicable to other aerosol environments. Instead, it presents the result as evidence that OC4 temperature strongly affects operational EC assignment in this specific dataset.

Comment 2 — Instrument type, protocol implementation, and optical correction

2-1: Line 71 describes a "thermal–optical carbon analyzer (Sunset Laboratory Inc., Model RT-3140)". "RT" typically refers to a real-time instrument. The method described in the manuscript, however, is clearly an off-line analysis of 1.5 cm² punches with sequential extractions. This inconsistency is critical, especially as most cited studies use laboratory analyzers.

The authors must clearly identify the exact instrument model and configuration (real-time vs laboratory unit). If a laboratory analyzer was used, the "RT-3140" wording is misleading and should be corrected. Any non-standard configuration should be described in sufficient detail to allow reproduction and fair comparison with the literature.

Authors' Response:

We appreciate this important comment. We agree that the original description of the thermal–optical analyzer was insufficiently clear and could lead to ambiguity regarding the instrument configuration. The model designation used in the original manuscript could be interpreted as a

real-time analyzer, whereas the measurements performed in this study were based on offline filter-punch analysis.

We have therefore corrected the instrument description in Section 2.2 to specify the exact laboratory (offline) thermal–optical carbon analyzer and configuration used in this study. The revised description now clearly states that OC and EC were quantified using a laboratory offline analyzer (Sunset Laboratory Inc., Model 4L, serial number 269-68) operated with thermal–optical transmittance (TOT) correction.

2-2: The manuscript states that thermal–optical transmittance (TOT) was used for charring correction with both IMPROVEA and NIOSH protocols. Most of the key IMPROVE-related studies cited here use reflectance (TOR) as the default optical correction. Transmittance and reflectance can yield significantly different OC/EC splits, even with the same temperature protocol. This issue is central and is not treated properly in the current version.

The authors need to:

- Explicitly confirm that IMPROVEA was implemented with TOT and not TOR.

- State clearly that, as a result, the measurements are not strictly comparable to earlier IMPROVEA/TOR results cited in the manuscript.

- Revise the discussion and conclusions wherever direct comparability with IMPROVEA/TOR literature is implied.

- Add a concise discussion on how the use of TOT, rather than TOR, may have influenced the observed protocol differences.

Authors' Response:

We appreciate the reviewer's comment regarding the optical correction mode. We agree that the distinction between TOT and TOR is important when comparing thermal–optical results among different studies, particularly for IMPROVE-related protocols.

We have explicitly clarified in Section 2.2 that both IMPROVEA and NIOSH protocols in this study were performed using thermal–optical transmittance (TOT), not thermal–optical reflectance (TOR), for charring correction. We also revised the manuscript to clarify that the IMPROVEA/TOT results obtained here are not directly comparable to previously published IMPROVEA/TOR values because TOT and TOR can produce different OC/EC split points and carbon partitioning even under identical temperature programs.

Furthermore, the discussion of protocol-dependent EC differences in Section 3.3 has been revised to consider the contribution of optical correction mode in addition to OC-phase temperature effects. Specifically, we now clarify that part of the difference between IMPROVEA/TOT and NIOSH results may arise from the different optical correction approach,

and that comparisons with previous IMPROVEA/TOR studies should therefore be made cautiously.

2-3: Table 1 lists only the temperature steps. For IMPROVEA, the OC4 step duration is modular and controlled by the optical signal returning to baseline, whereas NIOSH and EUSAAR2 apply fixed step durations. The manuscript focuses on changes in OC4 temperature, but completely omits the corresponding durations. This is a major omission because incomplete OC4 evolution due to short durations can strongly bias the results.

The authors should:

- Report the OC4 step duration for each protocol and each modified OC4 temperature.

- Clarify whether the duration was kept constant when the OC4 temperature was adjusted.

- Discuss explicitly how the chosen durations may have affected OC4 peak development and the differences observed between NIOSH variants.

Authors' Response:

We agree that the original description of the thermal–optical protocols was incomplete because only the temperature profiles were provided, without the corresponding step durations. Since the duration of each temperature step can influence carbon evolution and OC/EC partitioning, this information is important for reproducibility and interpretation of the modified OC4 experiments.

We have therefore expanded Table 1 to include the duration of each OC and EC step for the IMPROVEA, default NIOSH, and modified OC4 protocols.

