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Atmospheric Measurement Techniques Discussions

Interactive comment on "Characterizing black carbon in rain and ice cores using coupled tangential flow filtration and transmission electron microscopy" *by* A. Ellis et al.

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Response to: Interactive comment on "Characterizing black carbon in rain and ice cores using coupled tangential flow filtration and transmission electron microscopy" by A. Ellis et al. Anonymous Referee 1

We thank the referee for their constructive comments.

Referee comments are bolded, and the authors' response is below.

General Comments:

1. **It would be good to see some more discussion on the possibility that black carbon particles might aggregate, fragment or collapse during different sample manipulations. For example, the authors in section 3.3 write: "Black carbon particles in both the rain and ice cores appeared to be significantly aged in the atmosphere as indicated by the collapsed structure of the carbon spherules". Is it possible that the collapse happened during the processing of the sample, e.g. during the drop evaporation, instead of during atmospheric aging? I do believe the authors interpret the results correctly, but some additional discussion on this potential issue would be good. Several studies are available in the literature showing how the structure of black carbon can affect its optical properties (for the same mass) with obvious radiative forcing implications; therefore, this is a potentially important issue.**

We agree that section 3.3 would benefit from additional discussion of the potential shortcomings of the method outlined in this paper, i.e. release of particles into liquid solution and possible coagulation after melting due to aggregation or as the particles dry on the TEM grid. As stated in the introduction, the tangential flow filtration concentration method has been used to preserve fragile structures of particles (Benner et al., 1997) and to avoid aggregation of nanoparticles (Dalwadi et al., 2005), but disaggregation, aggregation, and aggregate collapse are still possible outcomes of the method. However, we see no obvious evidence of alteration. The following text and references therein have been added to the discussion for clarification:

"The tangential flow filtration concentration method has been used to preserve fragile structures of particles and to avoid aggregation of nanoparticles. Nevertheless, disaggregation, aggregation, and aggregate collapse are still possible outcomes of the method. However, we see no obvious evidence that these factor significantly into the results.

Tests of bond strength between carbon spheres in BC show that aggregates are unlikely to fragment into smaller units (Rothenbacher et al., 2008). Hence, disaggregation

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from this method is unlikely.

Both the rain samples and the ice core melt water samples were processed in an identical way, including the filtration technique to concentrate the samples and the evaporation technique to deposit particles on the TEM grids. Both rain and ice core samples contained significant variations in particle size, including large amounts of smaller BC aggregates (100 nm). This variety suggests that method-induced aggregation did not result in significant changes to the particle population.

The collapsed structure of the black carbon aggregates seen in the ice core samples is supported by reports of BC aging in the atmosphere (Johnson et al., 1991; Li et al., 2003; Martins et al., 1998). The BC contained in Antarctic ice cores has aged significantly from emission to deposition and would therefore likely contain collapsed aggregates.

As BC is wet deposited in the rain samples, the particles are likely hydrophilic. The transition from hydrophobic to hydrophilic is a result of atmospheric aging (Stier et al., 2006), suggesting that the BC in rain has also aged significantly before deposition and will contain collapsed aggregates as well."

2. **Concentration factor: How was estimated? Maybe I missed it, but it was not fully clear to me. Also, how good is the estimate? Maybe provide an uncertainty.**

The concentration is discussed in section 3.2. The estimate of concentration factor was based on the approximate average initial volume of the ice core melt water and the final sample volume of 1.5 mL for all samples.

The concentration factor would vary slightly based on the initial volume of the ice core melt water, which was different for each ice core sample used. This was due to variations in the size of each ice core.

The text has been clarified and the discussion now reads:

"Using TFF, the ice core samples were concentrated from an average initial volume of

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2 L to a final volume of 1.5 $\pm$ 0.1 mL, a factor of 1300. The concentration factor varied slightly due to the initial volume of the ice core melt water, which was different for each ice core sample used. This was due to variations in the size of each ice core."

Section 3.2 was also separated into three paragraphs for clarity.

3. **Is the application of the method only for microscopy or do the authors envision also some other application? How?**

The method could also be used to study particles in ice, rain, and sea water samples by other instrumental techniques such as single particle inductively coupled plasma mass spectrometry, Nuclear Magnetic Resonance (NMR), Raman spectroscopy etc.

4. **There are some studies available in literature showing how the mixing of black carbon with other particles such as dust, might affect their optical properties; these re- sources might be relevant to the discussion of the importance of the interesting finding reported in the beautiful figures 4, 5 and 6.**

The following has been added to the discussion (section 3.3) to highlight the importance of the results:

"The mixing of BC and other particulates shown in figures 5-7 is significant, as internal mixing of BC with other particles such as dust can affect their radiative forcing (Clarke et al., 2004; Scarnato et al., 2015). STEM-EDS can distinguish variations in BC composition that may routinely be overlooked."

Specific comments:

5. **Lines 18-19, page 6022: "Ice and snow from this site has been. . ." should probably read "Ice and snow from this site have been. . ."**

This has been corrected in the revised manuscript.

6. **Lines 4-5, page 6023: "Ice cores were approximately 1m in length 5 and 5 cm by 5 cm cross-section before decontamination" this seems a repetition of the**

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sentence on line 23 on the previous page.

This has been corrected in the revised manuscript, and the sentence on page 6023 has been removed.

7. **Line 23, page 6023: "Approximately 5mm was" maybe should read "Approximately 5mm were"?**

This has been corrected in the revised manuscript.

8. **Line 27, page 6024: Consider removing "a" in front of "SPI"**

This has been corrected in the revised manuscript.

9. **Line 13, page 6026: Period missing before "Three. . ."**

This has been corrected in the revised manuscript.

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