Response to comments of anonymous referees # 2

"Physical and chemical properties of black carbon and organic matter from different sources using aerodynamic aerosol classification" by Dawei Hu et al. describes a comprehensive set of measurements from a well-designed and rather clever set of experiments. I believe the measurements are important for the community (especially the BC morphology results) and I look forward to the subsequent paper on optical properties.

We thank the reviewer for the positive comments on our manuscript

However, the manuscript is in need of some attention to detail, and in some cases, significant revisions and potential re-analysis of data. I believe this manuscript will be suitable for publication in ACP after these questions and comments are addressed.

In the revised version, we have addressed the comments listed below.

Major Questions and Comments

Given the scope of the manuscript, the title does not adequately capture the science and I believe a more focused title will help steer readers towards this work when conducting literature searches. With the current title, I would believe that the authors aerosolized a variety of substances and passed them through an AAC, when in reality, the work is geared towards important combustion aerosols and a variety of instrumentation. Consider revising the title to reflect that.

We thank the reviewer to point this out.

The title is modified to: "Physical and chemical properties of black carbon and organic matter from different combustion and photochemical sources using aerodynamic aerosol classification"

Lines 29-31 of the abstract say "Here we present insights into the physical and chemical properties of the aerosols, with optical properties being presented in subsequent publications" and lines 131-132 of the introduction say "The characterisation and parameterisation of the optical properties of the particles will be the subject of a future publication" yet the introduction seems almost entirely focused on refractive index retrievals. It isn't until line 108 that the authors begin to make the case for morphology and mixing state as a prerequisite for understanding RI. If the optical properties are the subject of a future publication, then the bulk of this introduction belongs in whatever forthcoming paper the authors are preparing, not here. I suggest re-writing the introduction to focus on the literature surrounding the physical and chemical properties that form the basis for the results presented in this manuscript.

We thank the reviewer to point this out.

The introduction is rephrased in the revised manuscript (line 63-161 on page 3-7). More discussions regarding the physical properties of particles are added in line 80-108 on page 4 and 5.

"Although BC and BrC are very important for climate, they are poorly represented in atmospheric models (Zuidema et al., 2016). This is in part due to the complex microphysical properties of BC and the lack of accurate refractive index (RI) descriptions for both BC and BrC (Liu et al., 2020). Fresh soot particles often exist in the form of aggregates composed of primary spherules with an irregular and highly fractal geometry (Xiong and Friedlander, 2001;Wentzel et al., 2003). The morphology of these aggregates change markedly during the atmospheric aging process, influencing the corresponding particle size and optical properties (Zeng et al., 2019;Zhang et al., 2008). For example, after condensation of gaseous species such as sulfuric acid or water (under high relative humidity (RH) environments) on soot particles, or coagulation with the pre-existing particles, soot particles can experience restructuring and the shape of the soot particles becomes more similar to a spherical particle (Zhang et al., 2008). The morphology of BC particles can be measured directly by using Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) (Fu et al., 2006;Chen et al., 2018;Ellis et al., 2016). However, the SEM/TEM approach only provides particle shape information in two dimensions and do not provide real time characterisation. Alternatively, the particle morphology can be determined by measuring its size and mass with different techniques (Chen et al., 2018;DeCarlo et al., 2004). A conventional approach is to classify particles (generally using a differential mobility analyser, DMA, to select monodisperse particles on their mobility size) and then measure particle mass using a particle mass analyser (Zhang et al., 2008;Park et al., 2003;Park et al., 2004a;Park et al., 2004b;Chen et al., 2018) (Wu et al., 2019). From the resulting information about particle mass for different particle mobility sizes, the dynamic shape factor (χ, defined as the ratio of the drag force on the particle divided by the drag force on the particle's volume equivalent sphere) and fractal dimensions (D_f) can be retrieved (DeCarlo et al., 2004). Mobility-mass fractal dimension (D_{fm}) has been reported over a wide range of 2.2-2.8 for diesel exhaust particles (Park et al., 2004b). D_{fm} has been reported as higher than the $D_{f,}$ - defined as the scaling exponents between the radius of gyration of an aggregate and the radius of primary spherules composing the aggregate - but the two are not always directly equivalent, particularly in the transition regime (Sorensen, 2011)."