In addition, we clarified in Section 2.2 that only the maximum OC-phase temperature (OC4) was modified in the NIOSH-type experiments, while all other temperature steps, carrier gases, and step durations were maintained unchanged.

2-4: Laser stability, optical signal behavior, and split point determination are not adequately documented. These aspects are crucial for OC/EC separation and for the KRISS-temperature concept.

The manuscript must include:

- A short description of laser stability checks and criteria for rejecting thermograms (e.g. signal drift, noise, shifts).

- Information on oven cleanliness and any temperature-offset calibration performed. Earlier studies have shown that soiled ovens can lead to pre-oxidation and bias in split point determination. Given the focus on an "optimized" OC4, this information is essential.

Authors' Response:

We appreciate the reviewer's suggestion to provide additional information regarding analytical quality control and optical signal stability. We agree that these aspects are important because OC/EC separation depends strongly on the stability of optical correction and accurate determination of the OC/EC split point.

We have therefore added a QA/QC description in Section 2.2. Short-term FID response stability was evaluated using eight replicate injections of a fixed methane amount through the internal calibration system. The relative standard deviation of the methane calibration peak area was 1.7 %, indicating stable detector response during the analytical sequence.

In addition, all thermograms were inspected for abnormal laser-transmittance drift, discontinuities in optical signals, unstable FID baselines, and ambiguous OC/EC split-point behavior. Measurements showing abnormal behavior were checked and reanalyzed where necessary. Instrument blanks were also analyzed to verify low carbon background and acceptable oven cleanliness.

Regarding temperature calibration, no independent furnace temperature-offset correction was applied in this study. Therefore, all OC4 temperatures reported in this manuscript represent analyzer-set temperature conditions for the specific instrument configuration used.

Comment 3 — Filter area, homogeneity, and replicate analysis

3-1: The primary samples are large rectangular high-volume filters (20 × 25 cm). Only a single 1.5 cm² punch is analyzed per filter. With such a large area, non-uniform loading is a realistic and important concern, especially after sequential solvent extraction and handling. Yet, the manuscript does not state whether replicate punches were taken. This is a serious gap in the uncertainty analysis.

The authors should:

- State clearly whether duplicate or triplicate punches were analyzed for each filter.

- If replicates were analyzed, provide a brief summary of intra-filter variability and explain how it was propagated into the uncertainty budget.

- If no replicates were analyzed, discuss explicitly the likely magnitude of inhomogeneity and how this unaccounted variability affects the reliability of the results and conclusions.

Authors' Response:

We appreciate this important comment. We agree that intra-filter loading heterogeneity is an important potential source of uncertainty when a small punch is analyzed from a large-area quartz filter.

To evaluate this issue, we performed a replicate-punch homogeneity test using the same type of quartz filter used in this study. Four punches were taken from a single filter and analyzed for total carbon (TC, defined as the sum of OC and EC). The relative standard deviation of TC among the four punch locations was 0.11 %, indicating highly uniform carbon loading within the evaluated filter area.

This information has been added to Section 2.2. We also clarified that the standard deviations reported in Table 2 represent variability among 14 independent daily $PM_{2.5}$ samples and therefore mainly reflect atmospheric variability in carbonaceous aerosol loading and composition, rather than analytical repeatability or punch-to-punch variability.

Although the homogeneity test was performed using TC rather than EC alone, the very small variability indicates that punch-location heterogeneity was unlikely to be a dominant contributor to the protocol-dependent EC differences observed in this study.

3-2: For the backup filters, the procedure is not clearly described. It is not evident whether the whole backup filter was analyzed or only a portion of it. Since the backup filter plays a key role in the EC mass balance (with a large fraction of EC being recovered on it), this must be clarified in detail.

Please:

- Specify whether the entire backup filter was analyzed or a sub-area.

- If the entire filter was used, describe the analysis method and any checks for homogeneity.

- If only a portion was analyzed, explain the sampling strategy and the assumption of uniform loading, and discuss how this assumption influences the calculated "operational reference EC".

Authors' Response:

We appreciate this comment and agree that the terminology used in the original manuscript was potentially misleading. The filter referred to as the "backup filter" was not a downstream sampling backup filter installed after the aerosol collection filter. Instead, it was an **extraction-stage capture filter** used only during the static solvent-immersion procedure.

