Review R3

The article compares the mass concentration of the mini-CAST soot generator based on an experiment that evaluates both online and offline measurement methods. The primary motivation for the study appears to be the determination of correction calibration parameters for mass calibration of the PPS instrument, which is based on aerosol active surface area.

Although the experiments were conducted with technical accuracy, I believe the experimental design should have been more robust. In addition, the conclusions drawn are **overly general and simplistic**. Therefore, **I do not recommend that this manuscript be accepted for publication** in Atmospheric Research.

Below, I outline several points that do not meet the standards of a research article and should instead be considered for publication as a technical report in a more appropriate journal once the following revisions are implemented.

1. Experimental setup, heated sampling line, and mass of PM from OC/EC analysis:

The experimental setup, as described in the text, states: "This setup includes the soot generation source, the mini-CAST, followed by two heated lines maintained at 180 °C. One line is used for filter sampling, while the other feeds a dilution system that distributes the diluted and cooled aerosol to various measurement instruments: the TEOM, PPS, MA300, and SMPS." However, the schematic only shows a heated line leading toward the offline sampling system. This raises an immediate questions: **Was the heated line actually used in both branches (online and offline), or only in the offline branch? Why was a heated line used at all, given that it can significantly alter the chemical and physical properties of aerosols**?

Indeed, this is an important point, and the aim of this experiment was to test the filter sampling procedure that is applied in direct exhaust measurements, particularly for ship engines, where there is distance between the sampling probe and the collection filter holder. We need a flexible connection (as short as possible, and with a length of here of 1m) to open the holder and change filters. It must be heated to avoid condensation. In such exhaust measurements where temperatures are over 200 °C depending on the sampling location, the main issue is to avoid condensation of moisture and semi-volatile species. The procedure follows ISO 8178, which specifies a target temperature of 180 °C for the sampling line and a maximum residence time of 3 seconds.

For comparison, if the OC/EC analysis followed the IMPROVE protocol—where the OC1 fraction is defined at 140 °C—this fraction would be entirely lost within a 180 °C heated line. Furthermore, heating the sampled air can lead to misinterpretation of pyrolyzed carbon (PC) in thermal-optical OC/EC analysis, as the initial reflectance from the filter may already include pyrolyzed material, resulting in an overestimation of elemental carbon (EC).

If one sampling branch was heated and the other was not, this introduces a fundamental inconsistency that compromises the comparability of the results.

With a sampling flow rate of 7.7 L/min, a line length of 1 m, and an inner diameter of 6 mm, the aerosol residence time is approximately 0.22 s. This duration is extremely short compared to the 173 s of the first temperature plateau at 140 °C on the thermogram shown below, which is required to vaporize only 1.3% of the total carbon mass.
In the revised presentation of the results from this study, the TEOM measurement is considered the reference. All measurements are performed downstream of the dilution system (TEOM, SMPS, PPS, MA300), except for the gravimetric measurement, whose results are validated by comparison with the TEOM measurements, as discussed later in the article.

Additionally, the authors should provide a more detailed explanation of how they calculated mass concentration based on OC/EC analysis. Assuming that the total aerosol mass (PM) is equivalent to the mass of carbonaceous aerosols (CA), the following equation applies:

$$PM=CA= OA+EC= TC\cdot(OA/OC)-EC\cdot(OA/OC-1)$$

where:

$$OC = OC1 + OC2 + OC3 + OC4 + PC$$

$$EC = EC1 + EC2 + EC3 - PC$$

OA/OC is the organic aerosol to organic carbon ratio, which can be obtained either through complementary measurements (e.g., ACSM for OA, OC/EC analysis for OC) or sourced from literature.

This work is carried out within a context of mass concentration measurement in field measurement campaign, evaluated in laboratory conditions. The ACSM is designated for long-term monitoring to study the temporal changes and variability of OA sources. In our case, we used a mini-cast generator to generate carbonaceous soot particles, and the chemical composition was not a point we tried to investigate, knowing that an ACSM could be difficult to implement on future field campaigns. We sampled soot on a filter and analyzed it with the Sunset Laboratory Analyzer. We did not make any real-time measurements.