The authors claim that their experimental setup enables them to derive refractive index with "much lower uncertainty than has been achieved previously." How is this quantified? How does this particular experimental setup achieve this? What is the current state-of-the-art in RI uncertainty? Finally, how can any statement of this nature be made when this manuscript does not report measurement uncertainties?

We thank the reviewer to point this out.

Yes, we agree with the reviewer that without providing the refractive index data and measurement uncertainties, we cannot state that "much lower uncertainty than has been achieved previously". We used the AAC instead of the DMA to select particles prior to optical measurement, which avoids the multiple charge issue and thus reducing the uncertainty in the RI derivation.

Thus, in the revised introduction, the statement "thus enabling optical properties – in particular refractive index – to be determined with much lower uncertainty than has been achieved previously" is removed.

In addition, we modified this statement to: "Careful consideration of the impacts of multiply charged particles on subsequent RI derivations can go some way to reducing uncertainty in the resultant RI, but this nevertheless remains a significant contributor to uncertainty (Cotterell et al., 2020;Zarzana et al., 2014;Miles et al., 2011). Thus, the classification of particles without relying on electrical charge should reduce the uncertainty in refractive index retrievals from measured aerosol optical properties. Important additional considerations in the retrieval of refractive indices from optical spectroscopy data are the aerosol morphology (described above) and mixing state. The mixing state can be probed using the Single Particle Soot Photometer (SP2), which can measure the refractory BC (rBC) mass content and optical size of individual particles. However the SP2 needs an empirical calibration to retrieve the rBC mass from the incandescence signal (Laborde et al., 2012a). The conventional method to calibrate the incandescence channel of SP2 is using size selected Aquadag standards (Acheson Inc. USA) and then correcting to a calibration representative of ambient rBC by a constant factor of 0.75 (Laborde et al., 2012b). However, few experiments since have independently verified this across various soot types."

Line 118-132 on page 5 and 6.

The SP2 has been thoroughly described in the literature. Is all of section 2.1.3 necessary? At this stage in the maturation of the SP2, I believe it is more constructive to discuss the artifacts and other measurement caveats of the SP2, for example, Sedlacek et al. (2018). How were these charring artifacts handled in data analysis analysis?

We thank the reviewer to point this out.

The sentence of "The SP2 consists of an intense intra-cavity laser operating at a wavelength of 1064 nm and four optical detectors. Particles were drawn into the measurement chamber through a capillary, restricted with a particle free sheath flow and focused into a jet. The particle jet passed through the center of an intra-cavity laser beam operating at 1064 nm." is removed in the revised manuscript.

The sentence is modified to: "The refractory black carbon (rBC) mass concentration was measured by a SP2 (Droplet Measurement Technologies, Colorado, USA). The SP2 uses the laser-induced incandescence to measure the rBC mass and optical size of individual BC particles with an intra cavity Nd:YAG laser operating at 1064 nm."

Line 226-229 on page 10.

More discussion regarding the artifacts of the SP2 is added in the revised manuscript.

"For those particles which contain absorbing materials such as the refractory BC, they will absorb 1064 nm light and then heat up and emit visible thermal radiation (incandesce). This incandescence signal is directly proportional to the mass of rBC as determined by a calibration (Liu et al., 2010) with generated BC aerosols of known or independently-measured mass. In the atmosphere, besides BC, other materials (e.g., some metals and minerals) can incandesce at 1064 nm as well. However, as boiling point temperatures of these materials are rather different to that of black carbon, it is easy to distinguish them in measurements made using the SP2 equipped with an additional narrowband incandescence detector, such as the one used here (Liu et al., 2018). Recently, Sedlacek et al. (2018) demonstrated that charring of light-absorbing organic particles at 1064 nm can produce the refractory black carbon and then overestimate the rBC mass concentration, however this does not affect pure BC particles and we saw no evidence for an incandescence signal associated with the pure organic particles measured in this study. We investigated the effectiveness of this calibration from different types of BC particles in this study and report the outcomes of these investigations in Sect. 3.3."

Line 238-252 on Page 10 and 11.

