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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Size-selected black carbon mass distributions and mixing state in polluted and clean environments of northern India" *by* Tomi Raatikainen et al.

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We would like to thank Referee #3 for the constructive comments. The comments below are shown with italicized font and our replies with the upright font. The changes to the manuscript and Supplementary Material are given as a supplement with replies to Referee #1.

The manuscript presents measurements of refractory black carbon measurements collected at two sites in northern India using a relatively new approach featuring a singleparticle BC instrument. By placing an SP2 downstream of a DMA the authors were able to examine relationships between mobility diameter and SP2 data prod-

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ucts, such as refractory BC mass, non-rBC containing particle optical size, and derived rBC-containing particle size. Based on the measurement location and types of measurements conducted the manuscript has the potential to be a significant contribution, however requires substantial revision before I can recommend it for publication in ACP.

General Comments

The main weakness of the current manuscript is the inconsistent, incomplete and at times confusing treatment of the main, unique data product of the DMA-SP2 combination, the relationship between rBC and total particle "diameters". It is very important to highlight and appropriately account for the difference in the mobility diameter selected by the DMA, which depends on particle shape and physical size, and the mass of refractory material measured by the SP2. For a given selected mobility diameter rBC mass will depend on whether the particle is mixed with other materials and the effective density or shape of the rBC particle. At times the analysis assumes particles are spherical in order to compare rBC volume and total particle volume, but in other places the manuscript specifically states the particles are non-spherical aggregates. I think there is additional information (SP2 data products, ambient conditions) available to better identify situations where it is "safer" to treat the data in one extreme or the other (e.g., highly aged/spherical versus fresh/fractal). Reviewer #2 makes a number of very insightful comments regarding this aspect of the analysis, so I will not repeat many of her or his points here, however I would like to stress that this area of the analysis should be revisited, with particular attention paid to how uncertainties in the particle shape vs mixing affect the major conclusions of the paper.

We have clarified the text so that we no longer assume any particle shape, but rely on the measured parameters (other replies below).

There are many locations in the manuscript where the authors could be more specific without forcing the reader to consult tables and/or supplementary material. The methods section, not supplementary material, should give important details such as

the scan time being 30 minutes or that the sample was dried (to what RH?). Was an impactor used upstream of the DMA to remove larger particles that would affect the inversion? In addition, it would be stronger if more specific numbers were used rather than more general terms like more, less, or different.

Those details (scan time, RH and impactor) are now given in the methods section. Terms more, less and different have been replaced by numbers when possible.

Specific comments (page-line)

1-18: I recommend the authors use a different term here than elemental carbon, which to most readers will be interpreted as the operationally defined measurement, when I think they simply mean to say that the BC particles are initially externally mixed and "pure BC" for lack of a better term.

Elemental changed to pure (black carbon).

2-2: I suggest a slight re-phrasing, since being a CCN is not necessarily a requirement for cloud processing (e.g., collision processes)

Cloud processing part is now removed.

2-10: "from" to "for"?

Done.

2-29: Avoid use of "truly", because "size" is not a well-defined term (diameter, equivalent diameter, mass, surface area?). Better to say "mobility diameter" as that is the property relevant to the DMA used here.

Done.

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3-26: Suggest very briefly stating what is involved in the inversion without going into details placed in supplementary information to give reader a sense of what is being done here. For example, "Number concentrations measured by the SP2 were converted to rBC number distributions by accounting for charged particle fractions and the DMA transfer function using standard DMPS inversion methods (see Supplementary Material)". Note the inversion does matter for reporting averages like number fraction or volume fraction if they include all particles and not just those identified as +1 charged.

This section is now updated so that more details are given about the inversion method. Average number fraction and volume fraction meant bin averages (bin averages independent of the inversion), and not averages over mobility sizes (number-weighted average would depend on the inversion).

3-29: The manuscript should also cite our original HTDMA-SP2 methods paper here (McMeeking et al., 2011). I also recommend the authors mention other work where the SP2 has been placed behind different types of classifiers, such as the APM and/or CPMA, such as Ohata et al. (2016).

These papers are now cited.

4-1/3: Another important thing to note here is higher output concentrations going through only one DMA instead of the two used in the VTDMA and HTDMA studies, allowing for improved counting statistics and faster scan times.

The SP2 in the VTDMA study is actually measuring from the output of the first DMA, which means that they have equally good counting statistics with our method.

4-23: Please clarify: I think the authors are referring to the SP2 size resolution? They should also mention a range of output sizes would be expected due to the DMA transfer function and that would have to be accounted for. It would also be useful to cite an

example from literature supporting the claim that most assume a narrow distribution of rBC core sizes...I'm not sure this is really the case.

We have clarified the text so that the size resolution refers to the DMA. Width of the DMA transfer function is now given (FWHM about 45 nm for the 360 nm mobility size bin). The text about the assumed rBC core size distribution has been reformulated.

Section 3.1 – it would be useful to have the average BC concentrations at each site given here, along with variability metric. Also better to state which of the sites was higher than saying there was a difference between them. Finally the measurements were performed at different times, so it would be helpful to know if there is any general trend in concentrations during the region over this time using the Aethalometer data.