During extraction, the sample punch and a pre-baked quartz fiber capture filter were assembled in a custom holder, with the capture filter placed facing the particle-loaded side of the sample punch. This configuration allowed carbonaceous material physically detached from the sampled surface during solvent immersion to be retained and subsequently quantified.

The manuscript has therefore been revised throughout to replace "backup filter" with "extraction-stage capture filter". We also clarified in Sections 2.3 and 3.1, as well as in Fig. 1 and its caption, that this filter:

(i) was used only during the extraction procedure,

(ii) was not part of the atmospheric sampling filter pack, and

(iii) was not intended to correct gas-phase organic adsorption or semi-volatile organic carbon artifacts.

After extraction, the sample punch and the extraction-stage capture filter were analyzed separately by thermal–optical analysis, and the EC measured on both components was incorporated into the extraction-stage EC mass balance.

3-3: The manuscript reports that, on average, 37.4 ± 6.4 % of EC is recovered on the backup filter after extraction. This is a substantial fraction, introducing additional uncertainty. The authors should assess whether this fraction is stable across samples or shows systematic variation with load, OC/EC ratio, or other indicators. This variability needs to be incorporated transparently into the uncertainty estimates.

Authors' Response:

We appreciate the reviewer's suggestion to further evaluate the variability of the carbon fraction recovered on the filter. We agree that the terminology used in the original manuscript could lead to confusion regarding the role of this filter.

The filter referred to as the "backup filter" in the original manuscript was not a downstream sampling backup filter installed during atmospheric aerosol collection. Instead, it was an **extraction-stage capture filter** used only during the static solvent-immersion procedure. During extraction, the capture filter was placed facing the particle-loaded side of the sample punch to retain carbonaceous material physically detached from the sampled surface. Therefore, it was not used to correct gas-phase organic adsorption artifacts or semi-volatile organic carbon breakthrough during sampling.

The manuscript has been revised throughout to replace "backup filter" with "extraction-stage capture filter" and to clarify its role in the extraction-stage mass balance.

To evaluate whether the redistribution fraction depended on sample characteristics, we calculated the fraction of EC recovered on the extraction-stage capture filter as:

$$EC\ fraction_{capture} = EC_{capture}/(EC_{sample}+EC_{capture})\times 100$$

where both EC_{sample} and $EC_{capture}$ represent EC concentrations measured by thermal–optical analysis **after solvent extraction** of the sample punch and capture filter, respectively. The total EC used for the extraction-stage mass balance was therefore:

$$EC_{SE} = EC_{sample} + EC_{capture}$$

The relationship between this capture-filter EC fraction and carbonaceous aerosol properties was further examined. Total carbon (TC) was obtained independently from untreated sample filters analyzed using the NIOSH870 protocol. The OC/EC ratio was reconstructed using:

$$OC = TC_{bulk} - (EC_{sample} + EC_{capture})$$

and the corresponding OC/EC ratio was calculated using the extraction-corrected EC mass balance.

The capture-filter EC fraction showed a moderate inverse relationship with TC loading (R^2 = 0.45), indicating that the redistributed fraction was not simply proportional to the total amount of carbon collected on the filter. A weak relationship was observed with the reconstructed OC/EC ratio (R^2 = 0.22), suggesting that redistribution was not strongly controlled by the bulk carbonaceous composition within the limited dataset. However, because this analysis was based on only 14 samples, these relationships should be considered exploratory rather than evidence of a universal dependence.

Importantly, the capture-filter EC fraction was **not applied as a fixed correction factor**. Instead, EC measured on each extraction-stage capture filter was incorporated into the sample-specific extraction-stage mass balance to calculate SE-EC. Therefore, variability in the redistributed carbon fraction is

directly included in the operational definition of SE-EC. Therefore, the observed variability in redistribution was not treated as an uncertainty source requiring correction, but as an inherent component of the sample-specific SE-EC definition.

The revised interpretation has been added to Sections 2.3, 3.1, and 3.6. We also clarify that the physical and chemical identity of the redistributed carbonaceous material remains unresolved and should be further investigated using independent characterization methods in future studies.

Comment 4 — Brown carbon, charring, and extraction scheme

Lines 114–119 refer to brown carbon and charred OC in the context of solvent extraction, drawing on studies that often use water-only extraction or different pretreatments. In this work, both water and organic solvents are used, and the filters are sourced from a specific suburban environment. The connection to the cited mechanisms is not always convincing, and the current wording is confusing.