The SMPS has an even longer history of prior publication. Section 2.1.6 can be significantly shortened to include only the operational parameters such as scan time and flow rates, and the resulting bounds of the size distribution you are able to measure. Once this has been described, the manuscript would benefit from a discussion on the uncertainties introduced by the SMPS. Finally, please describe the inversion algorithm used. Is it the typical inversion algorithm that comes with the SMPS software, or is it custom? If it is custom, it should be discussed and cited.

The section 2.1.6 is modified to simply state: "Aerosol size distributions in the diameter range from 14.9 to 673.2 nm were measured by a commercial SMPS (TSI, USA, employing a model 3082 classifier unit, 3081 DMA and 3786 CPC) with sheath and sample flow rates of 3 L min^{-1} and 0.3 L min^{-1}, respectively. The DMA was operated in scanning mode with a scan time of 60 s and a retrace time of 4 s. The particle size distribution was corrected for multiple charge effects and diffusion loss using the standard inversion algorithm in the SMPS software (AIM version 10). Before the experiment, the SMPS was calibrated using NIST certified polystyrene latex spheres (PSLs, Thermo Fisher Inc.)."

Line 276-283 on Page 12.

Why was 180 °C chosen for the thermal denuder? The optimal internal temperature for a thermal denuder is the subject of ongoing research, yet the consensus is that it must be chosen based on some optimization of experimental parameters. In this case, I would guess that this optimization corresponds to complete volatilization of coating materials so that BC alone can be studied. However, it is never explicitly stated what the reasons are for choosing 180 °C, nor is the method by which the authors arrived at this temperature. For example, Sumlin et al. (2018) describes an approach using four different TD temperatures in an attempt to volatilize different mass fractions of organic matter. Please discuss the approach to choosing 180 °C.

For the purpose of this study, we wanted to remove as much of the organic coating material from the combustion-generated particles as possible and 180 °C is the maximum temperature for our self-built thermal denuder.

The following sentence is added for further clarification.

"In this study, the purpose of the TD is to remove as much of the organic coatings from the combustion-generated particles as possible, rather than probing the volatility properties of the coating. Therefore, all heating zones of the TD were set to their maximum temperature of 180 °C. This upper temperature is lower than that achieved by other commercial TD units and minimises the risks of charring."

Line 304-309 on page 13.

Furthermore on the subject of the TD, the authors state that the inner diameter of the heating zone is 0.15 meters. This is rather large, and it is almost certain that there is a temperature gradient across the radius. The temperature along the central axis may be several degrees colder than at the walls, and aerosol travelling at different points along the radius will experience varying degrees of thermal processing. Was this temperature gradient measured? How does this gradient affect the analysis?

We agree that there is a temperature gradient across the radius of the heating zone in the thermal denuder. The temperature reported here is that at the axial centre of the thermal denuder's heating zone. We calibrated the TD by measuring the temperature at the point of the central line before the experiment. We did not measure the temperature gradient across the radius in this study.

As the purpose of using TD in this study is remove coatings of coated BC particles rather than investigate the volatility of the particles, the temperature gradient would not influence on our results here.

The following sentence is added for further clarification:

"The TD was given 30 mins for its temperature to stabilize before sampling. The temperature of the TD was calibrated by measuring the temperature at the axial centre of the denuder's heating zone. In this study, the purpose of the TD is to remove as much of the organic coatings from the combustion-generated particles as possible, rather than probing the volatility properties of the coating. Therefore, all heating zones of the TD were set to their maximum temperature of 180 °C. This upper temperature is lower than that achieved by other commercial TD units and minimises the risks of charring."

Line 302-309 on page 13.

Finally, on the subject of the TD, the authors state that the residence time in the heating section was approximately 31 seconds. Given the measurements provided for both the inlet and outlet (0.037 m ID tube) and the heating section (0.15 m ID) it seems that the authors did not account for fluid velocity change within the heating section. If one considers only 1 liter min-1 flow through the 0.037 m ID tube, across the 0.51 m heating section (assuming steady and conservative flow), one arrives at 32.9 s, which is "approximately" 31 s as stated in the manuscript. However, that assumes that fluid velocity is constant throughout the TD – it is not, since the ID in the heating section is different than the inlet and outlet. The mean residence time in the heating section is likely somewhere on the order of nine minutes. Given this, and my previous comment, I am unsure that conclusions from the TD experiment are represented accurately. It is likely that this data can be re-processed, or at least re-interpreted, but the data may have been handled according to an incomplete understanding of the experimental setup. This must be corrected or addressed in the manuscript.

