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# *Interactive comment on* "Black carbon concentrations and mixing state in the Finnish Arctic" *by* T. Raatikainen et al.

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We would like to thank the referee for the useful and constructive comments. Below are the issues raised by the referee (quotes shown in italics) and our replies (plain text).

*There are a number of issues that I have annotated in the manuscript (Summary material), some that I list here, that are related to clarity of understanding in the manuscript, as well as interpretation of the results. These are listed here in the order they were annotated in the manuscript. The annotated manuscript also contains my minor edits where I have tried to provide suggestions for better readability.*

We have made several updates to the manuscript based on the annotated manuscript.

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*Major issue 1 I am making a very strong recommendation that the term "coating" either be completely removed when discussing the mixing state of particles or be clearly defined, something like Schwarz et al. have used in their publications. I have had a discussion with Dr. Schwarz on this matter (personal communication) and he has emailed me the following response to my question about his opinion about the use of the term "coating":*

*"In my papers, I always have a sentence that reads like "the materials internally mixed with BC (here referred to generically as "coatings" without implying any knowledge of morphology)".*

*There can certainly be chemical processes whereby inorganic or organic material might condense or be deposited on the surfaces of the elemental carbon particles during the aging processes, but it is just as likely that during the aging process coagulation is also occurring between the rBC and other non-refractory material. For example in the abstract, describing a "coated to core diameter of 2", suggests a particle consisting of a solid core and a shell. This might actually describe a very small fraction of the particles but is unrealistic based upon the multitude of microscopic analyses that would suggest that the morphology of these particles is much more complicated. As an author of several SP2 papers I am guilty of propagating this same concept that I would now like to try and change in terminology. Instead of referring to "coated" rbC, I think the more accurate and correct would be "Internally mixed" rBC, since the authors have already defined in their opening discussion the term "internally mixed" to mean non-refractory material mixed with refractory material. I would also be willing to accept an acronym for this type of material, e.g. IMrBC. The derivation of the fraction of mixing remains the same. Instead of referring to a "coating layer" you would change it to "mixed fraction" so that in the abstract, "coated to core diameter of 2" would become "Total mixed to core diameter ratio of 2". Note that Huang et al (2012) avoid the term "coated" and instead use "Internally mixed". The same should be done in this paper.*

We agree that the structure of the BC-containing particles is unlikely as simple as ex-

pected by the core-shell model. Therefore, we will also avoid term "coated". However, the replacement term "internally mixed rBC" can have different meanings for a single particle (is it not pure rBC, but mixed with other species) and for aerosol populations (all particles are containing rBC so that there are no rBC-free particles), which is the definition used in the manuscript. For clarity, we will continue to use terms external and internal mixing when referring to aerosol populations. For a single particle containing both rBC and non-absorbing material we will use term "mixed" (or similar depending on the context) instead of "coated".

Regarding the parameter describing rBC content in a single particle, term "mixed fraction" is unambiguous as it could refer to particle populations or single particles. Although rBC volume fraction would be independent of morphology, its magnitude (about 0.01) is not as convenient as that of the diameter ratio and the diameter ratio seems to be better for averaging (volume ratio depends more on particle size). So, we will express rBC content as "particle diameter to rBC core volume equivalent diameter ratio" (briefly: particle to rBC core diameter ratio). This is neutral in the sense that it does not expect any morphology for rBC. Also, particle diameter is the standard term for particle size. Clearly, the terminology needs to be clarified, but this is not the purpose of our paper.

*Major Issue 2*

*The authors have tried to describe the operating principles of the SP-2 and analysis of the scattering and incandescence signals in their own words but in doing so have incorrectly described a number of the fundamental aspects. One example, on page 15627: "Nonabsorbing particles scatter laser light so that the maximum scattering signal is proportional to the scattering cross section of the particle, which is calculated using the Mie approximation..".*

*This is misleading since it suggests that only those particles without rBC are used for sizing. Here and in a previous statement the authors suggest that only non-rBC scatter*

*light but this is obviously not true. I have noted in my annotated version all the places where there are inaccuracies; however, I would suggest that the authors only present the minimum that is needed to explain the operation of the SP-2 and how the basic parameters are derived. That includes removing the lengthy discussion on the LEO derivation of size. It is sufficient to state that the size is derived from the scattering signal using the leading edge technique described by Gao et al. Then the mixing fraction can be simply described as the ratio of the rBC mass diameter to the mixed particle equivalent optical diameter without the need for a lengthy justification since this is what other studies have already published.*

We have clarified this based on the referee comments in the annotated version of the manuscript. The description of the SP2 and data analysis is also significantly shortened (e.g. the LEO part is almost completely removed).

*Major Issue 3*

*There are no uncertainties discussed for the SP2, MAAP or Aethalometer. This is a serious omission. Given the uncertainties in deriving the mixing fraction because of the assumed refractive index and particle density, as well as the possibly very large uncertainties in deriving the eBC from filter based techniques, anytime quantitative comparisons are being made between measurements being made by different instruments or techniques, these have to be given in the context of the expected variations.*

*Secondly, the operating principles of the filter-based instruments need to be included in the instrumentation section. Briefly, with adequate references, just as with the SP2.*

We have added some discussion about the uncertainties. Some of the uncertainties are also discussed in Sect. 3.4, where SP2 and optical black carbon measurements are being compared. The filter based instruments have now more references to publications where their operation and uncertainties are fully described. More details are given about the SP2, because MAAP and Aethalometer are routinely used instruments and this study is heavily focused on the SP2 measurements.