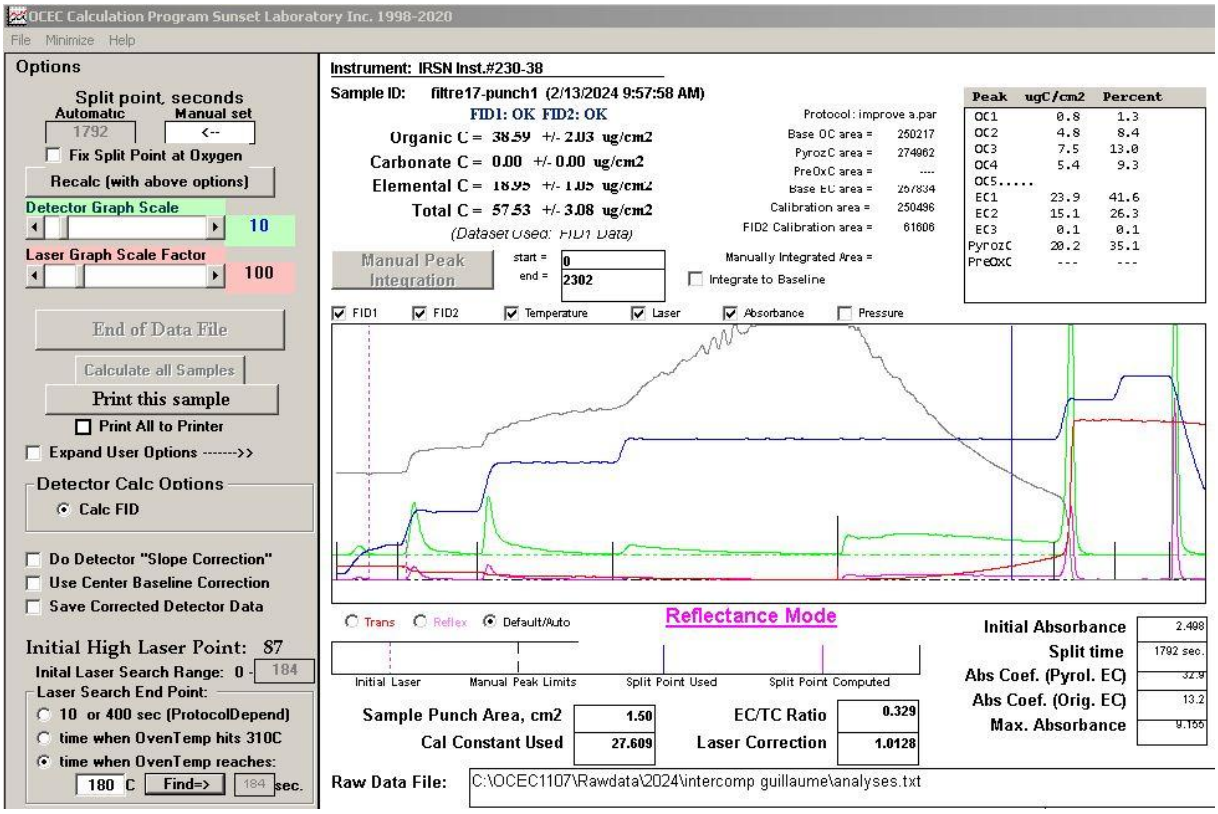
What OA/OC ratio was used in the mass estimation?

We estimated only the OC/TC using the Sunset Semi-Continuous Organic Carbon/Elemental Carbon (Sunset OC/EC) aerosol analyzer that utilizes the modified National Institute for Occupational Safety and Health thermo-optical method to determine total carbon (TC), organic carbon (OC), and elemental carbon (EC) at near real-time.

Was this ratio measured directly or adopted from previous studies? How do the authors justify the use of a heated line, and how do they address the uncertainties associated with the loss of the OC1 fraction and the potential misclassification of pyrolyzed carbon in thermal-optical analysis?

As mentioned above, the residence time in this short, heated line is no more than 0.22s in the condition of the experiment. In addition, we observed that the volatilization time at this temperature of 180°C is 184s, for a total vaporization of 0.8 µg/cm^2 over a total TC of 57.53 µg/cm^2 that represent 1.3% of the total mass, and 2% of the organic fraction OC.