We thank the reviewer to point this out. However, to be absolutely clear, the exact function of the thermal denuder was simply to remove as much coating as possible such that changes in morphology changes after coating and/or humidification could be detected. Given a clear distinction in results could be seen between different experimental runs, the set-up used was evidently successful in this regard, and it is not clear to us how the data could be reprocessed or reinterpreted in light of a more accurate estimate of the residence time.

That said, we have reviewed the setup of the TD, and added the following sentences for further clarification:

“The temperature in the heating section (0.51 m × 0.15 m ID) was controlled by four PID controllers (Watlow EZ-ZONE) with additional temperature sensors on the outside of the tube. It is necessary to ensure flow through the TD whenever it is heated, even when bypassed to allow measurements of the unheated sample. A constant 2-2.5 L min^{-1} flow of the sample air through it. A vacuum line maintained 2.0-2.5 L min^{-1} through whichever of the bypass or TD line was not in use. The residence time of the air sample in the heating section was 216-270 s. The TD was given 30 mins for its temperature to stabilize before sampling. The temperature of the TD was calibrated by measuring the temperature at the axial centre of the denuder’s heating zone. In this study, the purpose of the TD is to remove as much of the organic coatings from the combustion-generated particles as possible, rather than probing the volatility properties of the coating. Therefore, all heating zones of the TD were set to their maximum temperature of 180 °C. This upper temperature is lower than that achieved by other commercial TD units and minimises the risks of charring.”

Line 296-309 on page 13.

It seems that all measurements are reported without uncertainties. The authors should report uncertainties or justify their exclusion.

The uncertainties were analysed and added in the Table 1, Figure 4 and Figure 7 in the revised manuscript.

Finally, please make sure all references are properly formatted and include DOI numbers, if possible.

The references are reformatted with DOI numbers included.

Minor questions and comments

The name “Manchester Aerosol Chamber” is unfortunate, since it shares an acronym (MAC) with a commonly studied aerosol optical parameter, the mass absorption cross-section. Unless this acronym has been used for your chamber multiple times in other publications, I would suggest you consider renaming it.

We have deleted the acronym (MAC) in the manuscript as we only used it once. The acronym (MAC) in the Fig. 1 is replaced by the “Manchester Aerosol Chamber”.

Several parts of the Experimental Methods section contain results, especially section 2.3.4. I suggest re-writing these sections to focus on the methods, and thoroughly discuss the results in section 3.

We have re-arranged the section 2.3 and moved the results in the section 3.

The headings for sections 2.1.1, 2.1.2, 2.1.3, 2.1.5 and 2.1.6 should be spelled out, for consistency with other 2.1.X section headings.

This is revised.

The description about the AAC in section 2.2.1 is overly subjective. Furthermore, the AAC only produces a monodisperse aerosol in the sense of aerodynamic diameter. This is not "truly" monodisperse, since there are other measures of aerosol diameter that run contrary to this qualifier.

The term "truly" is removed and the sentence for AAC description is revised to: "The AAC (Cambustion Ltd, Cambridge, UK) is used to select aerosols within a narrow range of aerodynamic diameters and does not suffer from the issue of multiple charges that affects selection using instruments such as the CPMA and DMA."

Line 180-182 on page 8.

Line 278: The authors may consider stating the material that the space blanket (mylar, I'm guessing) is made from so that readers unfamiliar with the term will know what was used.

Yes, the material is mylar. This information is added in the revised manuscript.

Line 281: How was the illumination evaluated?

The illumination on the chamber was evaluated using both spectral radiometry and steady-state actinometry experiments. Briefly, the ambient environment daytime solar spectrum was first measured by spectral radiometry. The photolysis rate of NO_2 (jNO_2) was estimated in steady-state actinometry used as a confirmation of the light intensity in the chamber (Hu et al., 2014) measured by direct spectral radiometry. Such actinometric measurements were carried out by injecting ~ 70 ppb NO_2 into the chamber and irradiating for more than 3 hours, measuring the concentration of NO, NO_2 and O_3 continuously. The temperature and relative humidity was maintained at around 25°C and 50% respectively. More details can be found in section 3.3 in Shao et al. (2021). Fig. 4 in Shao et al. (2021) shows the total actinic flux measured in the Manchester Atmospheric Chamber (red line) multiplied by 3.5 compared with the Manchester midday clear sky measurements on a June day.

