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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 #2 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.

It is very exciting to see SP2-measured rBC mass loadings and microphysical state information coming out of India. This important yet under-reported region is a critical piece in the "BC puzzle". Raatikainen et al,. present SP2 measurements of mobility-diameter selected aerosol, and have obtained data which, if appropriately quality-

assured, will be of high value and interest to the wider community.

The manuscript needs substantial improvement. Most significantly, the quality of the rBC data set should be more carefully assessed: a ∼20% bias to a CPC was corrected simply based on the assumption that the CPC was correct. Potentially larger biases than this exist in the data.

We have now confirmed that this 20% bias is systematic and related to this specific SP2. The counting was verified by our other SP2-D, which shows the same concentration as CPC used in Indian campaign and as other calibrated CPCs. The over counting is size independent; however, the reason for this over counting is still unknown.

Generally, the manuscript should be proof-read for grammar. Imprecise vocabulary (e.g. "absorbing particles" for rBC-containing particles) should be revised (there are many light-absorbing particles that may not contain rBC). Background information about the performance of the SP2 should be more clearly summarized in the main text. I also found it difficult to follow how the size-resolved results were combined to reflect the ambient aerosol condition. The results should be more thoughtfully presented (for example, the section about BC volume fractions based on the assumption that the total particle volume is proportional to mobility diameter cubed is followed by a section indicating the lack of value of that analysis after inspection of SP2 LEO fit results).

We have improved the text and clarified the vocabulary. We have also clarified our terminology regarding the results. For example, volume fractions are not used anymore.

Specific comments:

1) "Absorbing" and "refractory" are terms that apply to rBC, but not all light-absorbing or refractory particles are either rBC-containing, or detected via incandescence in the SP2. For example, only a small fraction of dust particles incandescence in the SP2,

although most of them are refractory. The paper should be made more precise by avoiding un-specific vocabulary. Two examples: 1) page 2 line 13 – the SP2 will not help determine a number fraction of light-absorbing particles; 2) page 3, line 19: the Sp2 does not measure all "refractory absorbing material".

We have clarified this so that term rBC-containing is now used to describe those particles that are detected by the incandescence signal.

2) Page 1 line 18: BC mixing state also depends on source.

This is now clarified.

3) Page 2 Line 11 and page 4, Line 17 and page 9 lines 5 - 11: The light-scattering for rBC-containing particles from the SP2 is a direct measurement (this is essentially a measurement of the particle optical size), and requires no assumptions about particle index of refraction or morphology. However, interpretation of the light scattering in terms of particle composition etc. does require assumptions.

It is true that light scattering is measured directly, but these three parts of the text refer to particle size, which require assumptions.

4) Methods:

a. Please specify if the aerosol was dried before sampling.

It is now specified that the aerosol was dried (RH inside the DMA was about 25%). The ambient aerosol was dried in several stages, first drier (using silica-gel, Sigma Aldrich) was in main inlet line outside, second stage was 1 meter-long nafion drier (Perma Pure) inside the building, third drier (silica-gel, Sigma Aldrich) was in closed DMA sheath flow loop.

b. It is necessary to consider SP2 detection efficiency of rBC, which depends on laser

intensity and is influenced by mixing state (see Laborde et al., 2012 – the AIDA intercomparision in AMT, and Schwarz et al., 2010 – Detection efficiency of the SP2 in AMT). A first order estimate of laser intensity can likely be obtained from "YAG power" if Droplet Measurement Technology provided a calibration of this. Note that "YAG power" and laser intensity inside the chamber (where it is critical for rBC detection) are both temperature sensitive. The statement in the supplement that laser power changes equivalent to 17% in diameter suggests even larger laser intensity changes (depending on the size of the calibration aerosol but likely more than a factor 2; please present the relative change in laser intensity inferred from the ambient measurements and assuming constant index of refraction).

