

Author Comments on the reviewer response on “An algorithm for retrieving black carbon optical parameters from thermal-optical (OC/EC) instruments” by A Andersson et al., Atmos. Meas. Tech. Discuss., 4, 1233-1254, 201

Anonymous Referee 1.

We thank reviewer 1 for his/her review and for providing suggestions on how the manuscript can be improved and clarified. Comments to the points raised by the referee are outlined below, with the referee comments marked in italic.

Major comments

This manuscript centers on the use of the thermal (Sunset) analyzer to infer both absorption and elemental carbon content. This must be done with a deep understanding of the biases in measurements of both quantities. Authors are either unaware of, or do not cite, the extensive literature describing artifacts in the detection of EC. Many of those artifacts relate to absorption and the expected changes in absorption that occur during heating. These are clearly discussed by Yang and Yu (EST, 36, 5199, 2002). The retention of organic carbon past the EC split point, which could affect the apparent optical properties of inferred EC, is discussed by Subramanian et al (AST, 40, 763, 2006). The differences between reflectance and transmission offer some insight into optics as discussed by Chow et al (EST, 38, 4414, 2004). None of this literature is discussed, and simply citing it will not fix this analysis. All these factors must be considered in the design and interpretation of the measurements.

Authors suggest that the Ram and Sarin comparison of attenuation and EC is the first such effort and that their own investigation of the laser signal is novel. This also betrays a lack of knowledge of past studies. Attenuation has been compared in quite a few studies but it's often inconclusive and nobody has really relied on it. The point-by-point laser is discussed by Kirchstetter et al (Atmos Env 41, 1874, 2007) and Boparai et al (AST 42, 930, 2008).

We agree with the reviewer's sentiment that isolation and quantification of the highly condensed carbonaceous residue of incomplete combustion (termed intermittently EC, BC, SC in different communities/techniques) indeed poses a substantial analytical challenge, with

the separation of non-pyrogenic OC from the EC being a central obstacle. We are well aware of the raised and additional BC metrology issues, having published half a dozen BC analytical/measurements studies prior to this submission. We agree completely that there are concerns also about the functioning of the thermal-optical (TO; OCEC; Sunset) technique, as there is with any other of the 5-6 well-tested EC (BC) mass measurement methods. Nevertheless, the TO-Sunset method is the most applied method for EC determination in aerosols (large set of references already cited in submitted ms). Given the broad application in the field of atmospheric science and air monitoring of this method, there are multiple comments/assessments of the method. The submitted ms highlighted several of those, yet we intend to elaborate on several of the additional references that this reviewed opted to emphasize. Given its deficiencies, the TO-Sunset method has still proven useful to assess EC dynamics in the atmosphere as well being the method of choice for the major BC emission inventory databases (e.g., Bond et al. and GAINS). The manuscript presents a method that allows the enormous databases that exist on TO-Sunset runs to be tapped for a key optical property, specifically for the EC that has already been quantified and is a key component of carbonaceous aerosols for climate forcing.

The manuscript will be revised to elaborate on the aspects raised by the reviewer but also place that in a broader perspective of the usefulness of the TO-Sunset method.

Specific points

The paper contains several misconceptions discussed below.

p. 1237: "Light is attenuated not only by aerosol absorption, but also scattering" True in the atmosphere, but the statements here suggest that authors do not understand the principle of the integrating plate. Lin 1973 is cited here. I suggest that authors should read and understand this principle and following work by Clarke regarding integrating plate. Scattering does affect the signal but its contribution to attenuation is much reduced.

We agree with the reviewer that the scattering effects observed using an integrating plate type of setup is much less than what is expected for ambient air samplers. We will emphasize this point in the manuscript.

p. 1238: "Laser transmission in the OCEC experiment can continue to increase even after the carbon signal has leveled off" What chemical compounds could contribute to this increase? According to the figure it occurs late in the analysis, therefore at a high temperature. Very few compounds absorb light, are stable until this temperature (750C? 900C?), and decompose at this temperature. In fact, I cannot think of any. Ammonium sulfate would have decomposed early in the analysis. Iron oxides are stable but remain on the filter even at the end of the analysis. Brown carbon would have been removed already either by oxidation or volatilization. I can think of one explanation: The optical signal in most analyzers (DRI, Sunset) is rather unstable and sometimes temperature dependent. It is quite possible that this entire investigation examines an artifact of the laser and not any contribution by other aerosol components.