*Major issue 4*

*The analysis of the variations in the rBC parameters is cursory at best. The correlation with CO is interesting but the trajectory analysis fall short of providing much in the way of useful information on the history of the rBC prior to its arrival at the research site. In figure 4 I am assuming that the origin is being determined from the point where the air mass was 5 days previously but there is a very wide range of values in each of the sectors, particularly the one labeled continental Europe. This suggests that there is a lot more going on to drive the variations than just where the air was 5 days previously. Here are some of the questions that need to be addressed:*

*1) How far has the air traveled in 5 days along its trajectory and how does that relate to the three most important parameters – rBC mass, number fraction and mixing state? 2) From what altitude is the air coming, i.e. has it been near the surface most of the 5 days or has it descended from a higher altitude? How does this impact the three parameter? 3) How does the rBC to eBC ratio vary with the rBC/CO and eBC to CO ratios? If the overestimate of eBC by the filter methods is due to absorbing material that is not rBC, then this is likely seen in the air mass history. 4) What is the correlation between mixing state and rBC mass, mixing state and number fraction and mixing state and rBC/CO? These are all possible clues to the aging processes.*

Figure 4 shows the average direction and distance, which is not the same as those of the first trajectory coordinate point. Different trajectory parameters (also trajectory length and altitude (question 2), which did not show any correlation with the rBC parameters) were tested and the two parameters (described in section 2.3) were selected, because they have the best correlations with the rBC parameters. It is also clear that the trajectories cannot explain variations in rBC mixing state (question 1). This is now clarified.

Linear fit to eBC as a function of CO gives a slope of $4.35\,\mathrm{ng\,m^{-3}\,ppb^{-1}}$, which is slightly higher than expected (ideally, should be five times that for rBC). Likewise,

rBC/eBC to rBC/CO is about the same as rBC/eBC, which is about 0.2. As mentioned in the text, air mass history described by trajectories had no apparent effect on rBC properties except mass concentration, and therefore cannot explain the low rBC to eBC ratio. Furthermore, the ratio is more or less constant although air masses are not, so air mass history cannot explain the difference between eBC and rBC.

Regarding question 4, we have calculated all cross correlations between the mixing state parameters, but nothing relevant was found. This is also evident from Fig. 3. We have also tried to find explanations for rBC/CO, but nothing relevant was found. This will be clarified.

*Other Comments*

*Figure 2 should include the average size distribution from the SMPS. It is stated that there are significant numbers of particles below 75 nm from Fig. 2 but this is speculation without also showing the SMPS distribution that should go down to as small at least as 10 nm.*

We will clarify that the rBC core diameters (not particle diameters measured by the DMPS) are often smaller than 75 nm. This can be seen from the rBC core number size distribution, which have maximum at the 75 nm detection limit. The other reason for not including DMPS size distributions to figure 2, is that both size (rBC core vs particle) and number (rBC-containing vs all particles) scales are different. We have now given a reference to previous studies from Pallas where DMPS size distributions are shown.

*Page 15626, line 10, "The SP2 was connected to the PM10 sample line, which means that some ice nuclei (IN) and cloud condensation nuclei (CCN) are not detectable when the station is covered by clouds." And again on page 15631, line 25, "As explained in Sect. 2.2, SP2 measurements can be biased during the in cloud time periods, because some ice and cloud condensation nuclei become too large to be detected". I don't understand what this means. The presence of CCN and IN have nothing to do with the presence of clouds so these statements are incorrect.*

The statements mean that when the station is covered by clouds, cloud and ice particles larger than 10 microns are removed by the PM10 inlet. This means that those particles that have been forming these clouds (IN and CCN) are not detected by the SP2. We have clarified this part of the text by removing terms IN and CCN.

*In addition to figure 3 time series, since it is mentioned that there is a correlation between the rBC mass and the wind direction and CO, these parameters should be included in the time series.*

We have added trajectory directions (better than wind direction) and CO time series to Fig. 3.

*The rBC mass concentration is correlated with CO, and a correlation coefficient and slope given. Please show a figure with these data. These are numbers that can be compared to correlations that have been published elsewhere, i.e. Han et al (2009), Zhou et al (2009), Andreae et al. (2006), Kondo et al (2006), Chou et al (2010), Spackman et al (2008), Baumgardner et al (2002). The BC/CO ratios range anywhere from 1 – 10 ug/m3 BC to 1 ppm of CO.*

We have added a figure showing the correlation. We know that there are several papers published on this topic, and this is why we already had five references. The references in the paper were selected so that they are based on SP2 data and rBC (slopes could be different for eBC), but it seems that from the references given above the first five and the last are not related to SP2 measurements. However, reference to Spackman et al (2008) has been added. The selected references show that the smallest BC/CO ratios are typically larger than $1\,\mathrm{ng\,m^{-3}\,ppb^{-1}}$, which is already higher than our value.

*Please also note the supplement to this comment: http://www.atmos-chem-phys-discuss.net/15/C4720/2015/acpd-15-C4720-2015-supplement.pdf*

The manuscript has been updated based on these comments.

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