With a residence time of 0.22s, the corresponding vaporized fraction would be around 0.002 %.



2. Experimental Design and Showing Method Equivalence

In demonstrating the suitability of using the PPS, two critical steps are missing. The reader is concerned by the simultaneous variation of **two parameters at the aerosol source—namely, the mass concentration and the aerosol composition as a function of the oxidation flow rate in the miniCAST**. This affects the OC/TC ratio

and introduces uncertainty. Additionally, there is a lack of evidence demonstrating the equivalence between the **reference gravimetric method and the TEOM online method**.

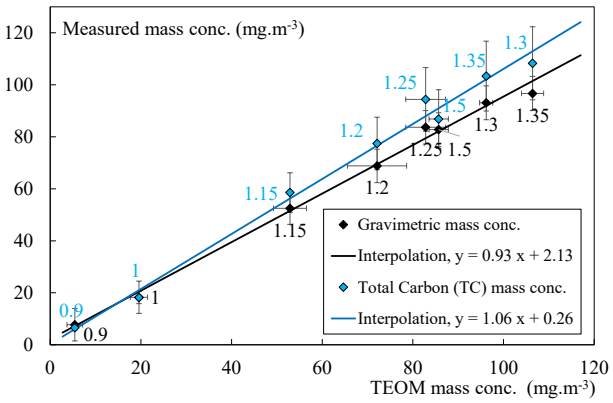
As a result, the reader cannot apply the calibration factors for the PPS in their own experiment, since two parameters are being altered simultaneously. Therefore, the experiment should be redesigned so that, for a fixed OC/TC ratio at the source, only the mass concentration is varied. This would allow for the determination of calibration factors under controlled conditions. This procedure should be repeated for multiple OC/TC ratios. Only in this way can the reader reliably apply the calibration factors in their experimental setup.

Thank you for your suggestion. In this paper we varied the oxidation air flow rate, which is the main operating parameters of the miniCAST that is found to be changed in most available studies using this generator. Changing this parameter indeed leads to the variation of two parameters at the same time, namely the OC/TC ratio and the mass concentration. As suggested, using a pure dilution of the generated soot on single miniCAST generation points would have been relevant to study the mass concentration linearity response of instrument. In another hand, changing the OC/TC ratio was interesting to study the aethalometer MA300 response. This discussion is interesting for future study. We added this suggestion to the work perspectives and as a discussion point on the present study, in conclusion:

"The results of this study show that the selected operating points led to simultaneous variations in mass concentration, size distribution, and OC/EC ratio. It would be relevant, by varying other gas flow rates of the miniCAST or the aerosol dilution conditions, to better decouple the parameters under investigation in future studies."

Furthermore, prior to this, the equivalence between the TEOM and the offline gravimetric method for measuring mass concentration should be demonstrated. Establishing this equivalence would validate the TEOM as a reference method against which all other measurements (SMPS, MA300, PPS) can be compared. It would also confirm the correct operation of the diluter and eliminate concerns regarding potential heating effects in the sampling line. For the comparison between the offline gravimetric method and the TEOM, authors should apply, for example, equivalence assessment tools as outlined in the European standard EN 16450:2017, which specifies requirements for automated measuring systems for particulate matter, including slope and offset of the orthogonal regression assessment. Only after establishing this equivalence can the results from SMPS, MA300, and PPS be interpreted with confidence and used to draw scientifically robust conclusions.

Thank you for this detailed and precise review of our submission. We provide responses to the various questions and comments below: we have considered your comment and based on ISO 16450 we have evaluated the slope and offset of the orthogonal assessment. The linear regression established between the reference and tested measurements satisfies the ISO 16450 validation criteria, with the slope b statistically compatible with unity ($|b - 1| < 2u_b$), and the intercept a close to zero and statistically compatible with it ($|a| < 2u_a$), where u_b and u_a are the standard uncertainties associated with the slope and intercept, respectively. So, we have established the equivalence between the TEOM and the gravimetric measurement. Finally, we concluded that the TEOM should be considered as the reference measurement, being online in the exact same conditions downstream the dilution system.