This part should be rewritten to:

- Clarify whether significant brown carbon or charred OC is expected for the sampling period and site considered here.

- Clearly separate water-soluble brown carbon, solvent-extractable OC, and mechanically redistributed carbonaceous material collected on the backup filter.

- Avoid general statements that implicitly assume that mechanisms from water-only extraction studies apply unchanged to a more aggressive, multi-solvent protocol.

Authors' Response:

We agree. The original discussion treated the effects of solvent extraction too broadly and did not sufficiently distinguish among the different carbon fractions affected by the procedure. Sections 3.1 and 3.2 have therefore been revised to separate three processes: removal of water-soluble OC, removal of organic-solvent-extractable OC, and physical redistribution of EC-like carbonaceous material during static immersion.

We also revised the interpretation of the thermograms. The shift of carbon evolution toward higher temperatures after extraction is no longer interpreted as evidence that chemically pure EC was isolated. Instead, we interpret it as an operational change in the thermal evolution behavior of the residual carbonaceous matrix after removal of more labile and extractable carbon fractions. This interpretation is more consistent with the operational nature of thermal–optical EC and avoids assigning the residual carbon uniquely to refractory soot.

The revised manuscript also clarifies that the redistributed material recovered on the extraction-stage capture filter was not independently characterized. It may include refractory soot, weakly bound soot aggregates, charred OC, light-absorbing organic carbon, or other extraction-affected carbonaceous material. This uncertainty is now explicitly discussed in Section 3.6.

Comment 5 — Thermograms, Table 2, and statistical significance

5-1: In Fig. 3, the OC peaks for C3 are very small. In contrast, Table 2 reports notable differences in OC4 concentration between NIOSH variants, especially at 650 °C. This is difficult to reconcile with the low OC4 signals seen in the example thermogram.

The authors need to clarify:

- Whether Fig. 3 describes a representative sample, and if all samples show similar thermograms.

- If not, why was this particular thermogram chosen, and how representative is it of the dataset?

- How can such small OC4 peaks produce the reported concentration differences in a statistically robust way?

Authors' Response:

We appreciate this comment and agree that the original manuscript did not clearly distinguish the purpose of Fig. 3 from the EC comparison presented in Table 2. We have revised the relevant sections to clarify that these two analyses address different aspects of the study.

First, Fig. 3 was revised to illustrate the effect of solvent extraction on thermal–optical carbon evolution. C0 represents the untreated bulk sample, whereas C3 represents the optimized solvent-extraction condition. Under C3, most extractable OC and potential charring precursors were removed before thermal–optical analysis, resulting in substantially reduced OC signals during the He phase, including the OC4 region. Therefore, the small OC4 peak observed in C3 should not be used to interpret the EC differences among the NIOSH650–NIOSH870 conditions.

Second, the EC differences among NIOSH650–NIOSH870 shown in Table 2 were obtained from untreated bulk samples (C0), not from solvent-extracted C3 samples. These differences reflect the sensitivity of operational OC/EC partitioning to the maximum OC-phase temperature and associated thermal evolution and optical split-point behavior. They are therefore independent of the small residual OC4 signal observed after solvent extraction.

We have revised Section 3.2 and the Fig. 3 caption to explicitly state that Fig. 3 demonstrates the effect of solvent extraction on carbon evolution, whereas Table 2 evaluates OC4-temperature dependence using untreated samples.

Regarding the statistical interpretation, we have clarified that the values in Table 2 represent the mean, standard deviation, and range of 14 independent daily $PM_{2.5}$ samples. Therefore, the reported variability primarily reflects day-to-day atmospheric variability in carbonaceous aerosol composition and loading rather than analytical repeatability. The revised manuscript avoids interpreting these differences as proof of absolute EC accuracy or statistical equivalence and instead discusses them as protocol-dependent trends relative to SE-EC.

The observed EC differences among NIOSH650–NIOSH870 were not derived from the magnitude of the OC4 peak in C3 thermograms, but from independent analyses of untreated samples under different OC4 temperature settings.