Average rBC concentrations and their variabilities are now given, and the location of the sites are now clarified. Unfortunately, we don't have Aethalometer data from Gual Pahari. Since our previous studies have shown that the sites have different annual cycles, Mukteshwar data should not be used alone. At least current measurements seem to be dominated by rapid variations rather than long term trends.

5-7: I found this confusing. What is really meant by "homogenous" here...the authors mention multiple times in the paper that BC has different mixing states and morphologies, which could both affect the rBC vs DMA size relationship. Please elaborate.

This bad example is now removed (better example given at the beginning of the results section) and we focus on describing Fig. 3.

5-18: It might be possible to determine whether the larger particles are indeed multiply charged particles based on the rough sizing metrics available from the SP2 itself (and could be further checked against known charging fractions).

Our aim was to say that larger particles have negligible contribution to the mobility size

bin mean values used in further calculations. For this it is irrelevant if these larger particles were multiply charged (they were) or pure compact rBC (such particles were not found as described in Sect 3.6).

7-3: "it is expected that particles are spherical" Can the authors support this statement? I'm not sure if they meant "assumed" instead of "expected", since they caveat the entire statement with "For simplicity, ..." Is this section exploring a hypothetical exploration of the data, or real? Unless there is any strong evidence that particles are spherical at these sites, especially the rBC particles, than suggest re-phrasing to "For simplicity, we treat particles as spherical...". See general comments above.

This section has been clarified. We are not expecting a particle shape, but report our directly measured parameters (e.g. rBC volume equivalent diameters and mobility diameters).

7-13: Sulfate is not really considered semi-volatile under typically atmospheric conditions... Further, primary semi-volatile organics would, if anything, evaporate as concentrations decrease away from the urban areas leading to increases in the rBC volume fraction, though this could be counter-acted by formation of additional secondary semi-volatiles. I think "secondary" would be more accurate.

Changed to "secondary".

7-21: Are these numbers for total particles or just for the selected mobility diameter. Is the comparison to the literature values cited just before this statement describing the same (e.g., all or size-selected)?

It is now clarified that this is for size-selected (360 nm) aerosol. Also, the different size ranges are now given.

7-23/24: Is there any evidence that BB is the dominant source? Biomass burning (de-

pending on type, fuel, efficiency) will also emit non-rBC containing particles. Could other sources still be important? These might emit higher number fractions of rBC-containing particles compared to biomass burning. Were there any patterns in week-day versus weekend traffic or activities in these regions that might affect the sources?

We don't have direct evidence of the dominant source, so now we now just mention regional BC emissions as an explanation for the high rBC particle number fraction. Our data set is too short for identifying weekday/weekend patterns (measurements took about six weeks in each location). Diurnal cycles are really the only patterns that we can see in our data.

8-15/16: I agree with the vertical mixing affecting aerosol concentrations, but don't see how dilution would affect the rBC number fraction, which would be independent of concentration, unless some aerosol micro-physical processes are going on. Is there evidence that the aerosol outside the nocturnal boundary layer has lower rBC number fractions and mixes into the surface layer?

rBC number fraction should decrease with altitude, because all major rBC sources are at the surface, but secondary organic aerosol formation can take place at any altitude.

8-21: It is not clear whether the authors are comparing the two sites here, or the periods when the Gual Pahari or polluted Indo-Gangetic plains particles affect the site to those when there is little impact?

We clarify that we are comparing the two sites (Gual Pahari and Mukteshwar).

9-3: Please be more specific about what is meant here by the phrase "current experiments"...is this recent work in the field or specific to the Indian measurements?

We clarify that these are the India measurements.

9-9/11: I think this particular section represents the general problems with how the treatment of the uncertainties in the different size classification methods affects the conclusions of the paper. How was the cutoff of the 10% difference determined to know a particle was non-spherical? Does it account for an expected range of rBC and nonrBC refractive indices, which will also affect the difference between optical and mobility diameters? The authors should also provide the uncertainty in the LEO method for their instrument based on a comparison of the full Gaussian scattering measurements and LEO results for non-rBC containing results to support criteria further.

The 10% limit was based on the SP2's sizing uncertainty, which is now clarified (also now giving a more conservative 20% limit). We have improved the description of the LEO results and included uncertainty analysis based on the range of refractive index values. LEO results are also compared with those without LEO for non-rBC particles.

9-31/10-20: Unless I have missed something I believe the analysis described here treats the rBC particles as purely rBC particles to calculate the mass fractal dimensions? This contradicts earlier discussions in the paper regarding volume fraction. It would be better to restrict the calculations to particles likely to have less other material (e.g., smaller LEO size, maximum rBC mass observed in each DMA mobility size). I don't see an easy way to distinguish the shape effect on DMA sizing from the effects of other materials mixed with the rBC if this is not done.

This part of the text has been removed.

Figure 4: Remove the spurious low point that is related to the gain-stage matching in the SP2. Better to show as a gap than as a non-realistic lower data point.

Done.

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