The reference of Shao et al. (2021) is cited in the revised manuscript.

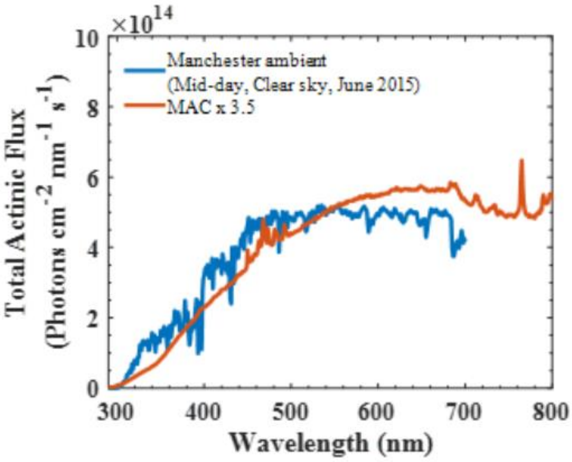

Figure 4: Total actinic flux spectrum in the MAC compared to the ambient light spectrum obtained in the city of Manchester (UK) mid-day with a clear sky in June 2015.

Reference:

Shao, Y., Wang, Y., Du, M., Voliotis, A., Alfarra, M. R., Turner, S. F., et al., 2021. Characterisation of the Manchester Aerosol Chamber facility. Atmos. Meas. Tech. Discuss. 2021, 1-50.

Line 357: Can the authors comment on what effect resin content might have on the resulting aerosols?

Many factors can influence the resulting aerosols, such as resin content, moisture content. In this study, we only focus on the influence of water content of wood samples on the physical and chemical properties of the particles from the wood combustion.

The following sentence is added in line 411-419 on page 18.

“Both Scots pine and Western red cedar are resin rich, while the Giant Redwood contains less resin, and the Poplar contains barely any resinous compounds. Hence, all should be capable of producing different volumes and types of aerosol particles. There are many factors that can influence composition and properties of generated aerosols during combustion, such as the wood resin content and moisture content, which would result in a highly extensive variable set. In the work presented here, we only focus on the influence of water content of wood samples on the physical and chemical properties of the particles from wood combustion. We assessed wood of two different fuel moistures: fully oven dried samples and moist samples with ~25% moisture content. ”

Line 366-367: How was the “sufficient concentration” to ignite the pyrolysate determined?

During the experiment, after the wood samples were placed under the radiant heat flux, a spark igniter was positioned in the released stream of the pyrolysate to attempt to ignite the wood samples. Immediately following the initial placement of the wood sample under the radiant heat source, pyrolysate is continuously released. “Sufficient concentration” refers to the pyrolysate concentration that is high enough to enable ignition of the wood sample. We have no metric to quantify this pyrolysate concentration.

The following sentence is added in line 423-430 on page 18 and 19 for further clarification:

“A continuously operated spark igniter that was positioned in the released stream of pyrolysate acted as a source of ignition. Immediately following the initial placement of the wood sample under the radiant heat source, pyrolysate was continuously released and the pyrolysate concentration immediately above the wood sample and in the vicinity of the spark igniter increased also. The sample ignited once this pyrolysate reached sufficient concentrations and was well mixed with the surrounding air, at which point the igniter was switched off and removed from the air flow.”

Line 380: Change “exemplar” to “example”.

This is revised.

Line 404: Change “300 s of the ignition” to “300 s after the ignition.”

This is revised.

Line 430: I suggest specifying the NO_2 came from a “compressed gas cylinder”. Also, what was the concentration of NO_2, and what was the balance gas?

The sentence is modified to: “During the experiment, NO_2 (10% v/v, with a balance gas of high purity N_2 (BOC, UK)) was injected directly into the bag from a custom-made gas cylinder via stainless steel tubing, and its concentration was measured using a chemi-luminescence gas analyzer (Model 42i, Thermo Scientific, MA, USA).”