The non-carbon contributions to the laser transmission accounted for by the current method are clearly caused at high temperatures. These effects are frequently observed but not for all samples/regimes (likely dependent on aerosol matrix). Furthermore, triplicate analysis shows a large consistency among samples where these effects are observed/not observed. Taken together this shows that it is unlikely that the observed phenomena are due to unstable optical/temperature effects by the laser. Rather this phenomenon is clearly linked to sample differences. As such it is also clear that these effects do not include any carbon contributions. Therefore these effects are very likely to be due to inorganic/minerogenic contributions. We agree with the reviewer that it would be interesting to know what these contributions are, but that question would require other instrumental techniques, which clearly is beyond the scope of the current study. However, we will make efforts to clarify the observational basis for discussing these high temperature non-carbon contributions to the laser transmission signal.

p. 1239: Even though no physical explanation has been offered, the next investigation tries to separate attenuation by carbon and attenuation by the unknown species. This treatment assumes that the two substances could be separated. It does not address the question of whether both substances might evolve from the filter at the same time.

How is this assumption justified?

The present study differentiates between carbon-containing compounds (detected by FID) and compounds that do not contain carbon, but still attenuate the laser transmission. Although the

molecular composition of the non-carbon contributions is not known per se, it is clear that they influence the laser transmission signal. It is a fact of observation that the carbon contributions and the laser-attenuating contributions do not evolve from the filter at the same time after all carbon contents are burned off. Thus, clearly there is a two state process: carbon-containing materials and non-carbon containing materials that therefore may be separated.

p. 1239: I found this section especially difficult to read and understand. What is a “novel contribution to the transmission?” What does the “response function” tell the analyst? If transmission increases and carbon decreases, shouldn’t the response function be negative? What is a “false positive”? It implies that a “true positive” is being sought, and what is it?

We will address these points in the manuscript to clarify the description of the current methodology. In short:

The novel contribution is the non-carbon fraction of the sample that affects the laser transmission at high temperatures. The response function is a measure of the time evolution of non-carbon contributions to the laser transmission. It is defined as the ‘time-derivative’ of the transmission signal divided by the ‘time-derivative’ of the cumulative carbon signal (i.e. the FID signal – this was not clearly explained in the manuscript). Since the laser transmission typically is monotonically increasing after the EC cut-off point, and since the FID is always positive, the response function is positive with a maximum where carbon contributions to the laser transmission is decreasing while the laser transmission is increasing. A false positive in the present context indicates a maximum in the response function that is due to noise rather than a real change. Such effects are suppressed by calculating the floating average.

p. 1241: I think authors have misinterpreted the shadowing effect. Although Weingartner discussed it for aged aerosols it seems to relate more to total absorption (and scattering) by aerosol on the filter.

We thank the reviewer for pointing out vagueness’ in our explanation of the shadowing effect and will clarify this issue.

p. 1241: “: : :can partially be controlled by ensuring that the sampling time/air flow rates match the ambient loadings.” I do not understand this at all. What has to be matched? A flow

rate does not match a loading. Maybe authors mean that the filter shouldn't be overloaded. Inter-site comparisons: Why were these sites chosen? The number of samples for each site is not given. More should be said about this.

Yes, we intended to describe overloading effects. We will clarify this section as well as more clearly motivate our choices of sites and the number of samples per site.

p. 1242-1243: The discussion of inter-site differences is not very satisfying (even if we could believe the measurements). Authors admit that no general conclusions are drawn. What are we supposed to do with the data? How are they useful? Most of the discussion emphasizes the large amount of variability between sites but doesn't provide new insights. It doesn't even provide confidence about data at any site.