We have added diagnostics about laser power to the supplementary material. Scattering signal amplitude for about 280 nm particles was 93% at Mukteshwar and 41% at Gual Pahari from the amplitudes obtained in the initial laboratory calibration. We have also examined the locations of the incandescence signals, which should be seen before particles cross the laser beam center. These show that the typical rBC-containing particles from mobility diameters above 220 nm reach their incandescence temperatures before the maximum laser power, which indicates sufficient laser power. Laser power was higher in Mukteshwar, so a lower detection limit can be used.

c. The supplemental results showing dependencies on detection from the SP2 on chamber temperature (figure S4) for the DMA set at a quite large size (285nm) are quite concerning since the scattering-aerosol detection limit was specified to be 180 nm in the main text. The suggestion that the CPC is a reference instrument and the SP2 is of low quality is not sufficient to simply correct the SP2 concentration without testing any hypothesis as to the origin of the offset (CPC's can undercount!). Over the temperature range specified, the SP2 LFE and Ashcroft differential pressure meter have much smaller temperature sensitivities than the 30% shown in the figure. Hence the basis for a correction, and for establishing the absolute uncertainty of the SP2 measurement is not clear. Note that the good correlation of Aethalometer and

Sp2 data is insufficient to rule out potentially large bias in either/both instruments, and does not validate the rBC size distributions, which have much smaller impact on rBC absorption than concentration; the Aethalometer result needs a large scaling factor that depends on total aerosol, and is highly site specific (see, for example: http://www.esrl.noaa.gov/psd/iasoa/node/81). It will be necessary for the authors to build a reasonable basis for evaluating the instrumental uncertainty. As part of this, I recommend including (in the supplemental material) peak-height distributions for the size-selected aerosol from the SP2 from these tests.

We don't think that the temperature dependency shown in Fig. S4 is related to detection efficiency. If this would be the reason, then we would expect to see an increase in the detection efficiency with particle size (Fig. S3), but this is not the case. Hypotheses were tested, but we could not find good explanation for the difference between CPC and SP2. For example, flow rates were calibrated for both instruments before the campaign, so these should have been correct (this explanation has now been removed). Also, both instruments seem to be operating correctly and concentrations were low enough for the CPC to avoid coincidence effects. Additional tests with another CPC and SP2 showed that this specific SP2 is always over counting, so the correction is justified. This is now clarified.

It is true that the absolute values of the eBC are uncertain and eBC is not the same as rBC, so now we focus on the correlation. Also, the lack of temperature dependency of the eBC/rBC ratio indicates that the measured rBC is not temperature dependent. Peak height distributions are now shown in the supplement.

d. Page 3, line 18: here the SP2 is indicated to detect both rBC-containing and rBC-free aerosol; this lead me to be confused about if the SP2-derived rBC-free concentration was used for anything other than comparison of detection efficiency with the CPC – was Sp2 rBC-concentration used with SP2 rBC-free concentration for the number fraction rBCcontaining particls?. Can the data sources for the various parameters be included

in a table or clearly summarized in the text?

This section is now clarified. SP2-derived number concentrations are used in all calculations, and CPC is for diagnostics and inversion.

e. Please briefly summarize the inversion for the reader here in the main text. I found the supplemental material also confusing, as the DMPS number size distribution comes from the DMA + the CPC: how is the ratio of "DMPS number size distribution to CPC concentration" particularly meaningful? The basic point is that SP2 concentrations are corrected to account for the number fraction of particles in a particular size bin with other than 1 electron charge? Please expand to explain how multiply charge particles are dealt with; this is likely a question that is in readers minds when looking at figure 3. This is at the heart of interpreting the "basic" SP2 data of rBC concentration and size distribution.

Brief summary of the inversion is added and the description of the inversion in Supplementary material has been clarified. The SP2 concentrations are calculated using the DMPS inversion results, which account for the multiply charged particles. We have also clarified that multiply charged particles have a negligible effect (can be seen from Fig. 3).

f. Section 3.1:

g. The Supplemental figure S1 should be updated to show that the Aethalometer sampled in parallel with the DMA.

Figure S1 describes the DMPS-SP2 measurement system, which does not include the Aethalometer (it is another independent instrument and only used in Mukteshwar).

5) Results:

a. Page 4, line 25: What is the basis for this assumption? Every SP2 user sees rBC associated with singly and doubly charged (at least) peaks when calibrating with Aquadag or other materials (this is the bare rBC case). In the case of size-selected internally mixed particles, why would a narrow rBC size distribution be assumed?

This comment has been removed and a better explanation is given in Sect. 3.2.

b. Section 32. Please address multiply-charged particles in the DMA. Page 5, line 18 – As these particles appear to be mostly bare, fractal rBC, how do you know that the ∼210 nm mode are not doubly-charged particles? This analysis would be helped by including the information from LEO fitting which was done. A prioriy one would expect that, unless there were dramatic changes in fractal dimension (which the authors rule out), a single size selected aerosol population will contain a continuum in which more massive rBC cores are associated with lesser amounts of non-rBC material, and smaller cores are associated with larger amounts of non-rBC.