5-2: The EC concentration range reported in Table 2 is relatively low, while the associated uncertainties are comparatively large. Several of the apparent differences between NIOSH variants are small relative to these uncertainties. It is not evident which differences, if any, are statistically significant. The current discussion tends to overinterpret trends that may be within the bounds of uncertainty.

Authors' Response:

We agree that the original manuscript did not sufficiently explain the meaning of the variability reported in Table 2. We have revised the description to clarify that Table 2 summarizes results from 14 independent daily $PM_{2.5}$ samples and that the reported standard deviations represent atmospheric sample-to-sample variability rather than replicate analytical uncertainty.

Analytical repeatability and intra-filter variability were evaluated separately through methane internal calibration and filter homogeneity tests, respectively, and these results are now described in Section 2.2. We have also revised the interpretation of Table 2 to avoid implying that SE-EC represents a validated absolute EC reference. The observed differences among OC4 conditions are now discussed as protocol-dependent changes in operational EC assignment. Because SE-EC is an operational comparator rather than an independently validated EC measurement, the results are interpreted in terms of convergence or divergence relative to SE-EC rather than statistical equivalence to true atmospheric EC.

5-3: The regression-based KRISS temperature of 615 °C is derived exclusively from this limited dataset. This must be made explicit. It is an operational parameter tuned to this specific aerosol type and to the particular implementation of the NIOSH protocol and optical correction used here. Without additional validation on other aerosol types and in other laboratories, the value cannot be promoted as generally applicable.

Authors' Response:

We agree with the reviewer. The regression-derived 615 °C OC4 setpoint was obtained exclusively from the present dataset, consisting of 14 $PM_{2.5}$ samples collected at a single suburban site during one sampling period. Therefore, it should not be interpreted as a universal OC4 temperature applicable to different aerosol types, sites, seasons, instruments, or thermal–optical implementations.

In the revised manuscript, the 615 °C value is described as a regression-derived OC4 crossover setpoint within a modified NIOSH-type protocol using TOT optical correction. It represents the temperature at which the SE-EC/bulk EC ratio approaches unity for the present dataset. This value is not presented as a chemically defined EC temperature or a replacement for existing optimized thermal–optical protocols. The Abstract, Results, Discussion, and Conclusion have been revised accordingly. In addition, Section 3.6 has been added to explicitly discuss the dataset-specific nature of this result and the need for validation using additional aerosol types, seasons, sites, instruments, and independent black-carbon measurements.

Comment 6 — Inter-protocol comparability and interlaboratory relevance

The manuscript states that lowering OC4 and introducing the KRISS temperature improves inter-protocol comparability and supports better interlaboratory reproducibility. In practice, changing OC4 and using a different optical correction mode defines a new protocol. This has serious implications for continuity with existing IMPROVEA and NIOSH datasets. Please clarify whether the KRISS temperature, in its current form, would effectively create a modified/new temperature protocol.

The recent interlaboratory work by Sipkens et al. (2024) is briefly mentioned but not used to place the uncertainties in context. That study reports reproducibility-related uncertainties on the order of 10–20 % for EC, OC, and TC. The manuscript needs to demonstrate that the additional method complexity yields a net benefit and does not merely shift or inflate uncertainties.

Recommendation

Given the issues outlined above, major revisions are necessary. The manuscript requires clearer, more complete documentation of the instrument and protocols, a more rigorous treatment of filter homogeneity and uncertainties, and refocusing of the conclusions to what the data can actually support.

Authors' Response:

We agree. The revised manuscript now explicitly states that changing OC4 defines a modified thermal–optical protocol. Therefore, the regression-derived 615 °C OC4 setpoint is not presented as a correction factor that makes NIOSH and IMPROVEA EC directly comparable. It is also not presented as a universal replacement for existing protocols.

The 615 °C value is now described as a dataset-specific OC4 crossover setpoint within a modified NIOSH-type protocol using TOT optical correction. This framing avoids implying that historical NIOSH, IMPROVE-A/TOR, IMPROVEA/TOT, and modified OC4 datasets can be directly converted or harmonized using a single temperature adjustment.

We also revised the discussion of Sipkens et al. (2024). The reported interlaboratory uncertainty range is now used only as context for the magnitude of protocol- and laboratory-dependent uncertainty in thermal–optical carbon analysis. We do not claim that the modified OC4 setpoint reduces interlaboratory uncertainty below this range. This limitation is now discussed in Sections 3.4 and 3.6.