The current work focuses on the methodology and use a smaller set of field observations just to demonstrate the algorithm. This field data show that large variations may be observed when comparing different sites as well as when analyzing time variations for a single site. However, extensive field applications, which are now underway, are necessary to draw conclusions about the optical properties of EC at any particular site. The current field data is rather intended as a proof of principle.

Section 3.4 Comparisons with other filter based methods. The first 3 paragraphs here are not very useful. They are general statements about artifacts and considerations. They don't help the reader understand how to interpret the results given in the paper. The final paragraph compares MAC given in this paper with MAC given by others, and then suggests that they are comparable if one chooses a new filter correction. This is unconvincing.

We agree that the description of these artifacts and considerations are not central to this manuscript. We will delete this section.

The rationale for comparing the current Stockholm MAC values with the one by Bond and Bergstrom is that the Stockholm values are expected to be caused by relatively freshly emitted EC contributions from a nearby motorway, whereas the Bond values reflect 'fresh' soot. I.e., the Stockholm values are not expected to be as well-aged as the ones collected at the other sites, and therefore should have lower multiple scattering correction factors. However, we

agree with the reviewer that such comparability with different results should not be overstated. We will delete this section.

The concluding paragraph is overstated. It says that a method was developed and successfully applied. It appears that an algorithm was developed and it did produce numbers, but no criteria for success (understanding, accuracy) were set and none were met. This conclusion also says that novel insights were provided. I regret that I could not find any.

The novel and important insight stems from the observation of a clear non-carbon high temperature contribution to the laser transmission in the common NIOSH protocol. This contribution may be quantified by high precision using the proposed algorithm. The precision of the current method is evaluated by triplicate analysis of the samples: The relative error in the calculated light attenuation using the method by Ram and Sarin (2009) for the current data set was 9% (Stockholm), 2% (Aspvreten), 5% (Sinhagad) and 4% (Hanimaadhoo), see Table 1. The corresponding values using the novel algorithm for accounting for non-carbon high temperature contributions to the laser transmission are 8% (Stockholm), 4% (Aspvreten), 3% (Sinhagad) and 27% (Hanimaadhoo). Thus, the novel algorithm clearly provides consistent values for the different sites. Taken together, this shows that careful considerations are needed to account for these non-carbon contributions when utilizing the widely spread techniques for evaluating BC/EC concentrations from filter-based absorption measurements. We regret that the understanding and accuracy of the current measurements was not clearly enough explained. We will make efforts to clarify these issues.

Anonymous Referee 2.

We thank reviewer 2 for carefully reviewing our manuscript and for proposing improvements. Comments to the points raised by the referee are outlined below, with the referee comments marked in italic.

Major comment:

My major concern is on the use of terminology in the MS. There is a lack of consistency on the use of notation and definition of various terminologies (as also realized by the authors) and those used in the literature. As a reviewer, I find very difficult to grasp and have to look back many times on the terminology used by the authors. I strongly recommend and urge the authors' to stick with the standard definition used in literature (see suggested nomenclature given in Table) or suggest authors to add a table on the nomenclature of various terminologies. This will also provide a good and fluent reading of the paper. Furthermore, methodology section of the MS is weaker and authors should provide fine details of their methodology as they claim development of a new algorithm.

We will adopt the more common terminology and will emphasize the details of the current algorithm.

Authors are suggested to provide details of the uncertainty in their measurement of optical properties.

Please see response below in connection to comment on Table 1 and Fig. 2a.

Specific comments:

*P1236, L21-22 and other places in the text: The term ATN is widely defined in literature as $\ln(I_0/I)$ or $100 * \ln(I_0/I)$ which is a unit less parameter. The term attenuation coefficient has a unit of m^{-1} (see equation 3 of the MS). I strongly recommend and urge the authors' to stick with the standard definition of Bond et al, 1999, Bond and Bergstrom 2006, Weingartner et al, 2003; Ram and Sarin, 2009 (all of them cited in the paper). Otherwise, authors are suggested to add a table on the nomenclature of various terminologies used in the MS I am providing the following table for the authors which can be useful in defining various parameters. Parameter Symbol Unit Optical-attenuation ATN unit less Attenuation coefficient*

bATN Mm-1 Multiple scattering effect C unit less Shadowing effect R unit less Absorption coefficient babs Mm-1 Mass absorption efficiency (MAE) iA_{s,abs} m2g-1

We will adopt the more common terminology in the present manuscript.