3. Lack of critical evaluation in the interpretation of filter photometer measurement results

The comparison of mass concentration measurements based on attenuation using the MA300 filter photometer is overly superficial. When using filter photometers with laboratory-generated aerosols, it is essential to carefully consider filter loading corrections, and the C parameter (multiple scattering correction factor), which depends not only on the properties of the filter substrate but also on the optical characteristics of the aerosol.

Indeed, these parameters were not sufficiently detailed in the originally submitted version, where we moved rather directly to the results. We propose to enrich the revised submission by specifying several factors, including some of those you requested. As suggested, we will also expand the discussion regarding filter loading and the associated correction factors, which we may have addressed too briefly.

In the newly submitted version of the paper:

"The MA300 aethalometer (AethLabs, San Francisco) is a real time portable analyzer that uses the filter-based light absorption principle: the mass concentration measurement is based on the optical attenuation ATN of a light beam passing through a cake of particles collected on a filtering fiber tape. The instrument has five analytical channels that operate at different wavelengths (375, 470, 528, 625 and 880 nm), and the measurement of absorption at 880 nm is interpreted as Black Carbon (Hansen et al., 1984). The MA300 draws a controlled flow through the collection spot on the filter tape, and when the light attenuation reaches a threshold value, the tape advances automatically.

The attenuation ATN is defined (Gundel et al., 1984) as $ATN = -100 * \ln(I/I0)$, with I and I0 respectively the measured intensity trough the loaded spot signal and the reference signal, through the empty filter (see Fig. 3). The instrument measures the transmission of light through the particle-loaded filter, from which the attenuation (ATN) is derived based on its rate of change over time. This attenuation is then converted into an absorption coefficient. Finally, the equivalent black carbon mass concentration is obtained by dividing the absorption coefficient by the mass absorption cross-section specific to black carbon (Drinovec et al., 2015). With this definition and for the 880 nm wavelength, the deposited Black Carbon BC mass concentration is then evaluated as:

$$BC = \frac{S \cdot (\Delta ATN/100)}{F(1-\xi) \cdot \sigma \cdot C \cdot (1-k \cdot ATN) \cdot \Delta t} \qquad (1)$$

Where S is the collection spot area (for the MA300, S=0.0707 cm2) , DATN the changes of attenuation during interval Dt, F the measured flow rate, and Dt the time interval between two measurements (Dt was 5 sec. in this study).

Since the airflow is measured downstream of the filter, it is necessary to account for lateral air leakage within the filter matrix beneath the optical chamber, represented by the parameter ζ, the leakage factor. The value of ζ is determined by comparing the inlet and outlet flows and is calibrated by the aethalometer manufacturer. Drinovec et al. reported values of ζ ranging from 2% to 7% (Drinovec et al., 2015). In Equ. (1), the σ (m2/g) and C are the mass absorption cross-section and multiple scattering coefficient factor (Weingartner et al., 2003). Filter-based light absorption techniques are subject to measurement artifacts due to scattering on the filter (Weingartner et al., 2003). These empirical parameters are related to the instrument design and filter material (Wu et al., 2024). The C parameter considers multiple scattering correction factor, which mainly depends on the properties of the filter substrate, and on the optical characteristics of the aerosol deposited on the filter. According to Drinovec et al. (2015), C strongly depends on the filter material used. Indeed, the optical absorption of aerosols collected on a filter is affected by light scattering within the filter matrix, which is dependent on the filter material, but with no significant spectral dependence (Drinovec et al., 2015). The value of C is determined by comparing the results of different measurement methods in laboratories and in ambient observatories, and Drinovec et al. report values in a range of 1-1.36 (for tetrafluoroethylene TFE/Quartz with variable ratio) up to 2.14 (for Quartz filter). For our measurement instrument, the sampling filter tape is composed of PTFE (polytetrafluoroethylene), and the manufacturer calibrated value of C is 1.3. The MAC (Mass Absorption Cross-section) or Mass Absorption Coefficient is defined as σair = σATN / C, with σATN the Specific Attenuation Cross-section, dependent on the wavelengths λ (σATN =10.120 m2/g for IR at l=880 nm, up to σATN =24.069 for UV at l=375 nm).

One of the identified drawbacks of aethalometers is the overestimation of BC concentration on a new filter and the underestimation when the loading is high, with the most accurate concentrations being obtained on slightly loaded filters (Arnott et al., 2005; Collaud Coen et al., 2010). Several models have been proposed to consider this loading effect when processing aethalometers data, such as Weingartner et al. (2003) and Virkkula et al.