Line 459-462 on page 20.

Line 432: Change “desirable” to “desired”.

This is revised.

Lines 451-454: I suspect that the increase in ozone concentration is attributed to the absorption of UV photons by O_2 in the chamber – this is a common method to produce O_3 from O_2. I cannot find any references in the literature on O3 production due to UV absorption by cresol. If the authors can provide a reference for O_3 production by cresol photochemistry, please do so.

As shown in Fig. 3, the increase of ozone concentration occurs only after the injection of the VOC (cresol). At the instance of cresol injection, the lights are off. Therefore, the abrupt increase in ozone concentration detected by the ozone monitor around the time of VOC injection is not caused by photochemistry. The signal detected by the O_3 monitor may be due to cresol absorbing light at the wavelength it uses.

Line 464: Change “desirable” to “desired”. What was the desired concentration?

This is revised.

Line 470: “particulate” is an adjective. Change to “particles”.

This is revised.

Line 471-472: What size did the particles stabilize to?

This information is added in the revised manuscript.

"After the condensed organics equilibrate with the surrounding VOCs and the particles stabilised at a certain size (295 nm in aerodynamic size), the aerodynamic particle size distribution of the dried organic coated BC particles, and that of the dried organic coated BC particles experienced the humidity cycling, was measured by AAC. Hereafter, a thermal denuder operated at 180 °C was added, and the organic coatings of the coated BC particles, that had either experienced the humidity cycling process or not, were removed by the TD, and then the size distribution of the BC core was measured by the AAC and SMPS."

Line 488-495 on page 21.

The caption on Figure 1 refers readers to the main text to thoroughly understand what is meant by the different groupings of instruments, however, the first reference to the figure in section 2 does not clarify the groupings whatsoever. The figure is therefore unclear: were different groupings of instruments used during different experiments? Were they grouped in this way during data analysis to calculate specific parameters? This needs to be clarified both in the figure and its caption, and in the main text.

In this study, we use the different groupings of instruments to achieve different target. This information is added in the main text, the caption in the Figure 1.

The following sentences are added in the line 170-177 on page 8.

"The right panel in Fig. 1 shows the various instrument configurations used in this study to target different measurements: Instrument set (1) was used for measurements of aerosol optical properties (and thereby enable the retrieval of refractive index for BC/BrC aerosols, subject of a future publication) and organic chemical measurement for wood combustion (setup (a)) and chamber (setup (c)) experiments. Instrument set (2) was used for dynamic shape factor measurements for BC and material density measurement for organic aerosols (setup (a) and (b)). Instrument set (3) was used for SP2 incandescence signal calibration (setup (b)). Instruments set (4) was used for BC restructuring experiments (setup (c))."

The caption in Figure 1 is modified to:

"**Fig. 1.** Schematic diagram of the experimental configuration for: (a) Wood combustion; (b) SP2 incandesces signal calibration and BC morphology investigation; (c) Brown carbon formation and restructuring of BC. The combinations of instruments described in (1), (2), (3) and (4) represent different measurement configurations used to enable characterisation of specific aerosol physiochemical parameters, as described in the main text. The instrument set (1) was used for measurements of aerosol optical properties (and thereby enable the retrieval of refractive index for BC/BrC aerosols, subject of a future publication) and organic chemical measurement for wood combustion (setup (a)) and chamber (setup (c)) experiments; instrument set (2) was used for dynamic shape factor measurements for BC and material density measurement for organic aerosols (setup (a) and (b)); the instrument set (3) was used for SP2 incandescence signal calibration (setup (b)); the instruments set (4) was used for BC restructuring experiments (setup (c))."

References

Sedlacek et al., Formation of refractory black carbon by SP2-induced charring of organic aerosol, Aerosol Sci. & Tech, 52:12, 1345-1350, 10.1080/02786826.2018.1531107, 2018.

Sumlin et al., Density and Homogeneous Internal Composition of Primary Brown Carbon Aerosol, Environ. Sci. Technol. 2018, 52, 7, 3982-3989, 10.1021/acs.est.8b00093, 2018.