The ∼210 nm mode is always the dominant mode (also for larger mobility diameters), so it must be related to singly-charged particles. Any other conclusion would have required unrealistic rBC size distributions, which were not observed. We clarify that particles observed close to 360 nm are more likely from doubly charged particles than from pure compact rBC, and all larger particles have multiple charges. Nevertheless, these particles are a minor fraction, so they have a negligible contribution to the mean values. We have now provided more information about the LEO fit, but the analysis is kept limited due the problems with increased instrument noise (all LEO results given in Sect 3.4).

c. Page 6, line 1: note that rBC mass is a better first order proxy for the absorption cross-section in each size bin.

rBC mass mean diameter has been chosen, because it is familiar for typical readers (at least for us).

d. Page 6, line 22 – 27: what are the values and total uncertainties observed here

This paragraph has been removed, because rBC and eBC are not directly comparable.

Page 6, line 30: Secondary rBC modes at larger sizes have been observed in China, these should be cited here: Wang et al., Shen, Black carbon aerosol characterization in a remote area of Qinghai–Tibetan Plateau, western China, Science of The Total Environment, V.479–480:151-158 (2014) and Huang et al., Black carbon measurements in the Pearl River Delta region of China, Journal of Geophysical Research, 116(D12208), doi:10.1029/2010JD014933, 2011. Is anything similar observed here?

Reference to the Wang et al. (2014) has been added (Huang et al., 2011, was already included). We also clarify that similar larger particles were observed in these sites.

e. Page 7, line 6 and line 25: the volume ratio goes as the ratio of diameters cubed, not as the linear ratio. This should be corrected throughout the paper. Line 21: The low ratio of rBC to total volume is in fact not distinctly different from previously published SP2 results based on LEO interpretation with Mie shell-and-core model. The assumption of this analysis (that Dm provides a route to total particle volume even for rBC-containing particles) is shown to be false in the next section; the results should be more clearly presented.

Correction to the volume fraction has been made. We will also clarify that the numbers in line 21 are for rBC-containing particle number fractions and not rBC volume fractions. The ratio of rBC mean diameter to the mobility size is a directly measured quantity, although its interpretation is not as simple as for spherical particles. We have clarified the text so that diameter ratios are no longer interpreted as rBC volume fractions.

f. Page 9 – why aren't any of the LEO results shown? What was the average scattering cross-sections? What fraction of rBC-containing particles were successfully fit? If

the particles are bare, the scattering cross-section to rBC mass relationship should match expectations for material with the index of refraction measured by Moteki et al., Method to measure refractive indices of small non-spherical particles: Application to black carbon particles, J. Aero. Sci., 2010. The analysis of page 10 requires the LEO data, or analysis of the evolution of scattering signal for individual rBC particles, to support the assumption that the rBC particles are bare.

More details about the LEO fit are given and some additional LEO results are shown, but the discussion is kept limited due to the problems with the LEO fits. Note that we have not seen bare rBC, but irregular or fractal rBC. We have decided to report particle sizes instead of scattering cross sections, because particle sizes are more familiar for typical readers (at least for us).

6) Conclusions: Please include quantitative values with uncertainties in this section.

Values and uncertainties are now given.

7) Table 1: the $\pm$ values are standard deviations? This should be stated in the caption. Please include absolute uncertainties for rBC concentrations at least.

The values are standard deviations. Typical absolute uncertainty (20%) is given for rBC concentration.

8) Figure 2: The time series does not seem to be extensively referenced in the text, perhaps this figure should be moved to supplemental material?

This figure was originally in the supplementary material, but it was moved here by the request of the Editor, so we will keep it here.

9) Figure 5: DMA data down to 20nm was taken. Why is the full range not shown if the clearly biased data below 200 nm is shown? I would prefer to see the whole range.

Here it seems that the CPC data was not used for total particle number – why not? And if not, how is rBC number fraction $\sim$50% down to 100 nm when the SP2 scattering particle detection limit is specified to be 180 nm?

Figure 5 and all SP2 calculations were limited to the 100 nm mobility size, because this is about the same as the SP2 detection limit for rBC, so the whole available range is already shown. Mobility sizes above 100 nm range were fully analyzed and the results were used to find the lowest size where results are still valid. Figure 5 shows very clearly why the lower limit has been set to approx. 200 nm. CPC data was not used, because concentrations are measured by the SP2. Any non-rBC particle count below 180 nm mobility diameter is related to multiply charged particles. Also, at 100 nm only a fraction of rBC is detectable.

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