P1238, L1: Again inconsistency with the use of notations. The term “I/I₀” is usually defined as transmittance while “ln(I₀/I)” is defined as absorbance or attenuation (ATN).

We will make efforts to keep the manuscript consistent with respect to terminology.

P1238, L4-5: Delete “the extinction coefficient, here referred to as”. Please see an earlier comment.

Please see above.

P1238, 3-6: Please amend the uses of attenuation and attenuation coefficient in the text accordingly.

Please see above.

Equation 3; P1238, L16-24 and P 1239, L1-4: The measurement of ATN and other optical properties in Ram and Sarin (2009) paper is based on the measurement of intensity of transmitted light (I) and intensity of incident light (I₀). The absorbance or attenuation is calculated when the sample is just put in the oven and sample is not heated. Thus, all the derived optical properties are independent of what happens to laser transmittance when sample is heated in an inert and oxidizing atmosphere. It would be interesting to know how the transmittance and optical properties changes when sample is heated. This is an important finding of the paper and authors should utilise this fact, in details, to discuss the changes in optical properties of aerosols.

This is an interesting observation that could be elaborated upon. Especially since BC/EC is formed during combustion at various temperatures. However, such analysis is complicated due to the heterogeneity of the samples. As is shown in this manuscript there are large non-

carbon contributions to the laser transmission at higher temperatures. We therefore think that the temperature response with respect to carbon contents and laser transmission first should be examined using standard BC samples, and potentially using a different temperature program than the NIOSH. Such detailed analysis lies outside of the scope of the present manuscript.

Table 1 and Fig. 2a: What is the uncertainty in the measurement of attenuation coefficient?

The uncertainties of the measurements of the attenuation coefficient are evaluated by triplicate analysis of the same filter. The standard deviation of this triplicate analysis is presented in Table 1 as mean value \pm standard deviation (columns ATN_{RS} and ATN_{EC}).

Authors are suggested to provide details of the uncertainty in their measurement, though they have provided standard deviation in real-time measurement. The numbers given in table 1, except at MCOH, are statistically indistinguishable and may be same within the error of two measurement techniques. What could be reason (s) for differences in calculated optical properties at MCOH, especially when the two techniques agree well at other locations? Could it be explained on the basis of mixing state(internal) due to aging/chemically processing?

For uncertainties, please see previous point. We have also noted that the high-temperature non-carbon contribution to the light attenuation is relatively larger at MCOC compared with the other sites. As we are not clear on what this non-carbon contribution is, it is hard to speculate what specific contributions could explain this variability. However, MCOH is the site at which the air masses are expected to have been transported for the longest time. Thus, we agree with the reviewer that chemical ageing might be a possible candidate for explaining such phenomenon. However, we dare not speculate on such in this methods manuscript (to be addressed in forthcoming field applications paper).

Authors are suggested to add ATN (calculated using transmission signal) vs EC concentration (in g cm^{-2}) plot of their own data (to validate the Beer-Lambert's law and use of the methodology).

We thank the reviewer for this suggestion and will add such a plot.

Technical corrections:

P1234, L10: please replace “in-organic” with “inorganic”

We agree.

P1235, L4: Please replace "opposed" with "compared" as Brown carbon also has a weak absorption like BC.

We agree.

P1235, L14: Punctuation is needed after “setup”.

We fail to find this part in the manuscript.

P1235, L24, 26 and other places: Please replace "extinction" with "absorbing" throughout the text. Extinction means the sum of scattering and absorbing properties of aerosols.

We agree.

P1236, L1: Delete "PSAP" as authors have already defined it at P1235, L11-12.

We agree.

Table 1: Please change the units of EC and OC to g m^{-3} . Also, the use of unit m^{-1} gives wrong impression as it means $(\text{m})^{-1}$, if written in this way. I would urge the authors to use Mm^{-1} instead.

We agree.