(2007) models, which have been most frequently used for loading effect compensation. Drinovec et al. (2015) developed a real-time method to compensate nonlinearity with high time resolution, by using a double collection on two spots in parallel at different flow rates. They introduced the new reference Aethalometer model AE33 (Drinovec et al., 2015). In this model, the k constant is real-time evaluated from the algorithm described in (Drinovec et al., 2015), for each wavelength, and this so-called "dual-spot technology" permits to eliminate the data artifact due to filter loading. AE33 is now considered one of the most popular instruments for the real-time measurements of aerosol BC. The aethalometer MA300 we used in this study is a portable version also using this patented "dual spot" technology that makes it possible to eliminate data distortions due to filter loading.

Aethalometers have been used to monitor black carbon concentrations in urban areas (Blanco-Donado et al., 2022), assess biomass burning contribution to emissions in urban areas (Favez et al., 2007), or to measure personal exposure in working environment (Gren et al., 2022). However, the ability of aethalometers to accurately quantify soot emissions remains an active research topic. The recent study by Aakko-Saksa et al. (Aakko-Saksa et al., 2022a) over a wide ship exhaust test matrix obtained with different fuels, engines, and emission control devices showed that measurement with an aethalometer could lead to overestimation of BC emissions."

These optical properties include aerosol coating effects, which may be transparent or light-absorbing, and cannot be adequately described by a simple OC-to-TC ratio, as suggested in the manuscript.

We are indeed aware of the effect described, and our intention is not to reduce the interpretation of results from this type of instrument to a single parameter. In the specific case of soot particles generated by propane combustion in the miniCAST burner, it is well established in the literature that the primary particle diameter, aggregate morphology, and the OC/TC ratio are the main descriptive parameters. However, in other studies involving post-generation treatments of particles (e.g., for coating formation, see Salo et al., 2024), the OC/TC ratio alone is indeed insufficient to fully characterize the aerosol.

Moreover, filter loading effects can differ between the two wavelengths used in the MA300. Therefore, the conclusion that one can simply select the wavelength that yields a result within ±10% of the gravimetric mass concentration is methodologically flawed and inappropriate for a journal such as Atmospheric Research.

The conclusion seems a little harsh to us; however, the initial point raised is indeed relevant and warrants further discussion. We will therefore expand upon this aspect of "filter loading effects" and the way it is addressed trough the "dual spot" approach, in the revised version of the manuscript. The aim is to provide a clearer justification of our scientific approach. Indeed, we do not assert a definitive conclusion regarding the selection of a single wavelength. The original objective was to evaluate to what extent the mass concentration estimated at 880 nm (typically associated with black carbon) can be considered representative of the total mass concentration of a carbonaceous aerosol, particularly in cases where the organic fraction varies significantly. We proposed a tentative quantitative threshold for this representativeness, but indeed this may be subject to further discussion.

The authors should provide a detailed description of the parameters used in their analysis, including the multiple scattering parameter, loading compensation parameter, and the mass absorption cross-section. Furthermore, a thorough comparison of different mass concentrations at a constant OC/TC ratio should be conducted and clearly presented.

We fully understand your request, although, for the sake of consistency with the presentation of other instruments, we had initially chosen not to include such a level of information. This additional data will be incorporated into the revised version of the manuscript. Concerning the recommendation to carry out variation of the mass concentrations at a constant OC/TC ratio, this involves changing the dilution factor for different OC/TC measurement points. So, we suggest proposing this direction in the study perspectives

Absorption at 880 nm can serve as a reliable indicator of black or elemental carbon mass across varying OC/TC ratios. In contrast, the signal in the UV range is expected to increase primarily due to enhanced scattering at higher OC/TC ratios.

This is indeed the conclusion we also arrived at, and we have attempted to go a step further by proposing a quantitative threshold, even though we acknowledge that the conclusion remains preliminary. In this study, we do have an objective measurement of the OC/TC ratio based on filter sampling and thermo-optical analysis; however, we do not currently have a methodology to quantify the organic fraction directly from the UV signal of the aethalometer. Thank you once again for providing a detailed review.